

Escuela de Ingeniería de Bilbao

Departamento de Ingeniería Química y del Medio Ambiente



Estudio del proceso de metanación empleando catalizadores basados en metales de transición soportados en alúmina y derivados del óxido de grafeno

Memoria presentada por
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Ya han pasado algo más de tres años desde que Pedro y Laura me dieron la oportunidad de entrar en el departamento de ingeniería química y del medio ambiente con un contrato predoctoral. Tres años desde aquel día en que me reuní con Laura en su despacho en dirección y me guio por los laboratorios y salas en las que tantas horas pasaría. Me presentó tantos y tantos rostros y nombres, que en aquel momento aún me resultaban desconocidos. Y con estas palabras que tanto me está costando redactar, esta etapa está llegando a su fin. Un fin que he llegado gracias a muchas personas que han creído en mí y que me han ayudado a crecer tanto como persona como investigador.

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A todos y todas, GRACIAS.

***A mi familia y amigos, por
ayudarme a ser quien soy***

*"Es justamente la posibilidad de realizar un sueño lo
que hace que la vida sea interesante"*

Paulo Coelho: El alquimista

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Abreviaturas

ΔH_r^0 Entalpía estándar de reacción

ρ_{Ni} Densidad del níquel

A

AC Active Carbon (Carbón activo)

AAEMs Alkaline Anion Exchange Membrane (membranas de intercambio aniónico alcalino)

AGO Amine Graphene Oxide (óxido de grafeno aminado)

Al_2O_3 Alúmina u óxido de aluminio

A_{Ni} Área superficial del átomo de níquel

Ar Argon

a.u. Arbitrary units (unidades arbitrarias)

AWE Alkaline Water Electrolysis (electrolisis de agua alcalina)

B

B Boro

Ba Bario

$BaCO_3$ Carbonato de bario

BaO Óxido de Bario

BECCS Bio-Energy with Carbon Capture and Storage (captura y almacenamiento de carbono para la obtención de bioenergía)

BGO Óxido de grafeno reducido por MeAB

BJH Método Barret-Joyner-Halenda

BET Método Brunauer, Emmett y Teller

BOE Boletín Oficial del Estado

C

C Carbono

Ca Calcio

CaO Óxido de Calcio

CAES	Compressed-Air Energy Storage (almacenamiento de energía por aire comprimido)
CCU	Carbon Capture and Utilization (captura de carbono y utilización)
Ce	Cerio
CeO ₂	Óxido de cerio
CFC's	Clorofluorocarbonos
CH ₄	Metano
Co	Cobalto
CO	Monóxido de carbono
CO ₂	Dióxido de carbono
[CO ₂] _{in}	Flujo de dióxido de carbono de entrada
Cr	Cromo
CrO ₃	Trióxido de cromo
Cr ₂ O ₃	Óxido de cromo (III)
CS ₂	Sulfuro de carbono
CSC	Captura y secuestro de carbono

D

DMC	Dimetil carbonato
DME	Dimetil eter
d _{Ni}	Diámetro de partícula de níquel
D _{Ni}	Dispersión del níquel
d _p	Tamaño de partícula
d _{XRD}	Tamaño medio de cristal determinado por la técnica XRD

E

EDX	Espectroscopía de energía dispersiva de rayos X
-----	---

F

Fe	Hierro
Fe ₂ O ₃	Óxido de hierro (III)
Fe ₃ O ₄	Óxido ferroso-férrico o magnetita
FES	Flywheel Energy Storage (batería inercial)

G

GEI	Gas(es) de efecto invernadero
GES	Gravitational Energy Storage (almacenamiento de energía gravitacional)
GHSV	Gas Hour Space Velocity (velocidad espacial)
GNS	Gas Natural Sintético
GO	Graphene Oxide (óxido de grafeno)

H

H ₂	Hidrógeno
H ₂ O	Agua
H ₂ S	Sulfuro de hidrógeno
HCl	Ácido clorhídrico
He	Helio
HFC's	Hidrofluorocarbonos
HNO ₃	Ácido nítrico
HR-STEM	High Resolution - Scanning and Transmission Electron Microscopy (microscopía electrónica de barrido y transmisión de alta resolución)

I

ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
Ir	Iridio

J

JCPDS	The Joint Committee on Powder Diffraction Standards
-------	---

K

K	Potasio
kWh	Kilovatios por hora
KOH	Hidróxido de potasio

L

La	Lantano
La ₂ O ₃	Óxido de lantano
LPES	Liquid Piston Energy Storage (almacenamiento de energía líquido-pistón)

M

MeAB	Metilamina borano
MeOH	Metanol
Mg	Magnesio
MgO	Óxido de magnesio
Mn	Manganeso
Mo	Molibdeno
MoO ₃	Óxido de molibdeno (VI)
Mtpe	Millones de toneladas de petróleo equivalentes

N

N ₂	Nitrógeno
N ₂ O	Óxido nitroso
Na	Sodio
N _{Avogadro}	Número de Avogadro 6,022×10 ²³ mol ⁻¹
NH ₃	Amoniaco
Ni	Níquel
NiAl ₂ O ₄	Aluminato de níquel
NiCo ₂ O ₄	Óxido de cobalto (III) - níquel
NiO	Óxido de níquel
NiS	Sulfuro de níquel
Nml	Mililitros normal (valor de volumen medido en condiciones normales)

O

O ₂	Oxígeno
O ₃	Ozono
OCDE	Organización para la Cooperación y el Desarrollo Económicos

P

Pd	Paladio
PD	Protocolo de detalle
PDF	Power Diffraction File
PE	Parlamento Europeo

PEMs	Proton Exchange Membrane o Polymer-Electrolyte Membrane (membrana de intercambio protónico o membrana de electrolito polimérico)
PET	Tereftalato de polietileno
PFC's	Perfluoro-carburos
PHES	Pumped Hydroelectric Energy Storage (almacenamiento hidroeléctrico de bombeo)
pI	Punto Isoeléctrico
PIC	Indicador controlador de presión
ppb	Partes por billón
ppm	Partes por millón
PtG	Power to Gas
PtL	Power to Liquid
PV	Efecto fotovoltaico
pzc	Point of zero charge (punto de potencial cero)

R

RCDE	Régimen de comercio de derechos de emisión
RCP	Representative Concentration Pathway (sendas representativas de concentración)
rGO	Reduced Graphene Oxide (óxido de grafeno reducido)
Rh	Rodio
Ru	Rutenio
RWGS	Reverse Water Gas Shift

S

S _{BET}	Área superficial medida por el método BET
SF ₆	Hexafluoruro de azufre
SEM	Scanning Electron Microscopy (microscopía electrónica de barrido)
SiC	Carburo de silicio
SiO ₂	Óxido de silicio
Sm ₂ O ₃	Óxido de samario
SOEC	Solid Oxide electrolyzer cell (celda electrolizadora de óxido sólido)
Sr	Estroncio

StF Solar to Fuel

T

TCD Thermal Conductivity Detector (detector de conductividad térmica)

t_{CO2} Toneladas de CO₂

TEM Transmission Electron Microscopy (microscopía electrónica de transmisión)

TGA Thermal Gravimetric Analysis (análisis termogravimétrico)

Ti Titanio

TI Indicador de temperatura

TIC Indicador controlador de temperatura

TiO₂ Óxido de titanio

TOF Turnover Frequency (frecuencia de recambio)

TPD Temperature Programmed Desorption (desorción a temperatura programada)

TPR Temperature Programmed Reduction (reducción a temperatura programada)

U

UE Unión Europea

V

V Vanadio

V_p Volumen de poro medio medido por el método BJH

W

WGS Water Gas Shift

X

X_{CO2} Conversión fraccional de dióxido de carbono

XPS X-ray Photoelectron Spectroscopy (espectroscopía fotoelectrónica de rayos X)

XRD X-Ray Diffraction (difracción de rayos X)

Y

Y_2O_3 Óxido de itirio

Z

Zn Zinc

Zr Circonio

ZrO_2 Óxido de circonio

Resumen

El dióxido de carbono (CO_2) es un gas presente de manera natural en la atmósfera, al proceder de fuentes naturales tan esenciales como la respiración celular o la descomposición de la materia orgánica, pero también incendios o volcanes. El ser humano ha contribuido al aumento de la cantidad de CO_2 atmosférico a causa de actividades como la agricultura o la ganadería. Desde la revolución industrial esta contribución se ha visto incrementada de manera significativa. Además, la necesidad de abastecer una mayor demanda de energía en poco tiempo, potenció el desarrollo de un sistema energético basado en las fuentes fósiles, generando una gran dependencia por estas fuentes, cuya combustión es una de las mayores contribuciones al CO_2 antropogénico.

El CO_2 es un gas de efecto invernadero (GEI), cuyo excesivo incremento en los últimos años ha provocado el aumento de la temperatura global, del deshielo de los polos, del nivel del mar o de la acidificación del mar entre otros, con las consecuencias que eso supone para la vida. Si no se revierte la actual tendencia, las consecuencias pueden ser catastróficas, y es por ello que se están desarrollando diversos proyectos para lograr reducir las emisiones de GEI y la transición de fuentes de energía hacia fuentes renovables más respetuosos con el medio ambiente. Con este objetivo se plantean sistemas de obtención de energía más sostenible y para la valorización del CO_2 como el Power-to-Gas (PtG).

El concepto PtG aparece como un sistema para la obtención de energía en lugares incomunicados o con dificultades de abastecimiento, pero también aparece como una solución a la problemática de las energías renovables para un abastecimiento de energía constante y un eficiente almacenamiento. El excedente de energía se emplea para la obtención de un combustible más fácilmente almacenable y transportable: el hidrógeno, mediante un proceso de electrólisis del agua. El transporte y almacenamiento de hidrógeno, aunque más eficiente, sigue estando limitado debido tanto a los bajos límites de inflamabilidad como a las bajas concentraciones permitidas en mezcla con el gas natural. Por ello, el hidrógeno se emplea como reactivo para la obtención de metano, mediante la reacción de metanación de CO_2 . El metano producido se puede transportar o almacenar por medio de gaseoductos o bombonas con el gas natural.

La reacción de metanación de CO_2 o también llamada reacción de Sabatier, es una reacción catalítica exotérmica, llevada a cabo generalmente a altas presiones y temperaturas, en el interior de un reactor que permita obtener un perfil isotérmico para un adecuado control de la temperatura de operación. Por otro lado, el catalizador debe ser eficiente y resistente a la desactivación derivadas de la temperatura de reacción, así y como del envenenamiento con gases que pueden acompañar a los reactivos. Con este objetivo, se debe hacer una buena elección del metal activo, promotor, soporte o modificador del soporte que componen el sistema catalítico, siendo este el centro de estudio de este trabajo de tesis.

Los catalizadores más ampliamente empleados en metanación se basan en el uso de metales nobles como metal activo, por su alta actividad y selectividad en la reacción de metanación. Entre ellos, destaca el uso de rutenio (Ru), rodio (Rh) y paladio (Pd) entre otros. Sin embargo, su alto coste ha llevado a la búsqueda de otras alternativas más económicas, que permitan alcanzar rendimientos similares. El uso de metales de transición, dando especial importancia al níquel (Ni), han demostrado ser útiles

alternativas más económicas, pero sin llegar a alcanzar los rendimientos de catalizadores basados en metales nobles. Estos metales son soportados sobre óxidos metálicos o zeolitas con alta área superficial, que facilita la mayor dispersión del metal sobre su superficie, siendo el soporte más utilizado la alúmina.

Otros metales de transición como el hierro (Fe), el cobalto (Co), el cromo (Cr) o el molibdeno (Mo) han demostrado ser activos en la reacción de metanación en mayor o menor medida y con selectividades diferentes. Además, su incorporación aporta una mejora en las características de dispersión o resistencia a la desactivación por la temperatura o por H_2S . Por esta razón se plantea el uso de estos metales como promotores en combinación con Ni, en vista de mejorar el sistema catalítico. De este modo se demuestra que la adición de Fe mejora el rendimiento para el catalizador $13\text{Ni}/\text{Al}_2\text{O}_3$, debido a la interacción con el Ni que promueve la presencia de centros activos. La adición de Co inhibe la formación del enlace S^{2-} del H_2S con el metal, lo que reduce el envenenamiento por azufre, consiguiendo la recuperación del 13% de rendimiento tras una etapa de regeneración del catalizador y eliminando el H_2S de los reactivos. El Mo demuestra ser menos activo y selectivo en la reacción de metanación, pero su adición en la cantidad óptima, permite trabajar a tiempos de residencia más elevados en presencia de H_2S .

La adición de Ru como promotor al catalizador de $13\text{Ni}/\text{Al}_2\text{O}_3$ produce un significativo aumento del rendimiento a metano, debido a una fuerte interacción entre Ru y Ni. Sin embargo, la mayor sensibilidad del Ru a la formación de enlaces con el H_2S presente facilita su desactivación.

El objetivo principal del soporte es la de dispersar el metal, para lo que se necesita una alta área superficial. Sin embargo, a pesar de disponer de gran superficie no siempre se garantiza que la fijación del metal sea homogénea, con la suficiente fuerza de unión para evitar su separación en reacción y con una correcta dispersión evitando la formación de aglomerados. Por ello, para la mejora de estas características que resulte en una mejora de la actividad catalítica, se adicionan diversos metales como modificadores del soporte entre ellos, alcalinotérreos como bario (Ba), calcio (Ca) y magnesio (Mg) o lantánidos como lantano (La) y cerio (Ce).

Según se observa en los resultados de este trabajo, los metales alcalinotérreos muestran una débil interacción con el soporte, que se traduce en un aumento de la actividad poco significativa. Por el contrario, los lantánidos muestran una fuerte unión con el soporte que facilita el anclaje de nuevos centros metálicos del metal activo, mejorando su dispersión y reducibilidad, alcanzando mayores rendimientos a menores temperaturas. Este efecto, es especialmente notable por la adición de La, alcanzando un rendimiento a metano del 98% a 572 K. Además, la fuerte interacción entre soporte, lantánido y metal activo dificulta la adsorción de las moléculas de H_2S en el metal, dificultando su envenenamiento, aunque no evitándolo, ya que una vez desactivados, estos catalizadores no recuperan su actividad.

La reacción de metanación, como se ha comentado anteriormente, es una reacción exotérmica que produce la elevación de la temperatura de reacción, dificultando su control. La formación de puntos calientes, que no necesariamente elevan la temperatura del sistema, pueden provocar la desactivación parcial o total del catalizador por sinterización. Para evitarlo, se plantea el uso de nuevos sistemas catalíticos, como sistemas monolíticos que mejoren la transferencia del calor. O más recientemente, se

están empezando a utilizar soportes de materiales más conductores como el grafeno y sus derivados. Los más destacados son el óxido de grafeno (GO), óxido de grafeno reducido (rGO) y óxido de grafeno aminado (AGO).

En este trabajo se han empleado varios derivados de óxido de grafeno tanto comerciales (facilitados por la empresa productora Grafenea) como de fabricación propia a partir de otros compuestos de óxido de grafeno. Se han preparado para su utilización como soporte en catalizadores de Ni, para conseguir una mayor eficiencia en la reacción de metanación debido a la mayor conducción del calor generado en la reacción y que evite la desactivación a causa de la temperatura. Sin embargo, la menor cantidad de grupos funcionales de oxígeno que permitan el anclaje del metal al soporte, producen una disminución de la cantidad de centros activos, su dispersión y por tanto de la actividad en estos catalizadores. Entre ellos, el catalizador que presenta mayor actividad es el basado en rGO comercial, siendo mucho menor que la obtenida para catalizadores soportados en alúmina. La adición de La, a diferencia de lo que ocurre en catalizadores soportados en alúmina, no produce la mejora de la actividad. Se debe a que la unión de La se realiza en los mismos sitios que lo hace el Ni y no sobre otros que aumentarían la incorporación de metal y su dispersión. Es por ello, que la resistencia a la desactivación por H₂S es mucho menor en este tipo de catalizadores, siendo necesario un estudio más amplio de este tipo de soportes para proceder a su uso en este tipo de aplicaciones.

Estructura de la memoria

La tesis se ha dividido en 7 capítulos, iniciándose por la contextualización en la **introducción general y estado del arte**, recogida en el **capítulo 1**. Del estudio de los problemas a resolver para implementar la tecnología PtG, y en particular por el estudio de los mejores sistemas catalíticos para la metanación, se derivan los **objetivos** recogidos en el **capítulo 2**. En el **capítulo 3**, se describen todos los **procedimientos experimentales** desarrollados durante la realización de la tesis, entre los que se incluyen no sólo la síntesis de catalizadores, catalizadores con promotores, soportes basados en óxido de grafeno o catalizadores con soportes modificados; sino que también se describen las técnicas de caracterización y los equipos empleados para el análisis de la actividad catalítica de las muestras.

El desarrollo de los objetivos específicos anteriormente mencionados ha permitido la obtención de los resultados recogidos en los **capítulos 4, 5 y 6**. Se han dividido en tres capítulos para facilitar su tratamiento y estudio en mayor profundidad. El **capítulo 4** pretende estudiar el efecto de añadir metales de transición como promotores al catalizador monometálico de Ni soportado sobre alúmina, con el fin de mejorar su actividad en la reacción de metanación de CO₂, su resistencia a la desactivación por H₂S y su capacidad de recuperación de la actividad. Por otro lado, en el **capítulo 5**, se busca conseguir mejorar la actividad del catalizador de Ni, de Ru y de Ni-Ru en la reacción de metanación de CO₂, además de mejorar su resistencia a la desactivación por H₂S, modificando el soporte de alúmina con metales alcalinotérreos y lantánidos. En el **capítulo 6** se analiza el sistema catalítico más idóneo basado en Ni para la metanación de CO₂, comparando el uso de soportes derivados de óxido de grafeno frente al soporte de alúmina y su modificación con La. Para finalizar, en el **capítulo 7** se recogen las principales **conclusiones** obtenidas durante la realización de esta tesis.

CAPÍTULO 1



Introducción y estado del arte

"Produce una inmensa tristeza pensar que la naturaleza habla mientras el género humano no escucha."

VICTOR HUGO

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El objetivo del presente capítulo es la contextualización del trabajo de investigación desarrollado en esta Tesis, centrado en el campo de la ingeniería de los materiales y procesos sostenibles. Para ello se comenzará enmarcando la necesidad de actuación en materia de clima y energía, a través del desarrollo de una serie de objetivos clave: la reducción de emisiones de gases de efecto invernadero, la incentivación de las energías renovables en favor de reducir las fuentes de energía basadas en combustibles fósiles y el aumento de la eficiencia energética. Estos objetivos forman parte de un programa de actuación establecido por la Unión Europea para mitigar los devastadores efectos del cambio climático en 2030, reforzándose con medidas internacionales, como las acordadas en la última cumbre del clima en 2019 en Madrid. En este marco se precisa de gran inversión en investigación, desarrollo y aplicación de energías renovables para solventar aquellos problemas derivados de su intermitencia, almacenamiento y distribución. Una de las soluciones que se plantean para solventar estas limitaciones, es la desarrollada en este trabajo, por la cual se transforma la energía excedentaria de fuentes renovables en energía química por el proceso conocido como Power-to-Gas (PtG). Este proceso consta de dos procesos: la hidrólisis del agua y la metanación de CO_2 , por medio de la reacción de Sabatier. Tras hacer un completo estudio de los diferentes elementos del catalizador: con la selección de los soportes, modificadores, promotores y métodos de producción más adecuados; se recoge un resumen de sistemas catalíticos recientemente empleados en la bibliografía con sus variables del sistema y condiciones de operación seleccionadas. Finalmente, se describe la desactivación de catalizadores.

1.1. Evolución de los gases de efecto invernadero (GEI) en la atmósfera

Los gases de efecto invernadero (GEI), entre los que se incluyen el dióxido de carbono (CO_2), el metano (CH_4) o el vapor de agua (H_2O), están presentes en la atmósfera desde el origen de la Tierra. Estos gases se producen de manera natural, siendo necesarios para la existencia de la vida. Cumplen una función imprescindible, frenando la pérdida de energía en forma de calor en la atmósfera, manteniendo una temperatura media apta para la vida (un valor medio global de 15°C) [1]. Entre ellos, cabe destacar el CO_2 por su mayor presencia en la atmósfera, con una proporción del 0,04% frente al 0,0009% del H_2O o el 0,0002% del CH_4 . La concentración del CO_2 ha cambiado a lo largo de la historia de manera significativa, con aumentos en períodos concretos, debido a diferentes factores: la actividad volcánica, deshielos, seísmos, incendios, aumento poblacional de seres vivos o descomposición de materia orgánica; o con disminución en otros períodos, asociados a una mayor extensión y crecimiento de la flora, tal y como se observa en la **Fig. 1.1** [2].

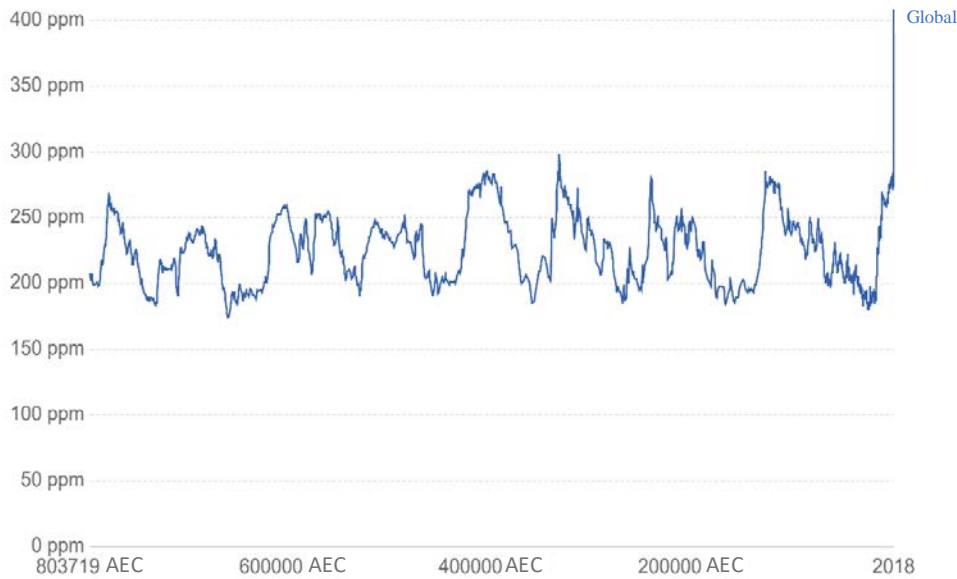


Fig. 1.1. Concentración atmosférica de dióxido de carbono (CO₂) a nivel global, medido en partes por millón (ppm) desde el 803.719 AEC (antes de la era común) hasta 2018 [2].

Sin embargo, esta tendencia histórica, determinada en base a estudios del aire atrapado en el hielo del Antártico, está sufriendo un drástico cambio en los últimos tres siglos [3]. Los datos indican que, aunque hayan existido periodos de mayor concentración de CO₂ en la atmósfera a lo largo de la historia, los valores siempre habían variado entre 190 y 280 ppm, nunca superando los 300 ppm. Previo al comienzo de la era industrial, era del orden de 280 ppm, coincidiendo con un periodo de estabilidad. El aumento que se produce a partir de ese momento se debe no sólo a las contribuciones de GEI de origen natural, sino a la contribución por emisiones de causa antropogénica, a los que se suman otros GEI como son el óxido nitroso (N₂O), ozono troposférico (O₃), clorofluorcarbonos (CFC's), hidrofluorcarbonos (HFC's), perfluoro-carbuos (PFC's) y hexafluoruro de azufre (SF₆) [3]. Es especialmente notable este aumento a partir de la proliferación de la industria en la Revolución Industrial, a mediados del siglo XVIII, tal y como se observa en la **Fig. 1.2** [4].

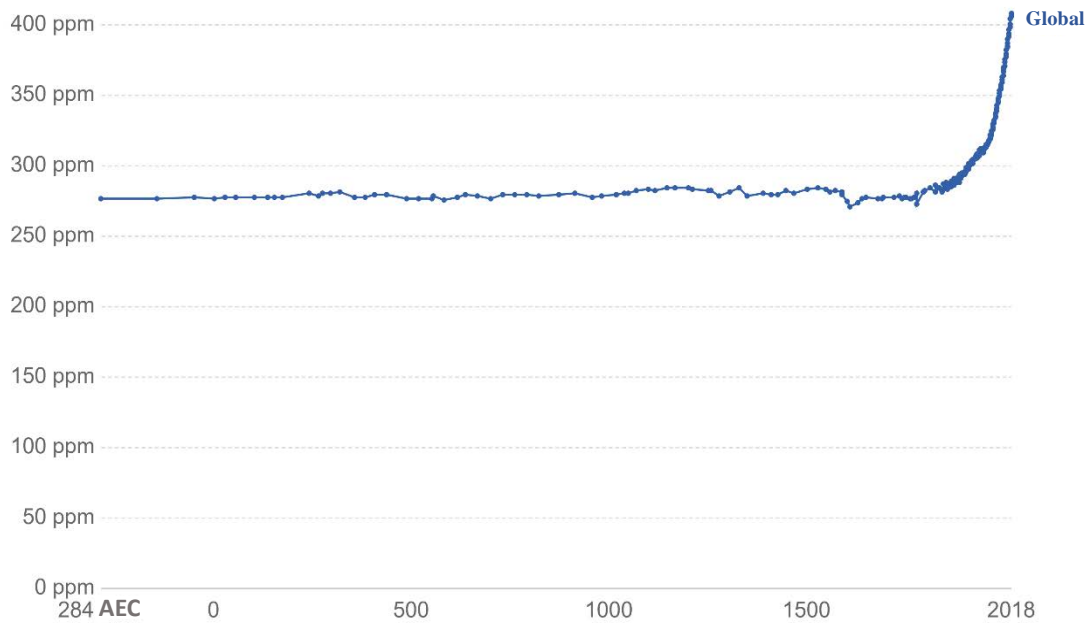


Fig. 1.2. Concentración atmosférica de dióxido de carbono (CO_2) a nivel global, medido en partes por millón (ppm) desde el 284 Antes de la Era Común (AEC) hasta 2018 [2].

La llegada de la máquina de vapor, los motores de combustión y la electricidad en sustitución del trabajo manual y animal, dieron paso a la Revolución Industrial y con ello la transformación del modelo energético, social, demográfico, económico y tecnológico [5]. El aumento poblacional, la aparición de nuevos medios y vías de transporte (como el ferrocarril o el barco de vapor) o la proliferación de la industria, derivaron en un aumento de la demanda energética que se suple por medio del aumento de la quema de combustibles fósiles, que rompe con el establecido ciclo del carbono, siendo por tanto la principal causa (junto con los incendios, deforestación, obtención de cementos, desgasificación del carbón y fugas) del aumento en la cantidad de CO_2 y CH_4 en la atmósfera [4]. En la última medición realizada en el observatorio Mauna Loa en diciembre de 2019 se ha observado un nuevo valor record en la concentración de CO_2 de 411,76 ppm (**Fig. 1.3, A**) [6] y en la de CH_4 de 1870,5 ppb (**Fig. 1.3, B**) [6], superando los 278,3 ppm de CO_2 determinados en 1734 [2] y los 680 ppb de CH_4 en 1730 [7].

Si las concentraciones de GEI siguen la tendencia seguida hasta la fecha, las previsiones de concentración de CO_2 y CH_4 para 2100 son de 950 y 3600 ppm respectivamente según los escenarios más pesimistas (RCP8.5, vía de concentración representativa) y de 500 y 1550 ppm respectivamente según los escenarios más optimistas (RCP2.6) [1,8]. La principal consecuencia del aumento de la concentración de GEI en la atmósfera es el aumento de la temperatura global media, la cual ya se ha elevado en 1°C desde la época preindustrial por el aumento de la concentración de GEI. De manera que, si esta concentración continúa subiendo en la misma proporción que hasta ahora, la temperatura se incrementará 1.5°C para 2040 y hasta 6°C en 2100 [9]. El aumento de la temperatura media global a su vez incrementa la fusión del hielo existente en los polos, glaciares y casquetes polares; que supone una elevación del nivel del mar de entre 0,45 a 0,73 m en 2100 para los escenarios RCP2.6 y RCP8.5 respectivamente, sumados a los 0,19 m que ha aumentado hasta 2014 [8]. El aumento de la concentración

de CO₂ en la atmósfera, sumado al aumento de la temperatura global media y el aumento del nivel del mar, provocará una disminución del pH de entre 0,14 a 0,32 en escenarios RCP2.6 y RCP8.5 respectivamente, debido a una mayor disolución de CO₂ en el agua del mar, ya habiendo bajado en 0,1 su valor en 2014 [8].

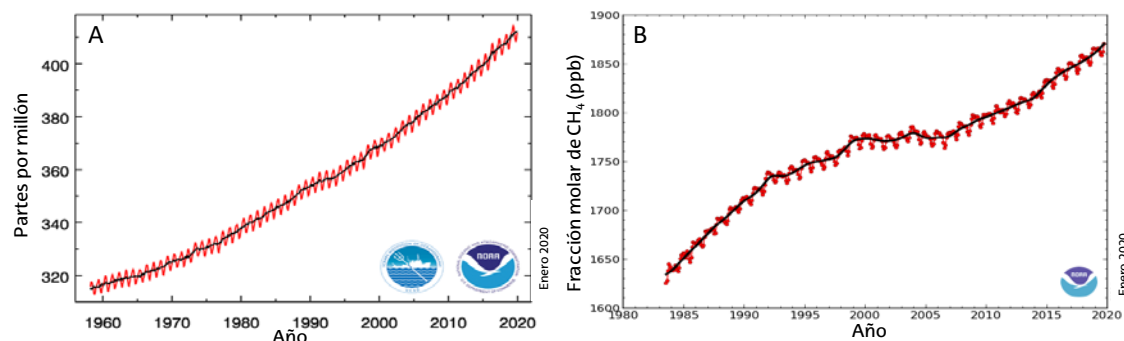


Fig. 1.3. Evolución de la concentración de CO₂ y CH₄ en la atmósfera en los últimos 60 y 40 años respectivamente, medidos en ppm y ppb de la fracción molar de CH₄ respectivamente, en el observatorio de Mauna Loa [6].

1.2. Medidas adoptadas para luchar contra el cambio climático

Los problemas derivados del cambio climático descritos en el apartado anterior son problemas actuales que atañen a todos los países del mundo. Es por ello, que las medidas para su remediación y recuperación deben ser acordados por el mayor número de países posible, por medio de compromisos realistas para su cumplimiento. Desde que se consideró el cambio climático como un problema grave, en la Primera Conferencia Mundial sobre el Clima en 1979, se han sucedido varias reuniones y acuerdos internacionales de carácter científico y político impulsadas por las Naciones Unidas para establecer las estrategias para hacer frente al cambio climático [1,3,4]. Entre los eventos más relevantes acontecidos desde 1979, destaca en primer lugar el desarrollo del Protocolo de Kyoto en 1997, por el cual se establecen límites de emisiones y herramientas para facilitar el cumplimiento con cierta flexibilidad [1,3].

El acuerdo de París se enfoca en dar continuidad a aquellos compromisos acordados en el Protocolo de Kioto, a partir del fin de su vigencia en 2020. En este marco se plantean en el artículo 2, tres objetivos principales [10]:

- Limitar el aumento de la temperatura global del planeta en menos de 2°C, a poder ser en 1,5°C, sobre los valores pre-industriales
- Mejorar la capacidad de actuación contra los efectos adversos del cambio climático y un progresivo desarrollo con reducción de GEI, siempre que no comprometa la producción de alimentos.
- Aumentar la financiación para superar las consecuencias climáticas y conseguir mitigar sus efectos, reduciendo los GEI.

Los países y/o agrupaciones de países establecen paquetes de medidas que contienen legislación vinculante que garantizará el cumplimiento de los objetivos climáticos y de energía asumidos, con el fin de alcanzar los objetivos establecidos en el Protocolo de Kyoto y posteriormente en el acuerdo de París. En el caso de la Unión

Europea, los principales objetivos que incluye la estrategia Europea 2020 son tres: reducir un 20 % las emisiones de gases de efecto invernadero respecto a los niveles de 1990, lograr que el 20 % de energía de la Unión Europea (UE) proceda de fuentes renovables y mejorar la eficiencia energética en el 20 % [11]. La reducción de los GEI pasa por un mayor control del Régimen de comercio de derechos de emisión (RCDE) que abarca el 45% de las emisiones, al corresponder con el sector de aviación y las grandes instalaciones de los sectores eléctricos e industrial, reduciendo sus emisiones un 21%. Según los últimos informes, la UE va camino de cumplir sus objetivos del compromiso del protocolo de Kioto y sus objetivos del 20% para 2020.

Los nuevos objetivos establecidos en el Marco sobre clima y energía para 2030 son mucho más exigentes, como contribución al Acuerdo de París. Los objetivos clave para el periodo de 2021 a 2030 son tres [12], siendo una extensión de los establecidos para 2020:

- Reducir las emisiones de GEI en al menos un 40 %.
- Lograr que al menos el 32 % de la energía proceda de fuentes renovables.
- Mejorar la eficiencia energética en al menos un 32,5%.

Alcanzar la reducción de los GEI en al menos el 40% requiere de una reducción en las emisiones del RCDE de al menos el 43 % con respecto a 2005, y el resto de sectores en un 30 %, siendo estos objetivos obligatorios para cada Estado miembro [12].

Finalmente, frente a las últimas consecuencias observadas de catástrofes naturales a nivel mundial, el Parlamento Europeo (PE) ha declarado el estado de emergencia climática y medioambiental, al que se han sumado otros países, incluido España, el día 21 de enero de 2020. En esta fase, la UE ha intensificado sus esfuerzos desde el punto de vista legislativo y presupuestaria para reducir las emisiones de GEI al 55 % en 2030 y eliminarlas para 2050, con el fin de limitar el calentamiento global a un máximo de 1,5°C [13].

1.3. Demanda energética y transformación de las fuentes de energía

El desarrollo tecnológico que supuso la revolución industrial, desencadenó la sustitución de la energía proporcionada por hombre y animales, por la obtenida por máquinas. Las principales fuentes de energía durante la Revolución Industrial se basaban en combustibles de origen fósil, especialmente de carbón. La creciente demanda energética requirió de un aumento de la infraestructura basada en estas fuentes de energía, tanto para su extracción como su aplicación, lo que provocó una fuerte dependencia de las fuentes de energía fósiles [14]. Este modelo energético ha seguido creciendo con el fin de satisfacer la ascendente demanda energética de los distintos países, como se observa en la **Fig. 1.4** para los últimos 45 años, creciendo en torno a los recursos disponibles. El aumento en el consumo total de energía es especialmente significativo en los países asiáticos no pertenecientes a la Organización para la Cooperación y el Desarrollo Económicos (OCDE), ascendiendo de 1634 Mtpe en 2002 hasta los 3317 Mtpe en 2017, situándose en segunda posición en el consumo de energía, detrás de los países miembros de la OCDE, con 3711 Mtpe en 2017. Esto resulta en un

consumo total de energía global en 2017 de 9717 Mtpce, que duplica el valor determinado el 1971.

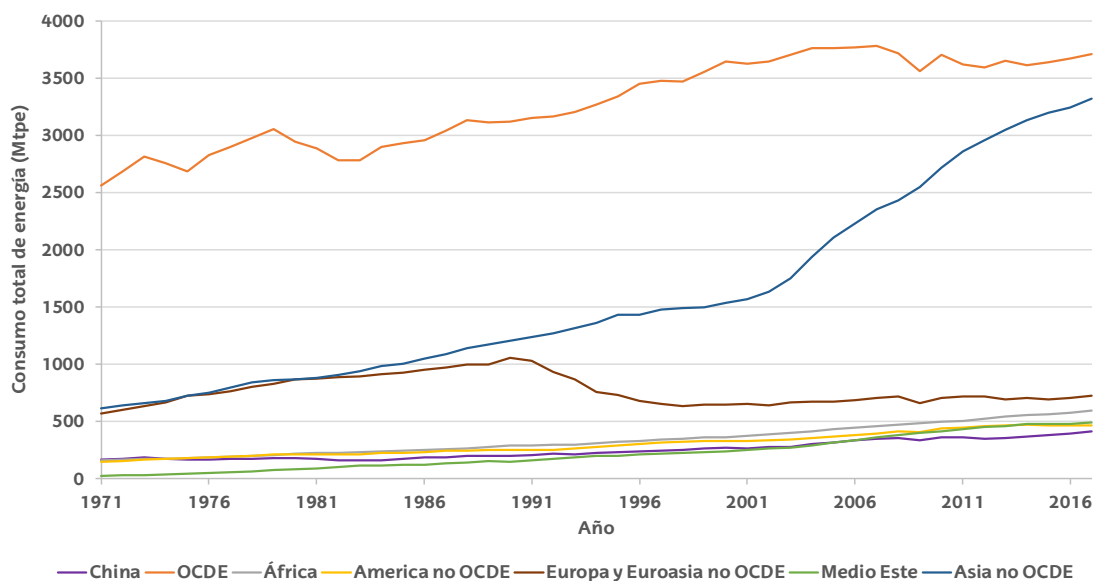


Fig. 1.4. Consumo total mundial de energía por región desde 1971 a 2017 [15].

Al pasar a considerarse el cambio climático como un problema grave en 1979, se le dio un impulso al desarrollo de las fuentes de energía renovables, suponiendo un cambio en el mapa energético, como se observa en la **Fig. 1.5**, donde se observan cambios progresivos en la cantidad de energía producida por fuentes renovables entre 1971 y 2017. Sin embargo, la adaptación de la industria a las nuevas fuentes de energía es un proceso lento y progresivo. Inicialmente está siendo necesario complementar la obtención de energía de fuentes renovables con fuentes de energía fósil, para poder suplir toda la demanda energética sin interrupciones. El desarrollo de la tecnología en este campo está haciendo grandes progresos, con el fin de ir sustituyendo las fuentes de energía tradicionales por fuentes limpias y renovables en distintos sectores, tal y como se plantea en el plan de medidas de la UE, descritas en el apartado anterior.

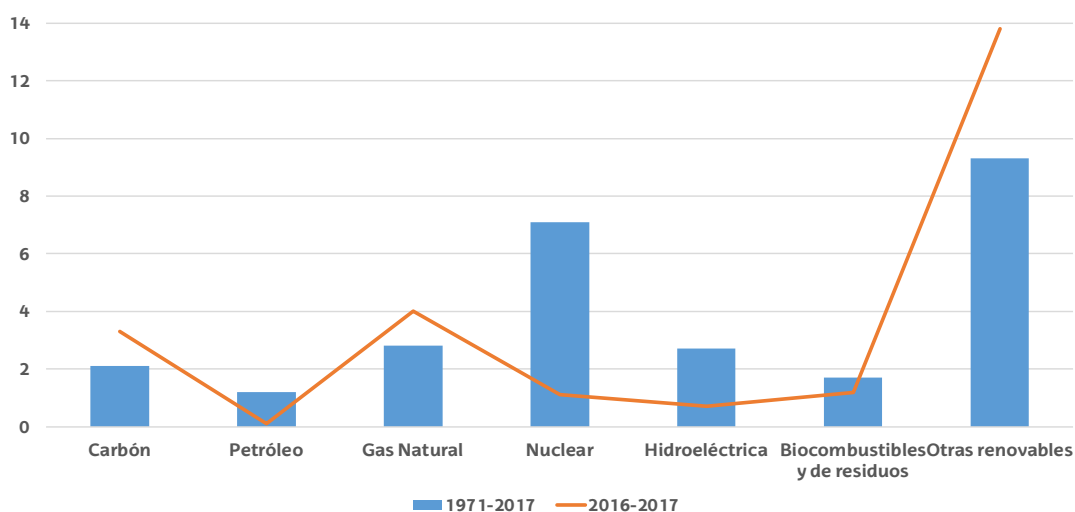


Fig. 1.5. Cambio en la cantidad anual global de producción de energía a partir de distintos combustibles entre 1971 y 2017 [16].

Las medidas adoptadas por los distintos gobiernos, están comenzando a modificar los sistemas productivos de la energía, tal y como se observa en la **Fig. 1.6**, al comparar las fuentes de suministro energético por combustible entre 1971 y 2017. Desde 1971 hasta hoy, se observa un fuerte aumento del suministro total de todos los tipos de energía, desde los 5514 Mtpe de 1971 hasta los 13971 Mtpe de 2017, con el fin de asegurar el aumento de la demanda energética. Atendiendo a la proporción de unas fuentes a otras, se observa una disminución del suministro de petróleo (del 44,2 al 31,8 %), a costa de un aumento en el gas natural (del 16,2 al 22,2 %), energía nuclear (del 0,5 al 4,9 %), hidroeléctrica (del 1,9 al 2,5 %) y otras renovables (del 0 al 13,8 %), tal y como se observa en la **Fig. 1.6**. La fuerte demanda energética requiere de fuentes de energía estables y con alta densidad energética. Esto, sumado a la estructura industrial basada en el carbón, resultan en un significativo aumento en su suministro (de 1435 a 3786 Mtpe), y una estabilidad basada en la proporción con respecto al resto de fuentes de energía, del 26,0 al 27,1 %, entre 1971 y 2017.

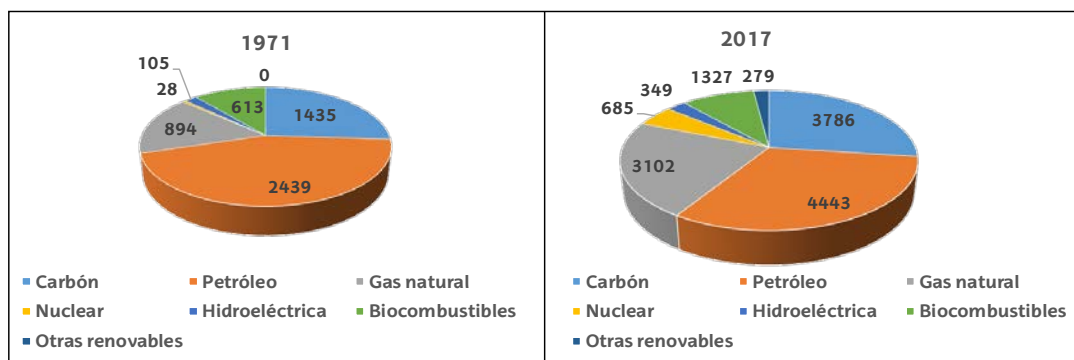


Fig. 1.6. Comparativa del suministro total de energía primaria por combustible entre 1971 y 2017, en millones de toneladas de petróleo equivalentes (Mtpe) [17].

Y es que, a pesar de las medidas adoptadas por la Unión Europea para incentivar las energías limpias y renovables, en sustitución de las fuentes de energía fósil, más contaminantes, se observa que el consumo total mundial de derivados del petróleo sigue aumentando desde 2592,65 Mtpe en 1990 hasta 3970,18 Mtpe en 2017, en mayor medida que el resto de fuentes de energía tal y como se observa en la **Fig. 1.7**. El carbón tras un periodo de caída ha remontado, recuperando y superando el consumo a partir del 2000, situándose en 1020,37 Mtpe. Las otras grandes subidas, en cuanto a consumo, se corresponden con la electricidad (de 934,43 Mtpe a 1837,64 Mtpe), seguida del gas natural (de 943,51 Mtpe a 1502,34 Mtpe). Aunque en menor proporción, el aumento del consumo de biocombustibles y de aprovechamiento de residuos es progresivo en el tiempo (de 790,24 Mtpe a 1037,76 Mtpe), al igual que el correspondiente a energías renovables como solar o eólica (de 3,38 Mtpe a 45,29 Mtpe). A pesar del bajo valor de estas energías, en relación con el resto, su aumento supone un incremento del 1240 % desde 1990 a 2017.

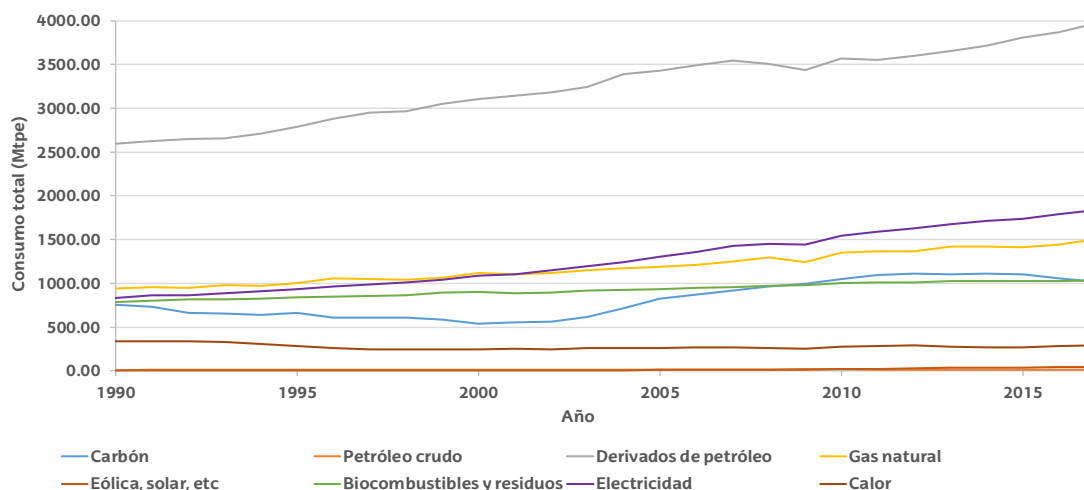


Fig. 1.7. Evolución del consumo mundial total de energía entre 1990 y 2017, por fuente [18].

Aunque la tendencia general siga siendo la de emplear combustibles fósiles como principal fuente de energía, ante el progresivo aumento de la demanda energética, las fuentes energéticas que más crecen son las basadas en tecnologías limpias y fuentes renovables. Esta idea se apoya en la creciente preocupación ante el cambio climático, por la fuerte contribución al efecto invernadero por parte de los combustibles fósiles, que arrastra a la movilización de recursos por parte de todos los países, para que de forma progresiva se pueda frenar el consumo de las fuentes de energía fósil, en pos de las renovables [3].

1.4. Fuentes renovables de energía

Se considera fuente renovable, por definición, toda energía que procede de procesos naturales que se regeneran constantemente, como es el caso de la solar, eólica, biomasa, geotérmica, hidroeléctrica, del mar (olas y mareas), y biocombustibles, o a otros vectores energéticos derivados de los anteriores, como el hidrógeno y sus derivados, procedente de fuentes renovables [19]. Presentan grandes beneficios desde un punto de vista ecológico, debido a que son fuentes de energía de procedencia natural, limpia e inagotable. Además, dada su naturaleza es posible su uso de manera descentralizada, a razón de poder proveer de energía a poblaciones pequeñas o menos accesibles [20].

La **energía solar** es la fuente renovable más abundante, pudiendo captarla de forma directa (de la fuente, el sol, directamente) ascendiendo esa energía a $3,8 \cdot 10^{23}$ kW o indirectamente (procedente de la captada por la tierra), que se corresponde con una energía de $1,8 \cdot 10^{14}$ kW. Es una energía disponible en cualquier lugar del mundo, incluso en aquellos lugares donde no existe red eléctrica, manteniendo un precio constante. Se puede emplear como fuente de energía térmica directa, para elevar la temperatura de los fluidos; como fuente de energía térmica indirecta para transformar la energía de la radiación solar en energía eléctrica; o como fuente eléctrica por la transformación de la energía solar directa haciendo uso del **efecto fotovoltaico (PV)**, el cual depende de que la interacción entre los fotones posea una energía igual o mayor a la correspondiente a la banda prohibida del material fotovoltaico. Pese a que la luz solar es gratuita y que los módulos PV generan electricidad sin emisiones, ruido o vibración, los costes de

generación de energía son significativamente altos, debido entre otras cosas a la baja densidad energética de los módulos PV y a que la fuente de energía depende de las condiciones meteorológicas, de la estación y de la hora, lo que convierte a esta fuente en una fuente intermitente o variable [20].

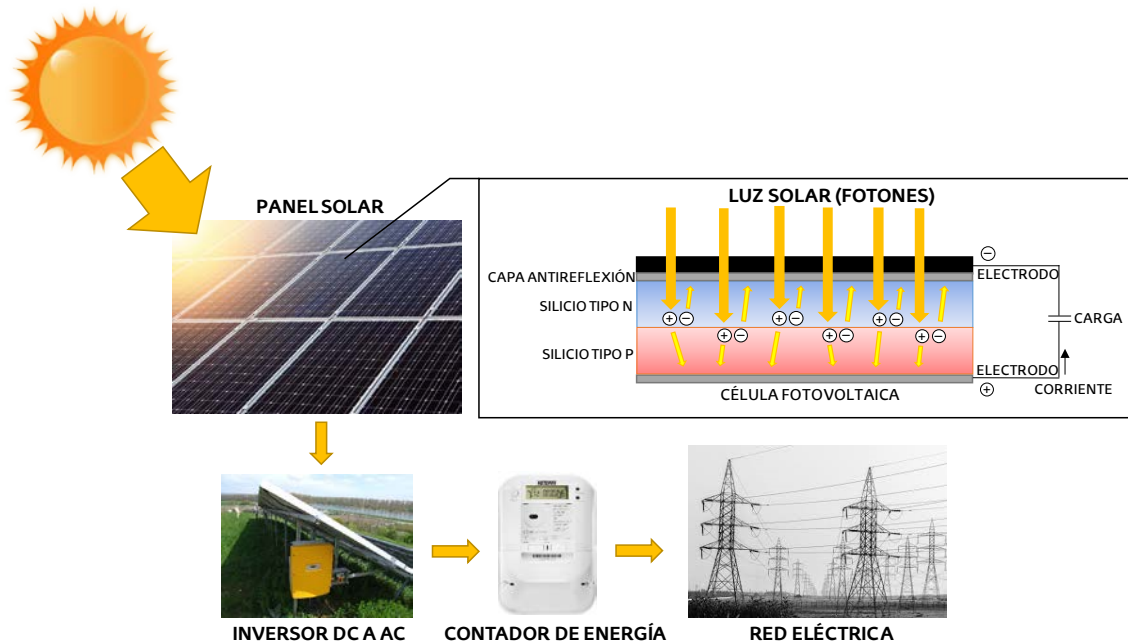


Fig. 1.8. Esquema de funcionamiento de una célula fotovoltaica, transformando la energía solar en energía eléctrica, y su incorporación a la red eléctrica [21].

La **energía eólica** se emplea para la generación de energía eléctrica, por la transformación de la energía motriz ejercida por el viento en energía rotacional, a través del uso de turbinas eólicas. Esto permite proveer energía eléctrica a poblaciones más aisladas. Aunque para garantizar un suministro continuo de energía, es necesario combinar esta fuente con otras, debido a su falta de continuidad en el tiempo. El potencial mundial de producción de energía eólica se estima que es de 26.000 TWh/año, no variando su precio con el tiempo y permitiendo el ahorro de grandes cantidades de petróleo y por tanto de grandes cantidades de emisión de GEI [20].

La **energía hidroeléctrica** es una tecnología madura, popular para la obtención de más de un sexto de la energía eléctrica mundial de forma fiable y a precios competitivos desde hace más de un siglo, y además, ha permitido la obtención de energía mecánica desde hace más de 2.600 años [22]. La energía potencial gravitacional almacenada en el agua es transformada en energía rotacional, que a su vez se transforma en energía eléctrica a su paso por la turbina, con una eficiencia de hasta el 95 % en condiciones óptimas de trabajo. El potencial mundial de producción de energía hidroeléctrica es de 15.955 TWh/año, siendo la cantidad generada en 2018 de tan solo 4.200 TWh [23]. No siempre se ha considerado como energía renovable, debido a su fuerte impacto ambiental. Sin embargo, sí que debe de formar parte de esta categoría, al no considerarse una fuente limitada, ni contribuir con emisiones de GEI [24].

Por el término de **bioenergía** se incluyen 3 productos principalmente: biogás, biodiesel y biomasa. El **biogás** procedente de la digestión anaerobia de diferentes

materiales de desecho (residuos orgánicos, abono animal o biomasa vegetal), es la tecnología más beneficiosa desde un punto de vista medioambiental y económico (por el máximo aprovechamiento de recursos de desecho) de todas las formas de bioenergía. El biogás puede producirse fácilmente cuando existe demanda, y en caso de exceso, almacenarse o transportarse por la infraestructura del gas natural, al estar compuesto principalmente por CH_4 (40-70 %) y CO_2 (30-60 %) [20]. El **biodiesel** es un combustible líquido empleado en sustitución parcial o total del diésel de origen fósil, al no contribuir con nuevas emisiones netas de GEI al ciclo del carbono, al proceder de la transesterificación de aceites de origen vegetal (catalizado por ácidos y/o bases), su ventaja adicional es que sus propiedades físico-químicas se asemejan a las del diésel tradicional [20]. La **biomasa** se puede transformar en líquidos por un proceso de pirólisis o en carbón vegetal (charcoal) y un gas de bajo poder calorífico (o gas productor), por un proceso de conversión termoquímica, que tiene lugar en los gasificadores, pudiendo emplearse para la combustión, tras un proceso de purificación previa a la combustión [20].

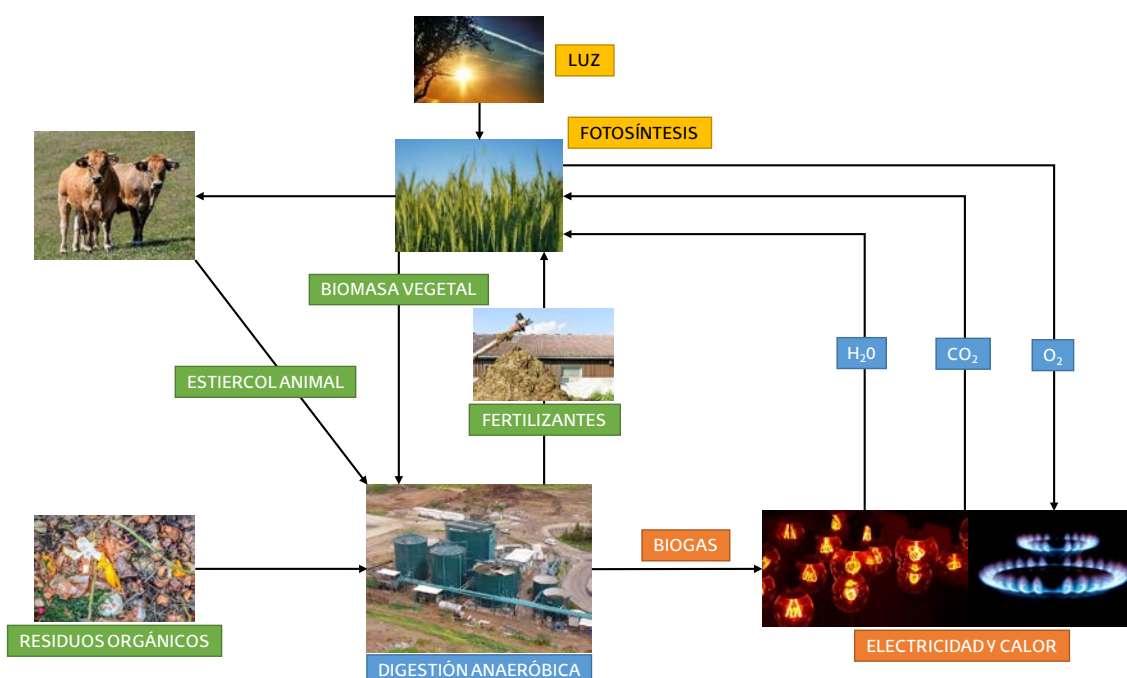


Fig. 1.9. Representación esquemática del ciclo sostenible de la co-digestión anaeróbica de estiércol animal y residuos orgánicos, adaptado de [20].

El **hidrógeno** es uno de los vectores energéticos más prometedores por su carácter limpio y sostenible, al poseer mayor densidad energética (140 MJ/kg) que los combustibles sólidos, líquidos y gaseosos más habituales (50 MJ/kg), todo ello sin liberar contaminantes como productos de reacción: sólo agua [25]. El hidrógeno es uno de los componentes más abundante de la naturaleza. Sin embargo, el hidrógeno gas no se encuentra en la naturaleza, sino que se presenta formando parte de otros compuestos. Su obtención se hace por la ruptura del enlace que lo une a otros elementos. Las fuentes principales para la obtención de hidrógeno son fuentes de energía primaria, entre las que se incluyen carbón, gas natural y petróleo, pero también fuentes de energía renovables intermitentes y biomasa [26]. Los principales procesos de obtención de hidrógeno renovable y no renovable son la electrólisis de agua, fuentes biológicas, pirólisis y

gasificación de biomasa, gasificación de carbón, reformado de petróleo/nafta o reformado con vapor de gas natural y metano [25]. La **electrólisis del agua** es el proceso más limpio para la obtención de hidrógeno, sin embargo, debido a su alto consumo energético y bajo ratio de producción, no se considera el proceso más competitivo desde un punto de vista económico [25] a día de hoy. Con el empleo de electricidad procedente de otras fuentes renovables como la solar o la eólica, se está aumentando la viabilidad de este proceso para el almacenamiento químico de la energía intermitente de estas fuentes.

Tal y como se ha mencionado anteriormente, el uso de energías renovables facilita el acceso a la energía a núcleos poblacionales menores o menos accesibles, sin aumentar las emisiones de GEI. Sin embargo, son fuentes intermitentes y variables, cuya producción depende de diversos factores, como de la meteorología, de la época del año o de la hora del día, como ocurre en la energía eólica y solar. Debido a esto, para garantizar la continuidad del suministro energético procedente de energías renovables, es imprescindible el correcto almacenamiento del excedente para su uso en momentos de menor producción [27].

1.5. Almacenamiento de energía

Existe gran variedad de tecnologías de almacenamiento, pudiendo clasificarlas según diferentes criterios (tiempo de almacenamiento, naturaleza de la energía almacenada, etc), que son diferenciados por la forma de energía a la cual se transforma para su almacenamiento. Bajo este criterio se recogen las siguientes categorías: almacenamiento de energía mecánico, eléctrico, térmico, biológico y químico. La elección de la tecnología adecuada dependerá de la función del almacenamiento, la fuente de energía, medio de transporte y el espacio de almacenamiento energético disponible [28].

1.5.1. Almacenamiento mecánico de energía

El almacenamiento de la energía eléctrica se realiza de la forma más fácilmente almacenable, como es el caso de la energía mecánica. El problema principal de estos sistemas de almacenamiento es la pérdida de energía de hasta el 50 %, que se produce debido a la ineficacia en su transformación [29].

El **almacenamiento hidroeléctrico de bombeo** (PHES del inglés, Pumped Hydroelectric Energy Storage) se basa en la elevación de masas de agua a unos depósitos, mediante el empleo de bombas, durante periodos de baja demanda. En periodos de mayor demanda, el agua se libera y se dirige por un sistema de turbinas para generar energía eléctrica (*Fig. 1.10*) [29]. La eficiencia de este tipo de instalaciones se encuentra entre el 65 y el 85 %, que puede alcanzar incluso el 87 %, siendo el sistema de almacenamiento de energía más común [27]. De este sistema derivan los **sistemas de almacenamiento de energía gravitacional** (GES del inglés, Gravity Energy Storage), adaptados de los anteriores y basados en el uso de la energía gravitacional, evitando los problemas del espacio de almacenamiento. Uno de los sistemas basados en esta tecnología, es un sistema cerrado que emplea un pistón deslizante de gran tamaño, suspendido en un eje sellado y sin fugas (*Fig. 1.11*). La carga se hace empleando la electricidad para elevar el pistón en el eje. Cuando se necesita energía, se libera el pistón

que fuerza el flujo de agua a través de una turbina que hace girar el motor/generador para producir electricidad, con una eficiencia del 80 % [27].

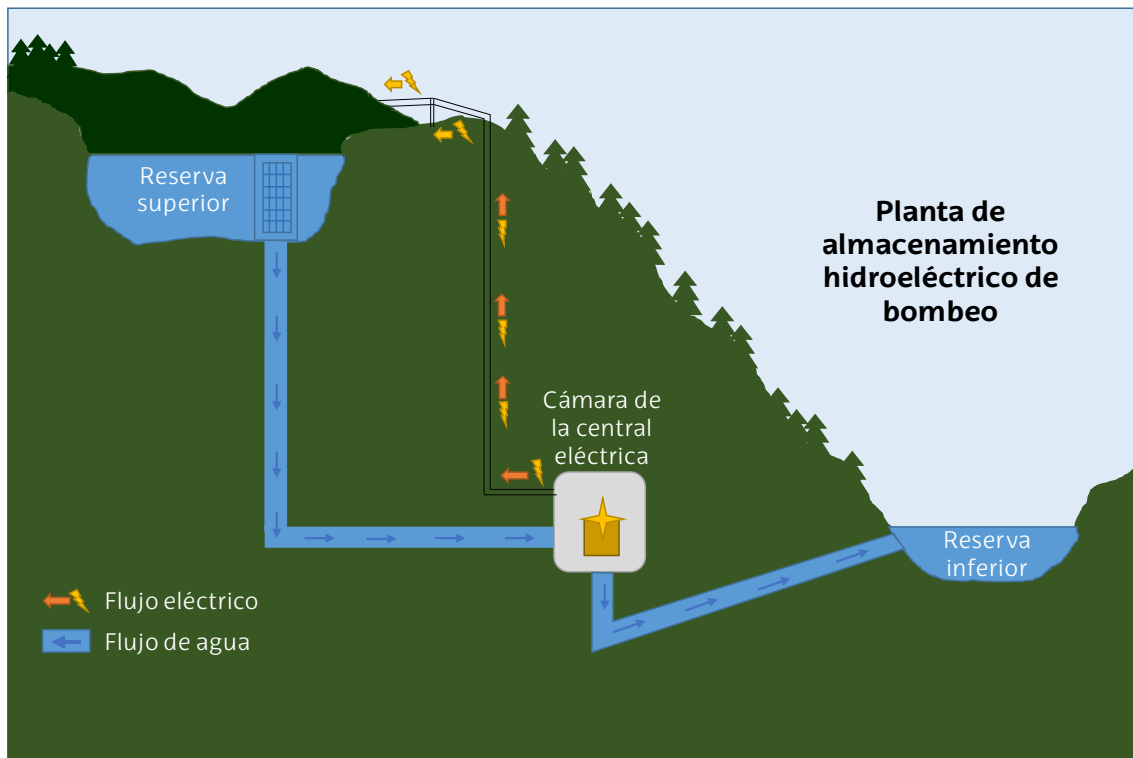


Fig. 1.10. Esquema de una planta de almacenamiento hidroeléctrico de bombeo, adaptado de [27].

La **batería inercial** (FES del inglés, Flywheel Energy Storage) transforma la energía eléctrica en energía cinética rotacional, transfiriéndole momento angular al rotor del motor, que actúa como componente de almacenamiento, volviendo a transformarse esa energía cinética, en energía eléctrica a través del generador (motor) cuando es necesaria [27]. Éstos son sistemas de almacenamiento de energía eficientes, pero para cortos periodos de tiempo, debido a la presencia de fuerzas de fricción que reducen la eficiencia del sistema con el tiempo, a pesar de operar en condiciones de baja presión o incluso vacío para reducir este efecto [29].

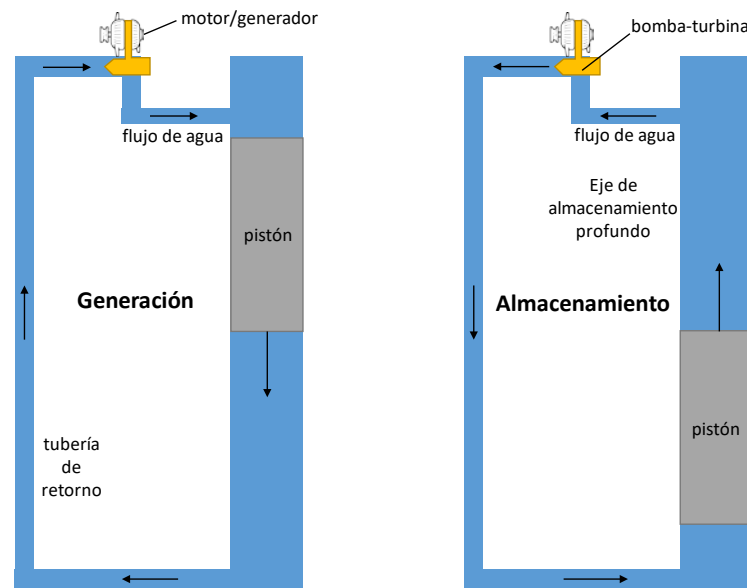


Fig. 1.11. Esquema del funcionamiento de una planta de almacenamiento de gravitacional, adaptado de [27].

El **almacenamiento de energía con aire comprimido** (CAES del inglés, Compressed Air Energy Storage) emplea la energía eléctrica para comprimir aire y almacenarlo, en momentos de baja demanda. Cuando la demanda aumenta, se libera el aire comprimido almacenado, a través de una turbina de gas, donde se expande, liberando energía con una eficiencia que puede alcanzar el 70 % [27].

Actualmente se está empezando a implantar el sistema de **almacenamiento de energía mediante el sistema líquido-pistón** (LPES del inglés, Liquid-Piston Energy Storage). Es una tecnología novedosa, basada en la compresión de un gas (generalmente nitrógeno o aire) en el interior de un depósito, empleando para ello un líquido bombeado a presión, en momentos de baja demanda eléctrica. La energía se almacena como gas comprimido, el cual se libera expandiéndose cuando es necesaria la energía, forzando al líquido a pasar a través de la turbina que acciona el generador para proporcionar electricidad. La eficiencia energética de este sistema puede llegar a alcanzar el 73 %, aunque cuenta con la limitación de tener menor densidad energética y posibilidad de fugas [27].

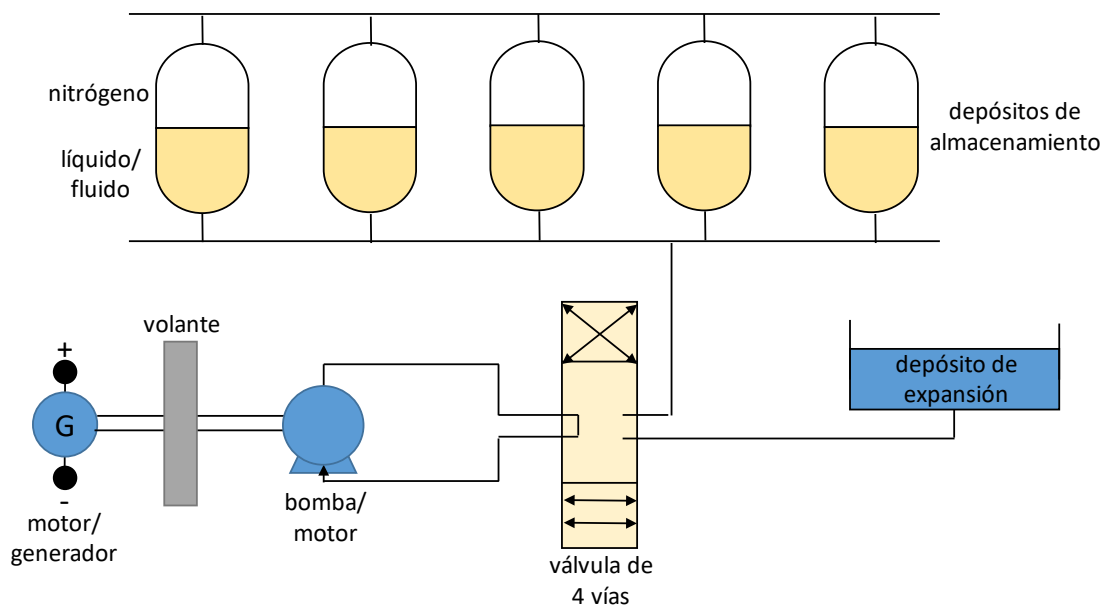


Fig. 1.12. Esquema de funcionamiento de un sistema de almacenamiento de energía líquido-pistón, adaptado de [27].

1.5.2. Almacenamiento eléctrico de energía

El almacenamiento de la energía eléctrica, de esta forma, se realiza en forma de cargas eléctricas entre dos placas metálicas o conductoras, separadas entre sí por un medio aislante o dieléctrico, con un determinado voltaje aplicado. Es por ello, que la capacidad de almacenamiento dependerá del tamaño, distancia y material de las placas [29].

Los **supercapacitores**, condensadores electroquímicos de doble capa o ultracapacitores, almacenan energía en los dos condensadores en serie de la doble capa eléctrica que se forma entre cada uno de los electrodos de los iones electrolíticos. Estos sistemas pueden almacenar grandes densidades de energía, en comparación con los condensadores convencionales, y pueden responder rápidamente a cambios en la demanda de energía. Los altos costes de estos sistemas, además de su rápida descarga (del 5 % diario), hacen que sean sistemas útiles para almacenamientos de energía a corto plazo [27]. Actualmente se están intentando solventar los problemas derivados de la desactivación y mejorar la densidad de almacenamiento, introduciendo carbono nanoestructurado como separadores de láminas de **grafeno**. Como en el ejemplo de la Fig. 1.13, compuesto por láminas de grafeno hidrogenado con cobre nanoporoso (hnc-G), separadas entre sí por la capa del electrolito polimérico y a su vez cubiertas por ambos lados por láminas de tereftalato de polietileno recubierto con oro (Au-PET) [30]. Sin embargo, aún los costes de aplicación son demasiado altos y debido a la alta porosidad, la densidad será demasiado baja, llenándose del electrolito que aumentará la masa y el volumen del dispositivo final. Debido a esta situación, aún se requiere de mayor ingeniería de estos compuestos antes de su aplicación [31].

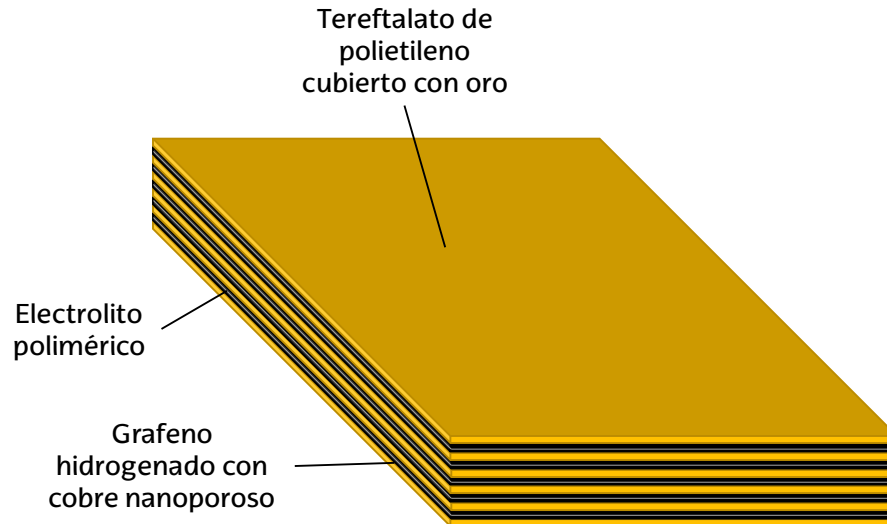


Fig. 1.13. Representación esquemática de un ejemplo de supercapacitor con grafeno [30].

Por otro lado, las **baterías** suministran energía eléctrica, almacenada como energía química, obtenida por medio de las reacciones electroquímicas. Hay baterías de diversos tamaños y capacidades de almacenamiento, alcanzando un rango de eficiencia de entre 60 y 80%, según sea el ciclo operativo y el tipo de celda electroquímica. Entre las baterías más comunes, destacan las baterías de sulfuro de sodio, de electrodos de cloruro de níquel y sodio, redox de vanadio, de hierro cromo, de zinc-bromuro, de zinc-aire, de plomo-ácido, de litio, de níquel-cadmio, etc [27]. Debido a las características hidrofílicas, la electronegatividad y los abundantes grupos funcionales del **grafeno** y sus derivados, se ha empleado en la preparación de diferentes tipos de baterías, dando lugar a una mejora de la capacidad de transmisión de la energía, en la estabilidad del ciclo, en la actividad electroquímica e incluso puede proteger los materiales activos del contacto directo con el electrolito. Esto hace de las baterías modificadas con **grafeno**, una tecnología con gran potencial, en la que se está haciendo grandes avances, pero que aún es necesario un mayor desarrollo [31].

1.5.3. Almacenamiento magnético de energía

Estos sistemas están basados en el almacenamiento de la energía en un campo magnético. La viabilidad de esta tecnología va ligada al desarrollo y utilización de materiales superconductores, que reduzcan la resistencia eléctrica al mínimo, de este modo se reducen las pérdidas al máximo posible. La cantidad de energía que puede almacenarse en este tipo de sistemas va a depender de dos factores: la intensidad del campo magnético y de la permeabilidad del material [29].

Los **superconductores magnéticos** se basan en el empleo de campos magnéticos para el almacenamiento de energía a temperaturas inferiores a la temperatura crítica de superconducción (aproximadamente 3 K) acercándose de este modo a una resistencia cercana a cero. La alta eficiencia de esta tecnología requiere de un alto coste de capital y de operación [27].

1.5.4. Almacenamiento térmico de energía

Son sistemas de almacenamiento de energía en forma de calor, basados en el almacenamiento del excedente de energía procedente de fuentes intermitentes. Pueden basarse en el calor sensible, latente o termoquímico, siendo las principales variables que determinan estos sistemas la escala y el método de almacenamiento empleado. La capacidad de almacenamiento de estos sistemas depende principalmente de la **cantidad de tiempo** que sea necesario almacenar la energía no siendo sistemas adecuados para el almacenamiento de energía a largo plazo, debido a las pérdidas de energía en forma de calor [29].

En los sistemas basados en **calor sensible**, el almacenamiento se consigue con un aislamiento físico que impida la pérdida de calor del material. Los materiales se pueden almacenar en estado líquido (agua caliente, fluidos oleosos y sal fundida) o en estado sólido (almacenamiento por llenado de metales y rocas). Es un sistema de almacenamiento común por su bajo precio, pero que precisa de grandes volúmenes debido a su baja densidad energética [27,29,32].

Los sistemas basados en **calor latente** se basan principalmente en el almacenamiento de la energía de cambio de fase líquido-sólido de los materiales, debido a que requiere menor volumen para el cambio de fase, manteniendo ese estado hasta que sea necesario su uso. Las dificultades de estos sistemas se centran en mantener el material dentro del sistema, inestabilidad química, reducida capacidad de almacenamiento y altos costes [27,29,32].

En los **sistemas de almacenamiento termoquímico**, la energía es almacenada a través de la etapa endotérmica de una reacción reversible, liberando esa energía durante la etapa exotérmica, por lo que es un buen sistema para el almacenamiento de la energía a largo plazo, pudiendo obtenerse altas densidades de energía, dependiendo de los compuestos seleccionados para la reacción [27,29,32].

1.5.5. Almacenamiento químico de energía

En este tipo de sistemas, la energía a almacenar se emplea en una determinada reacción química reversible para obtener un compuesto químico, el cual se almacenará para la obtención de energía en momentos de mayor demanda. Las baterías son un ejemplo de almacenamiento electro-químico, como ya se ha visto en el punto 1.5.2, que permite el almacenamiento de una gran cantidad de energía en un pequeño espacio [29]. Los compuestos químicos almacenados tienen alta densidad energética, lo que hacen de este sistema de almacenamiento una buena alternativa frente a otros sistemas de almacenamiento. Los componentes químicos más empleados para su almacenamiento son hidrógeno, metano, amoníaco, metanol, etanol, butanol u otros hidrocarburos [27].

La **tecnología Solar-to-Fuels (StF)** se basa en la producción de combustibles sintéticos a partir de energía térmica, basándose especialmente procedente del sol, dióxido de carbono y agua. Esta tecnología se basa principalmente en procesos de electrólisis y procesos reductivos fotoelectroquímicos, termoquímicos y fotocatalíticos, todos ellos basados en la energía solar como fuente de energía. De este modo se diferencian dos vías: i) la obtención de gas de síntesis empleando energía solar

fotovoltaica (Power-to-Liquid, PtL), y ii) la obtención por reacciones de reducción con energía solar tanto de CO₂ como de H₂, que permiten obtener gas de síntesis por el proceso de gasificación húmeda (WGS) y gasificación húmeda inversa (RWGS) respectivamente [32].

La **tecnología Power-to-Liquid (PtL)** se emplea para la obtención de combustibles líquidos por procesos de síntesis tipo Fischer-Tropsch, empleando para ello gas de síntesis (syngas), que se obtiene por la reacción de gasificación húmeda inversa (RWGS). Los productos principales derivados de esta tecnología son metanol, gasolina, queroseno, dimetil éter (DME) como diésel y algunas ceras [32].

La **tecnología Power-to-Gas (PtG)** transforma el excedente de electricidad procedente de fuentes renovables en un compuesto químico gaseoso, generalmente metano, para su almacenamiento. Este producto se puede emplear directamente como combustible, o para volver a generar electricidad. Para ello, el proceso de transformación se conforma de tres etapas. En primer lugar, el excedente de electricidad se emplea para la electrolisis del agua, obteniendo de este modo hidrógeno [33]. El hidrógeno obtenido, junto con dióxido de carbono, se transforma por un proceso de conversión catalítica en metano. Finalmente, el metano se transforma en energía en una nueva etapa, según el uso que se le vaya a dar [32].

1.6. Power-to-Gas

El hidrógeno, con su alto poder calorífico (entre 120 y 141,8 MJ/kg a 298 K), superior al de combustibles de uso común como la gasolina (44 MJ/kg a 298 K) [34], abre una vía para el uso directo de este compuesto tanto en aplicaciones industriales, como para su uso en transporte, como combustible o para su incorporación en la red de gas natural [35]. Un aspecto limitante del transporte y almacenamiento de hidrógeno son su baja densidad energética por unidad de volumen (10,8 MJ/m³), sus valores límite de detonabilidad (4-75%) y de flamabilidad (18,2-58,9 % vol en aire) o su temperatura de autoignición (673 K, 844 K en aire) [34]. Otra opción apunta a la reacción del hidrógeno con dióxido de carbono procedente de fuentes industriales o naturales, para la obtención de metano. La reacción de CO₂ con H₂ se denomina reacción de metanación, en la cual se libera energía en forma de calor, debido al carácter exotérmico de la reacción. El metano resultante, al igual que en el caso del hidrógeno, se incorporará en la red de transporte y de almacenamiento del gas natural para su posterior aplicación [33]. El esquema descrito de la tecnología PtG se recoge de manera esquemática en la Fig. 1.14.

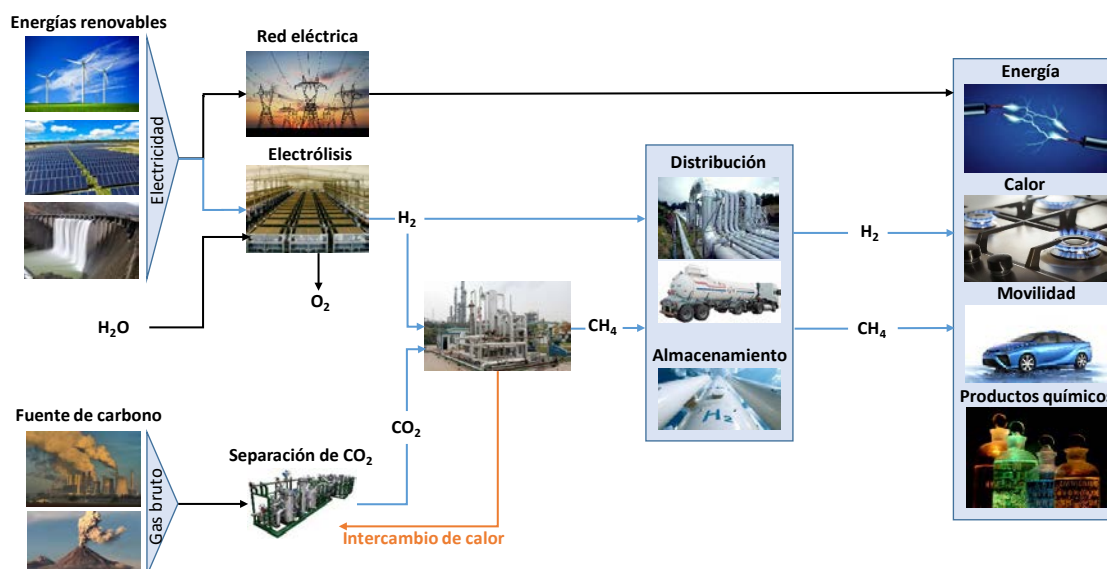


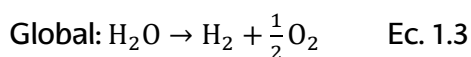
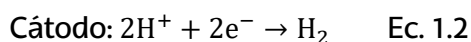
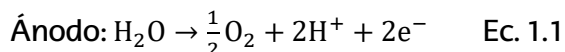
Fig. 1.14. Diagrama esquemático de la tecnología Power-to-Gas.

En resumen, el proceso de transformación de la energía excedente procedente de fuentes renovables, para su almacenamiento como metano, mediante la tecnología PtG, se lleva a cabo en dos etapas.

- Producción de hidrógeno, a través de la reacción de **electrólisis del agua**.
- Producción de metano, a través de la reacción de **metanación** de monóxido y/o dióxido de carbono con hidrógeno.

1.6.1. Electrólisis de agua

La electrólisis del agua es una reacción electroquímica, donde el agua es el reactivo que se divide bajo una cantidad de energía eléctrica suficiente entre dos electrodos. En el cátodo se produce la reacción de reducción, que da lugar al hidrógeno a partir de los protones presentes en el agua (Ec. 1.1). En el ánodo, las moléculas de agua se fraccionan en sus componentes fundamentales: oxígeno, protones y electrones (Ec. 1.2). De este modo, la reacción global es la suma de ambas, que da como resultado la reacción de electrólisis del agua (Ec. 1.3) [36], una reacción endotérmica que requiere de energía $\Delta H_r^0 = 285,8 \text{ kJ/mol}$ [37].



Existen principalmente cuatro métodos desarrollados para la electrólisis de agua, analizados en varios trabajos con diferentes materiales y condiciones de operación, entre los que se incluyen la **electrólisis de agua alcalina** (AWE del inglés, alkaline water electrolysis), las **membranas de intercambio protónico** (PEMs del inglés, proton exchange membranes), las **membranas de intercambio aniónico alcalino** (AEMs del inglés, anion exchange membranes), y la **electrólisis de agua en electrolizadores de óxido sólido** (SOE del inglés, Solid Oxide Electrolyzer).

- **AWE** es una tecnología madura, constituida por dos electrodos, compuestos generalmente por níquel, unidos entre sí por un diafragma de asbesto y sumergidos en una disolución acuosa de KOH, de una concentración del 25 al 30 %, como electrolito (*Fig. 1.15*). Con esta técnica la pureza de hidrógeno más alta alcanzada es de entre el 99,5 y el 99,9 %, con una eficiencia de entre el 52 y el 62 % [38]. Estos sistemas, al emplear electrolitos básicos, presentan menores problemas de corrosión que los basados en ácidos, aumentando la durabilidad. El uso de metales de transición, como el níquel, como electrolito reduce costes con respecto a otros sistemas [37].
- En el caso de los **sistemas PEMs**, los electrolitos se separan entre sí por una membrana polimérica que facilita el intercambio de protones (*Fig. 1.15*). Este sistema, presenta ciertas ventajas con respecto al sistema AWE, al presentar mayor densidad de corriente, mayor rango de operación y mayor pureza de hidrógeno, del 99,999 %. Además, la eficiencia de estos sistemas es de entre el 57 y el 64 % [38]. Sin embargo, los electrolitos al estar compuestos por metales nobles, y al aumentar la corrosión debido a los ácidos que componen el electrolito que reducen la durabilidad, aumenta los costes de mantenimiento del sistema [37].
- Los **sistemas AEMs**, aunque similares a los PEMs, se diferencian en la membrana de separación de los electrolitos, ya que en este caso es permeable al transporte de aniones OH^- , en lugar de protones H^+ (*Fig. 1.15*). Las ventajas de estos sistemas son que no presentan precipitación de carbonatos debido a la ausencia de cationes metálicos, presentan menores pérdidas óhmicas, mayor eficiencia (entre el 62 y el 82%), la membrana es más económica que la PEM, y es más fácil de operar al no necesitar de una solución concentrada de KOH. Además, al emplear electrodos de metales de transición los costes se reducen significativamente en estos sistemas [38].
- La **tecnología SOE** se basa en el empleo de alta temperatura, para lograr la electrólisis del agua en forma de vapor, de este modo se logra una mejora en la eficiencia comparado con las otras opciones analizadas (alcanzando incluso el 100 % en algunos casos). Además, se produce un mayor aprovechamiento de la energía, al emplearse la parte de la electricidad que obtiene energía en forma de calor en su uso para el propio sistema. A pesar de todo, debido a las severas condiciones de operación, esta tecnología presenta menor durabilidad, lo que dificulta su comercialización [38]. La eficiencia alcanzada por este sistema, es superior al 90 % [36].

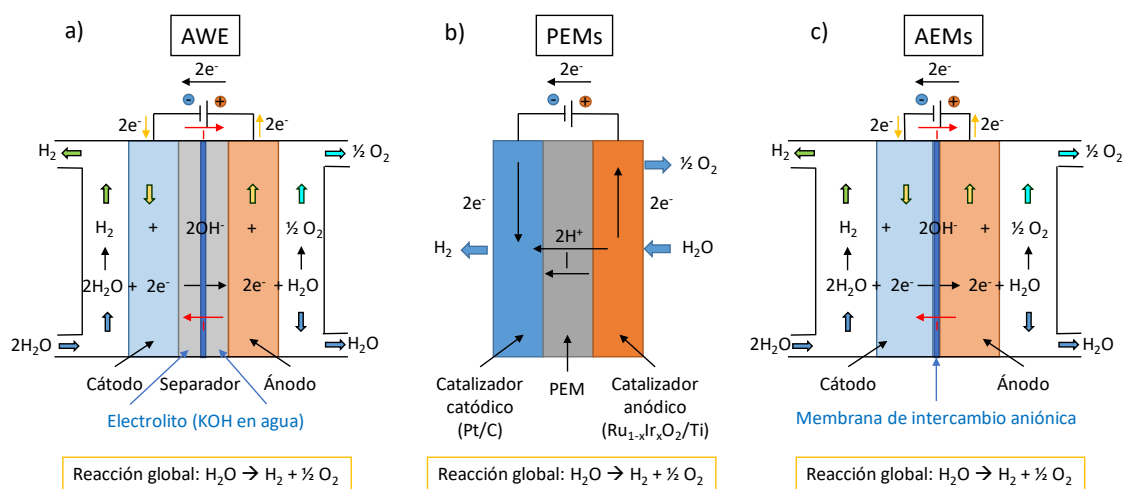


Fig. 1.15. Diagrama esquemático de a) una celda electrolítica de agua alcalina (AWE), b) una celda electrolítica de membrana de intercambio protónico (PEMs), y c) una celda electrolítica de membrana de intercambio aniónico (AEMs).

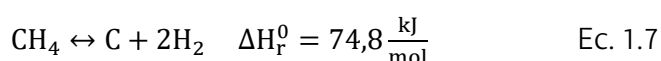
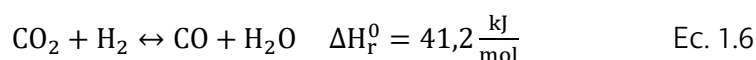
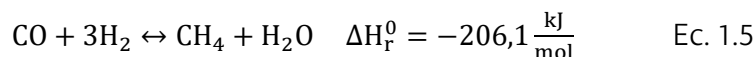
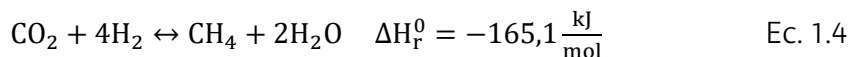
El hidrógeno procedente de la electrólisis del agua, tal y como se ha observado anteriormente, podría emplearse directamente en su aplicación como combustible para generar calor, energía motriz, volver a producir energía eléctrica o como reactivo de otros compuestos químicos. Su almacenamiento y/o transporte puede llevarse a cabo a través de la red de gas natural, limitado por la proporción de hidrógeno que limite la ley del país que corresponda, en base a mantener la seguridad en toda la instalación [39]. La cantidad máxima de hidrógeno que se puede incorporar a la red de gas natural varía de manera significativa en cada país, de manera que los valores más bajos están limitados en Bélgica y Reino Unido con el 0 % vol, seguido por Suecia con el 0,5 % vol Suiza y Austria permiten una incorporación de hasta el 4 % vol, Francia hasta el 6 % vol, y es en los Países Bajos donde el límite es más alto, al alcanzar el 12 % vol Por su parte, Alemania permite un nivel máximo del 5 % vol, pero con posibilidad de inyectar niveles del 10 % vol [40]. En España la normativa que rige la calidad que debe cumplir el gas natural para poder ser inyectado es el PD-01 "Medición, Calidad y Odorización de Gas" recogida en el Boletín Oficial del Estado (BOE), la cual establece un porcentaje de hidrógeno máximo del 5 % vol [41].

Siempre que la cantidad de hidrógeno producida sea mayor a la admitida por las infraestructuras existentes de gas natural, en base a los límites establecidos, será necesario el diseño y la construcción de una red específica de transporte y almacenamiento de hidrógeno [42].

1.6.2. Metanación

El hidrógeno obtenido en la electrólisis del agua puede emplearse en una segunda etapa de reacción conocida como reacción de metanación, en la cual se hace reaccionar con monóxido y/o dióxido de carbono para producir metano o gas natural sintético (GNS) [43]. Estos productos, al igual que el hidrógeno, podrán emplearse para la obtención de energía en forma de calor, electricidad, movilidad o para la obtención de otros productos químicos [44]. Son excelentes portadores de energía, con mayor facilidad de incorporación en la red de distribución y almacenamiento de gas natural que la que dispone el hidrógeno, al incorporar más del 80% de metano [45,46].

La reacción principal de metanación, conocida más comúnmente como reacción de Sabatier, se corresponde con la **hidrogenación de dióxido de carbono** (Ec. 1.4). Esta reacción puede ser obtenida como la combinación de la reacción de **hidrogenación de monóxido de carbono** (Ec. 1.5) y la reacción **“reverse water-gas shift”** (Ec. 1.6). Finalmente, la **reacción de Boudouard** (Ec. 1.7) destaca por ser la principal mecanismo de desactivación, por la deposición del carbono sobre el catalizador y su sinterizado, agravado por la temperatura [45,46].



Debido al fuerte carácter exotérmico de las reacciones de hidrogenación de monóxido y dióxido de carbono, es necesario un adecuado control de la temperatura, ya que a medida que esta aumenta menor será la conversión hacia la obtención de metano (basándose en el principio de Le Châtelier).

Existen tres métodos principales para llevar a cabo la reacción de metanación: **metanación biológica**, **metanación catalítica isotérmica** y **metanación adiabática de lecho fijo** [47].

La **metanación biológica** se da en plantas pequeñas de energía, siendo características por ser sistemas autocatalíticos, debido a la acción de los organismos metanógenos hidrogenotróficos autotróficos [48]. Éstos organismos, en medio acuoso, son capaces de generar su propio alimento, empleando como fuentes de energía y de carbono el hidrógeno y dióxido de carbono, por burbujeo, respectivamente, generando como subproducto metano y agua, a temperaturas de entre 273 y 395 K, con una temperatura óptima de crecimiento entre 288 y 371 K [48]. Esta tecnología se encuentra aún en fase de pruebas a escala piloto y de laboratorio [47].

La **metanación catalítica isotérmica**, se constituye de tres etapas de metanación llevadas a cabo en el interior de un reactor de lecho fluidizado, con el cual es posible alcanzar condiciones prácticamente isoterma [49]. En estas condiciones, los procesos de intercambio de masa y de calor se facilitan, permitiendo operar a menores temperaturas y bajas presiones con buenos resultados [49]. Esta tecnología se encuentra aún en fase experimental, y en desarrollo con pruebas a gran escala [47].

La **metanación adiabática de lecho fijo** es una tecnología madura a escala industrial, que se lleva a cabo principalmente en el interior de un reactor de lecho fijo en el que se pueden alcanzar las condiciones de energía necesarias para alargar el tiempo de vida útil del catalizador. La posibilidad de modificar condiciones de presión y temperatura en este tipo de sistemas, permite mejorar la conversión y la selectividad a metano [49,50].

1.7. Metanación catalítica de dióxido de carbono

La metanación de los óxidos de carbono (CO y CO₂) ha sido ampliamente estudiado desde que en el año 1902 fuese desarrollada por Sabatier y Senderens, con el fin de mejorar la eficiencia del proceso de gasificación del carbón [45,51]. Sin embargo, no fue hasta 1970 cuando cobró mayor importancia con la crisis del petróleo, otorgándole mayor relevancia a la metanación para la producción de GNS como fuente de energía [46,51]. Desde entonces ha seguido siendo estudiada durante décadas, hasta que, en 1994, Koji Hashimoto, presenta el concepto de Power to Gas por primera vez para solventar los problemas derivados del transporte y almacenamiento de las energías renovables en Japón, sin requerir de nuevas infraestructuras o sistemas de combustión alternativos [51].

En los últimos años, la metanación de dióxido de carbono está atrayendo mayor atención con el fin de reciclar el CO₂ presente en la atmósfera, con el objetivo de mitigar el calentamiento global y sus efectos. Esto ha provocado una renovación del concepto Power to Gas, cuando en 2009, Michael Sterner, enfocó el uso de esta tecnología hacia el aprovechamiento del excedente de energía renovable, empleando distintas configuraciones, en base a las fuentes de dióxido de carbono [52].

Los principales parámetros que van a determinar la configuración y eficiencia del sistema de metanación son: las fuentes de carbono, el tipo de reactor y el catalizador, con sus métodos de obtención y condiciones de operación. Estos parámetros se desarrollarán más ampliamente en las siguientes secciones.

1.7.1. Fuentes de dióxido de carbono

El hidrógeno es un reactivo necesario para llevar a cabo la reacción de metanación, pero también es necesaria una fuente de carbono, siendo el dióxido de carbono el principal compuesto empleado. Existen diversas fuentes de dióxido de carbono, considerándose como óptima aquella que sea barata, con menores requerimientos de energía, alta pureza y con capacidad para adaptarse a la demanda fluctuante. La cual, depende de la intermitente producción de hidrógeno con el excedente de energía procedente de fuentes renovables.

Las principales fuentes de dióxido de carbono disponibles son aquellas procedentes de **plantas de energía que emplean combustibles fósiles**, de la **biomasa**, de **procesos industriales** y del **aire** [42].

La captura, secuestro y almacenamiento del dióxido de carbono procedente del efluente de las **plantas de energía de combustibles fósiles** han sido ampliamente estudiados. Las principales técnicas desarrolladas se basan en la separación del gas objetivo del resto de componentes, mediante absorción física y química, adsorción, separación por membrana y separación criogénica. Los costes de separación se estiman que son del orden de 20 a 60 €/t_{CO2}, con una necesidad de energía de 100-240kWh_{el}/t_{CO2}, de manera que se producen unas pérdidas de eficiencia en el proceso de metanación del 2 al 5%. El mayor coste asociado a esta fuente, es su transporte de la fuente a la planta de metanación [42].

La transformación de la **biomasa** genera **biogás** con distintas composiciones, en base al proceso empleado, clasificándose principalmente en tres categorías: fermentación, gasificación y combustión. Por un lado, la gasificación y la combustión técnicamente son similares a estos procesos basados en fuentes fósiles. Por otro lado, la fermentación de la **biomasa** consiste en un proceso anaeróbico, desarrollado por microorganismos, en un ambiente libre de oxígeno y que genera como producto **biogás** y/o **bioetanol**, todo ello sin necesidad de aporte de materia o energía [42]. Los componentes principales del producto de la digestión serán metano y dióxido de carbono. Sin embargo, también están presentes otros gases en menor proporción como sulfuro de hidrógeno (H_2S), amoníaco (NH_3), hidrógeno (H_2) y monóxido de carbono (CO), entre otros, que es necesario eliminar previamente a la etapa de metanación [53].

La separación de dióxido de carbono de los efluentes de la combustión de **procesos industriales**, se realiza mediante el empleo de tecnologías de captura y secuestro de carbono (CSC). Las industrias que mayor contribución de emisiones de dióxido de carbono tienen son las industrias siderúrgicas y del cemento [46]. Estas emisiones se seguirían produciendo de no ser reutilizadas, lo que permitiría que este tipo de industrias redujeran su huella de carbono. Sin embargo, al igual que en las **plantas de energía de combustible fósil**, la mayor dificultad radica en el transporte para su uso en la producción de metano, pudiendo solventarse emplazando esta tecnología *in situ* [42].

La obtención de dióxido de carbono del **aire** es una tecnología posible, pero energéticamente ($3000-5000 \text{ kWh/t}_{CO_2}$) y económicamente (1000 €/t_{CO_2}) costosa, debido a la necesidad de concentrarlo desde el valor de 400 ppm que se encuentra de forma natural [54]. La principal ventaja de este método es la capacidad de abastecimiento de CO_2 sin restricciones, que reduce la concentración de este gas en la atmósfera. Sin embargo, los altos costes económicos y energéticos, dificultan la viabilidad de esta tecnología actualmente [42].

Actualmente, la principal fuente de dióxido de carbono para su empleo como materia prima en la reacción de metanación, es el proceso de fermentación de **biomasa** para la obtención de **biogás**. Con el fin de solventar la problemática asociada al transporte de dióxido de carbono, se han comenzado a construir plantas de energía PtG junto a plantas de tratamiento de biogás, tal y como se observa en proyectos como los desarrollados por Etogas, BTU, FESPE o BASF entre otras [52].

A medida que sigan desarrollándose las tecnologías CSC existirá mayor disponibilidad de dióxido de carbono puro como materia prima en cualquier lugar, evitando las dificultades derivadas del transporte del mismo, permitiendo un mayor aprovechamiento del mismo y reduciendo su problemática en la atmósfera [54].

1.7.2. Reactores para la metanación de dióxido de carbono

La metanación se puede llevar a cabo por tres procesos fundamentales, tal y como se describe al principio del apartado 1.7. De esos tres sistemas, los más frecuentes son la metanación catalítica isotérmica y la metanación adiabática de lecho fijo. En base al tipo de operación del lecho se han desarrollado principalmente dos reactores para la metanación [47]. Sin embargo, hay otros tipos de reactor como la configuración "**bubble column**", **reactores biológicos** o **reactores estructurados**, aunque frecuentemente

son menos utilizados en metanación [55]. Todos estos tipos de reactores se explicarán a continuación más detalladamente.

1.7.2.1. Reactores de lecho fijo

Este tipo de sistemas se caracterizan por estar compuestos por una serie de reactores adiabáticos (entre 2 y 5), con enfriamiento intermedio y, a veces, con recirculación de gases. En base a este modo de operar adiabático, el catalizador se introduce en el reactor en forma de pellet de pequeño tamaño, distribuido de forma homogénea. De este modo, es posible controlar la temperatura de operación en el rango de 523 a 773 K, a pesar de la alta exotermicidad de la reacción, evitando picos de temperatura o "hot spots" que facilitarían la desactivación del catalizador. La transferencia de masa entre el catalizador sólido y los reactivos gaseosos, es una dificultad de este tipo de sistemas a solventar [46,55]. Existe otro tipo de reactor de lecho fijo que también puede emplearse en metanación: el **reactor de lecho fijo refrigerado**. Este sistema mejora el proceso adiabático, empleando platos refrigerados, pero que elevan su coste [46]. Es posible encontrar diversos ejemplos de reactores de lecho fijo para la reacción de metanación, aplicados en la industria. Algunos de ellos se describen a continuación.

- **Air liquid**, anteriormente **Lurgi**, en 1970 desarrolló un proceso de metanación basado en dos reactores de lecho fijo, refrigerados y con reciclado del gas, que se sigue comercializando a día de hoy. Especialmente en aplicaciones en refinerías de crudo, o plantas de gasificación de carbón [51].
- En 1973, **British Gas (BTG) and Conoco**, desarrollaron un proceso de metanación parecido al de **Lurgi**, basado en el empleo de 3 reactores adiabáticos, con enfriamiento intermedio y reciclado de gas. Se ha testado principalmente en aplicaciones industriales de gasificación de carbón [51].
- La empresa danesa **Haldor Topsøe**, desarrolló en 1978 otro concepto de reactor de metanación, que se sigue comercializando, similar al proceso de **Lurgi**, pero basado en el empleo de 3-4 reactores de lecho fijo en lugar de 2 y centrado en la metanación a alta temperatura (973 K) [51].
- Para evitar el reciclado de gas y el enfriamiento intermedio, **Ralph M Parsons (RMP)** sugirió un concepto de reactor compuesto por de 4 a 7 reactores de lecho fijo adiabáticos en serie, controlando la exotermicidad de la reacción con enfriadores de gas intermedios, y una alimentación de gas por etapas en los reactores. Sin embargo, hasta ahora no se ha comercializado ninguna planta de estas características [51].
- **Imperial Chemical industries and Koppers** desarrollaron en 1970 otro proceso de metanación, basado en el empleo de varios reactores de lecho fijo en serie con enfriamiento intermedio, y limitando el aumento de la temperatura del catalizador en el interior del reactor, introduciendo una corriente de vapor entre los reactores [51].
- **Clariant and Foster Wheeler** desarrollaron un proceso de metanación disponible comercialmente, basado en la tecnología desarrollada por **Imperial Chemical industries**, por la cual se emplean tres reactores de lecho fijo en serie, controlando la temperatura con la incorporación de vapor [51].
- El sistema de metanación planteado por **Johnson Matthey (Davy Technologies)**, está basado en la evolución del proceso desarrollado por **British**

Gas and Conoco, por el cual se emplean tres reactores de lecho fijo adiabático con enfriamiento de gas intermedio y recirculación del gas [51].

- El proceso de metanación desarrollado por **Linde**, se caracteriza por emplear un **reactor de lecho fijo refrigerado**, integrando un intercambiador de calor y un segundo reactor de lecho fijo adiabático. En este sistema, se controla la conversión del monóxido de carbono y el calentamiento del interior del reactor, introduciendo el efluente gaseoso entre los dos reactores. Este concepto no se ha comercializado, pero ha servido de base para el desarrollo de reactores isotérmicos para sistemas de síntesis de metanol [51].

1.7.2.2. Reactores de lecho fluidizado

El reactor de lecho fluidizado se caracteriza por establecer un perfil prácticamente isotérmico en el interior del reactor, que facilita el control de operación del sistema. Esto se consigue a través de la fluidización de las partículas del catalizador sólido, por medio de un régimen turbulento mediante la incorporación de un flujo de gas. La fluidización del catalizador en el interior del reactor genera un rozamiento contra la pared, produciendo la abrasión de ambos, teniendo como consecuencia la desactivación del catalizador y el debilitamiento del reactor. Además, el régimen turbulento del lecho puede ocasionar un burbujeo que dificulte la completa conversión del CO_2 . Ahora bien, debido a su mecanismo, este tipo de sistemas presentan dos ventajas: una adecuada liberación del calor de la reacción y una alta superficie específica del catalizador, lo que lleva a una reducción de las limitaciones de transferencia de masa [46,55]. Hasta la fecha, este tipo de reactores no se han aplicado aún en procesos de metanación, pero sí que han sido ampliamente estudiados a escala piloto. Los más significativos se describen a continuación.

- Uno de los primeros procesos de metanación con empleo de lecho fluidizado desarrollado en la industria fue el **Bi-Gas-Process**, desarrollado por **Bituminous Coal Research Inc**, desde 1963. Se caracteriza por contar con un reactor que contiene dos intercambiadores de calor en el interior del lecho. Debido a su sofisticado proceso de control ha sido ampliamente estudiado en centros de investigación y testado en laboratorio [51].
- **Thyssengas** desarrollaron otro concepto de reactor de lecho fluidizado, en el que se introduce un intercambiador de calor interno. En 1977 se construyó la primera planta basada en este proceso y posteriormente fue operada comercialmente una planta piloto con este concepto [51].

1.7.2.3. Otras configuraciones de reactores

Existe otro tipo de reactores, basados en distintas configuraciones o mecanismos, que se aplican para sistemas de metanación. Los más destacados se describen a continuación.

El reactor tipo "**bubble column**" es un sistema que opera en procesos de metanación con tres fases: gaseosa con los reactivos, sólido con el catalizador y líquido, empleado como medio portador de calor. Este líquido promueve un sistema isotérmico, al transportar el calor liberado en la reacción exotérmica, impidiendo que la temperatura del lecho varíe de forma significativa, sin ocasionar grandes problemas de abrasión, como ocurría en los sistemas de **lecho fluidizado**. Sin embargo, debido al existir tres fases de

la materia, puede existir mayor resistencia a la transferencia de materia que afecte negativamente a la cinética del proceso global, y que complique el diseño y operación del sistema [55].

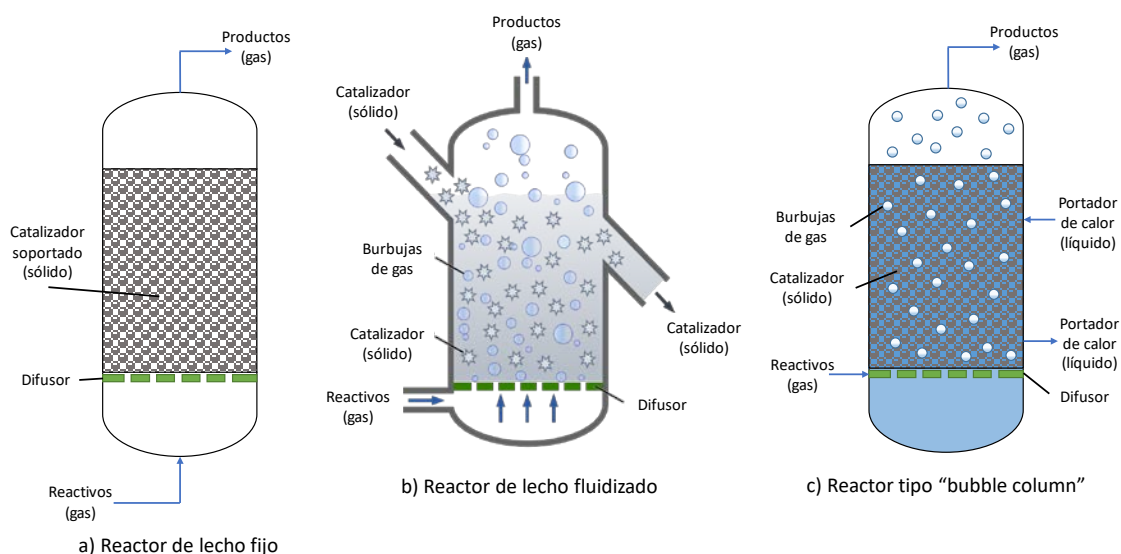


Fig. 1.16. Esquema de funcionamiento de a) reactor de lecho fijo, b) reactor de lecho fluidizado y c) reactor tipo "bubble column".

Los **reactores biológicos** o **biorreactores**, son sistemas basados en el empleo de microorganismos para la obtención de determinados productos. En el caso de la metanación biológica, los microorganismos encargados de transformar la biomasa en metano, son las bacterias metanogénicas, de la familia de las *Archaea*. Estas bacterias son capaces de sintetizar las enzimas necesarias para la degradación anaerobia de la materia orgánica a metano. Se han desarrollado a escala piloto y en laboratorio, logrando un ratio de conversión de hidrógeno del 80 al 90% con un adecuado control de las condiciones de pH, temperatura, presión total y presiones parciales de los reactivos. Las ventajas principales de este sistema son las moderadas condiciones de operación que reducen los costes de operación, de entre 303 y 333 K y presión atmosférica, y la alta tolerancia frente a sustancias contaminantes. Sin embargo, al consistir en un sistema de tres fases, la transferencia de masa está limitada, especialmente entre las fase gas y líquida; la fase sólida, al componerse de organismos vivos precisan de unas condiciones y componentes adecuados, que limitan la estabilidad a largo plazo y la selectividad de las reacciones [55].

Con el fin de solventar una de las desventajas principales de los reactores adiabáticos, que consiste en la aparición de puntos calientes en el lecho catalítico y pérdidas de carga durante la reacción, se plantea el uso de **reactores estructurados**. Los **monolitos**, debido a la alta conductividad del calor a través de la estructura metálica interna, mejoran el transporte de calor en dirección radial, en hasta 2 a 3 veces el orden de magnitud del lecho fijo. Sin embargo, debido a la dificultad del proceso de deposición del catalizador en la estructura metálica, el proceso de sustitución del catalizador desactivado es bastante complejo, limitando la implantación de este tipo de sistemas [46]. Los **monolitos** tienen principalmente dos configuraciones: por **extrusión** (cerámicos, metálicos o grafeno) [56–58] o por **enrollado** de láminas planas y corrugadas [59]. Los primeros, al ser una única pieza, la conductividad térmica es mejor, pero en los

segundos, la impregnación de catalizador y su sustitución, es algo más sencilla [60]. Los últimos estudios en esta línea, para la metanación de CO_2 , se centran en la impresión 3D del catalizador directamente (con níquel y alúmina) [61].

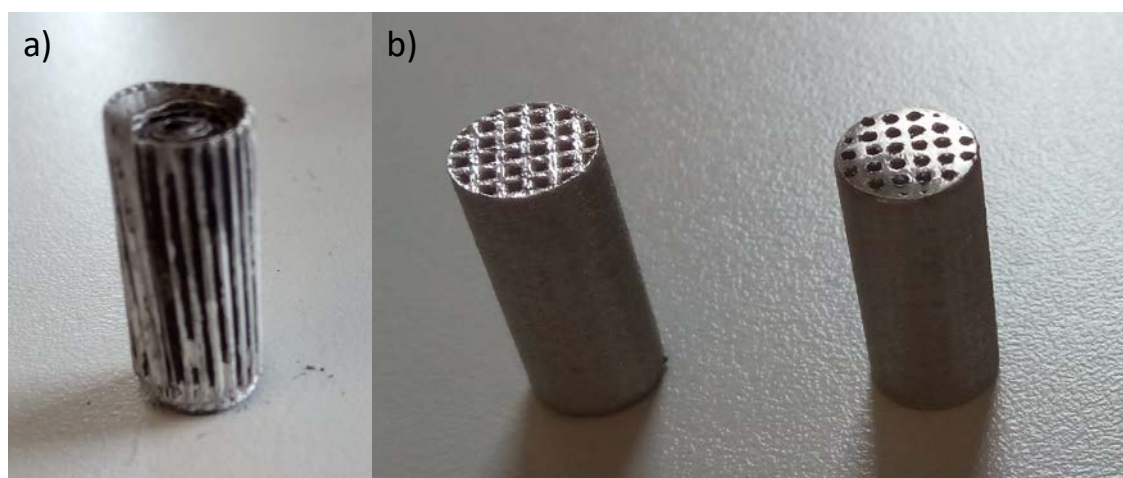


Fig. 1.17. Fotografías de a) monolito de láminas planas y corrugadas enrolladas impregnado con catalizador y b) monolito obtenido por impresión 3D con hilos de aluminio.

1.7.3. Catalizadores para la metanación de dióxido de carbono

1.7.3.1. Metales activos

En las primeras investigaciones llevadas a cabo por Sabatier y Sanderens, descubrieron que el níquel era un metal activo que catalizaba eficientemente la reacción de metanación de monóxido y dióxido de carbono con hidrógeno, para obtener metano y agua. Años después, se han desarrollado amplios estudios entre los diferentes metales, especialmente entre los de transición, determinando que los metales más importantes en la reacción de metanación (en orden de mayor a menor) por su actividad son: rutenio (Ru), hierro (Fe), níquel (Ni), cobalto (Co) y molibdeno (Mo); y por su selectividad son: níquel (Ni), cobalto (Co), hierro (Fe) y rutenio (Ru) [51].

Metales nobles como el **rutenio** (Ru) [43,62–69], el **rodio** (Rh) [66,70,71] o el **paladio** (Pd) [66], se han empleado en diversos trabajos, por su alta actividad en la reacción de metanación de CO , CO_2 o sus mezclas, especialmente en el caso del rutenio [51]. El rutenio presenta la actividad más alta en la reacción de metanación, sin embargo, su selectividad es la menor, debido a las diferentes reacciones secundarias que tienen lugar en función de las condiciones de operación. Además, sus altos precios (del orden de 700 (Ru) a 30.000 (Rh) veces más caros que el níquel), dificultan la aplicación de estos catalizadores a escala industrial [72].

En cuanto a lo que actividad/precio se refiere, el **hierro** [73,74] es el metal más adecuado. Sin embargo, su baja selectividad hacia la producción de metano, derivan su uso preferentemente hacia reacciones con mayor selectividad, para aprovechar su alta reactividad, como el proceso Fischer-Tropsch o la síntesis de amoníaco [51].

El **níquel** [43,62,67,74–80] ha demostrado ser un metal con alta actividad, y especialmente selectividad, en la obtención de metano, en numerosos trabajos. Es por

ello, y por su comparativamente bajo precio, que se considera como el metal más adecuado en su aplicación como catalizador comercial para reacciones de metanación [51].

A continuación del **níquel**, el siguiente metal más activo y con mayor selectividad en la reacción de metanación es el **cobalto** [73,81–85]. Esto hace que sea frecuente su uso en catalizadores para metanación, aunque en menor medida que el **níquel**, debido a su mayor precio [51].

Finalmente, el **molibdeno** [85,86], en comparación con los anteriores metales es el menos activo. Por otro lado, su selectividad está más orientada a la obtención de hidrocarburos de dos átomos de carbono o más, que a la de metano. A pesar de todo, su interés radica en su alta tolerancia a los grupos sulfuros, frente a la mostrada por el resto de metales, que se desactivan con mayor facilidad ante la presencia de estos grupos [51].

1.7.3.2. Soportes

Los metales activos son elementos importantes para conseguir un catalizador que alcance altos valores de actividad y selectividad en la reacción de metanación. Sin embargo, es el soporte un elemento fundamental para asegurar una buena dispersión del metal que mejore su actividad, al reducir la concentración del calor en puntos calientes o "hot spot", que facilitarían su desactivación. Es por ello un punto clave la elección del soporte adecuado, con una alta superficie específica que garantice la correcta interacción entre metal y soporte. Los soportes más comunes son óxidos metálicos, que presentan alta área superficial, siendo reportados en numerosos trabajos, como es el caso de la **alúmina** u **óxido de aluminio** (Al_2O_3) [62,65,66,70,75,78,79,81,87–92], **óxido de titanio** (TiO_2) [71,93–99], **óxido de silicio** (SiO_2) [77,94,100–102], **óxido de cerio** (CeO_2) [92,100,103–106], **óxido de itrio** (Y_2O_3) [92,107] o las **zeolitas** [108–111].

En los últimos años, se están empezando a incorporar soportes basados en derivados del carbono, como es el caso del **grafeno**, **óxido de grafeno** (GO) u **óxido de grafeno reducido** (rGO). El grafeno, y sus derivados, han despertado un gran interés debido especialmente a sus propiedades conductoras. La hibridación de los orbitales sp^2 del carbono, derivan en la formación de 3 enlaces simples tipo σ , dando un ángulo de enlace de 120° , que perfilan una estructura bidimensional con su particular forma hexagonal tipo panal de abejas. Pero además, presenta un enlace doble π deslocalizado, que en su conjunto constituyen una banda de conducción y una banda de valencia, que otorgan a este elemento propiedades altamente conductoras [112]. Estas propiedades conductoras del calor y la electricidad, que permiten disipar el calor liberado en la reacción exotérmica, sumadas a la alta área superficial y resistencia mecánica, plantean un gran potencial para este elemento como soporte. Sin embargo, en la bibliografía es más frecuente el uso de GO y rGO, debido entre otras cosas a su menor coste de producción que el grafeno y a una mayor presencia de grupos hidroxilo, epoxi y carboxilo, que actúan como centros de anclaje y nucleación de los centros metálicos, que facilitan una buena dispersión [112]. En su aplicación en metanación, en el trabajo de Hu et al. [76] se observa un aumento en la actividad del catalizador soportado sobre rGO, frente a los soportes de Al_2O_3 o **carbón activo**, especialmente en aquellos que incorporan cerio (Ce) como promotor. En el trabajo de Ma et al. [113], se emplea de forma alternada GO y SiO_2 con

Ni, que según concluyen, debido a la formación de Ni filosilicatos con el **GO** mejora la dispersión del Ni con más fuerte interacción, dando mayor estabilidad a la reacción de metanación a más alta temperatura. En el trabajo de Primo et al. [114] se ha mostrado el MoS₂ soportado sobre **grafeno defectuoso** como un catalizador selectivo para la metanación de CO₂, con aumento de la actividad con la temperatura.

1.7.3.3. Promotores y modificadores del soporte

El metal activo como punto importante en un catalizador, puede emplearse de forma individual o combinada con otros metales para promocionar el efecto reactivo del mismo, mejorando su actividad y/o selectividad. La adición de metales de transición junto con el metal activo, ayuda en algunos casos a mejorar la dispersión del metal sobre el soporte, además de poder mejorar su reducibilidad, de forma parecida a lo que ocurre al adicionar metales nobles, pero con un menor coste. Este hecho se puede observar en el trabajo de Lu et al. [73], al incorporar pequeñas cantidades de **lantano** (La), **cerio** (Ce), **cobalto** (Co) o **hierro** (Fe). La adición de determinadas especies como **Co**, **La**, **Ce**, **molibdeno** (Mo) o **boro** (B) a los respectivos catalizadores, puede modificar la estructura superficial con el fin de mejorar la resistencia al envenenamiento por el grupo sulfuro en la reacción de metanación, tal y como observaron en sus trabajos Wang et al. [115], Velinova et al. [116], Wolf et al. [117], Alarcón et al. [87], Bartholomew et al. [118], Wang et al. [119], Li et al. [86], Liu et al. [120] y Wang et al. [121]. La adición de **V₂O₃**, además de mejorar la actividad del catalizador, mejora su estabilidad térmica y la resistencia a la formación de coque, que reduzca la actividad del **Ni**, tal y como se determinó en el trabajo de Liu et al. [122].

Algunos metales se adicionan directamente sobre el soporte, antes de incorporar el metal activo, con el fin de facilitar su anclaje para mejorar la actividad, la dispersión y la estabilidad térmica. Liang et al. [123] observaron un aumento de la actividad del catalizador de **Ni** soportado en **Al₂O₃**, tras la incorporación de metales alcalinotérreos como el **magnesio** (Mg) y **calcio** (Ca), pero especialmente con la de **estroncio** (Sr) y **bario** (Ba). En los trabajos de Panagiotopoulou et al. [93] y Anle et al. [100], se ha demostrado que la incorporación de metales alcalinos como el **sodio** (Na) mejora la actividad y selectividad del catalizador de **Ru** sobre **TiO₂** y **Ni** sobre **SiO₂** y **CeO₂** respectivamente, en la reacción de metanación, por promocionar la aparición de especies intermedias más reactivas. Le et al. [124] determinaron que metales como **manganeso** (Mn), **Ce**, **zirconio** (Zr), **magnesio** (Mg) y **vanadio** (V) tienen un efecto positivo en la mejora de la actividad y selectividad de catalizadores de Ni sobre Al₂O₃, pero tanto **potasio** (K) como **zinc** (Zn) tiene un efecto negativo, por lo que no todos los metales son adecuados para mejorar la actividad. Con respecto a los metales lantánidos, hay varios trabajos que destacan su contribución en la mejora de la actividad y la estabilidad térmica, permitiendo una reducción de la temperatura de operación. Como en el trabajo de Garbarino et al. [88] con la adición de distintas cantidades de La sobre Al₂O₃; en el de García-García et al. [78] con la incorporación de **Ce** o **Zr** sobre **Al₂O₃**; en el de Quindimil et al. [108] incorporando **La** sobre **zeolitas**; y en el de Westermann et al. [109] que incorporan **Ce** sobre **zeolitas**.

1.7.3.4. Métodos de preparación

La elección de un adecuado metal activo, el soporte y todos aquellos promotores y/o modificadores que se quieran incorporar, son esenciales para lograr una alta reactividad y selectividad del catalizador producido, derivando en una adecuada dispersión del metal en el soporte y distribución del tamaño de partícula. Para lograr este objetivo, es necesaria una adecuada elección del método de preparación en base a sus componentes. Los principales métodos de preparación de catalizadores son: **impregnación, deposición-precipitación y coprecipitación** [125].

El **método de impregnación** es el más extendido y simple, pudiendo distinguir entre dos modos de preparación. La **impregnación incipiente** o **impregnación seca** emplea una cantidad de disolvente igual o ligeramente superior al volumen de poro del soporte. Por otro lado, cuando la cantidad de disolvente empleada en la preparación del catalizador es mayor al volumen de poro, está en exceso, se habla de **impregnación húmeda**. En ambos casos es importante el posterior proceso de separación del disolvente del catalizador, para evitar eliminar partículas de metal no incorporadas, pero sí eliminar el resto de componentes [126].

El **método de deposición-precipitación** consiste en la reducción de la solubilidad de la sal del metal precursor con el fin de que ésta precipite sobre el soporte y no en la disolución. Para ello se suele emplear cambios de pH, adición de agentes precipitantes, adición de un agente reductor o cambiar la concentración de un agente complejante. Pero para que la deposición se haga sobre el soporte es necesaria una buena interacción entre metal disuelto y superficie del soporte, y que la concentración del metal en el medio sea la adecuada, para facilitar una precipitación homogénea [125].

La **coprecipitación homogénea** de los cationes metálicos básicos, se consigue por medio de su transformación al óxido correspondiente, por la solubilidad mutua de algunos cationes en algunas fases de hidróxido, siendo los más frecuentes los hidroxicarbonatos, hidroxitonatos o hidroxiclорuros. De este modo, metales activos y soporte, ambos presentes en la disolución, precipitan de forma conjunta y homogénea, haciendo este método más reproducible [125,126].

Existen otros métodos también empleados para la síntesis de catalizadores, que según para qué aplicaciones, pueden ser los más adecuados. Como, por ejemplo, el **método sol-gel**. Se basa en la formación de coloides, que a medida que se elimina el disolvente por evaporación va dejando un gel en el que se encuentran todos los elementos que componen el catalizador [126].

1.7.3.5. Revisión de sistemas catalíticos

Anteriormente se han determinado los metales activos más relevantes para la reacción de metanación. Del mismo modo, se han descrito los soportes más comúnmente utilizados por su alta área superficial para asegurar una buena dispersión del metal activo. Y finalmente, se han descrito algunos de los promotores y modificadores, con mayor contribución para la mejora de la reactividad del metal activo, dispersión y/o resistencia a la desactivación. Sin embargo, es la combinación de todos estos elementos, y su interacción en base al método de preparación utilizado, lo que hacen que un sistema

catalítico, sea realmente reactivo y selectivo para la obtención de metano. Atendiendo a la bibliografía, se recogen en la **Tabla 1.7.1**.

algunos ejemplos de catalizadores aplicados a la reacción de metanación, indicando método de preparación, temperaturas de reacción, presión del sistema, conversión de CO₂, rendimiento a CH₄ y fuente bibliográfica.

Sistema catalítico	Método de preparación	Temperatura (K)	Presión (bar)	Conversión de CO ₂ (%)	Rendimiento a CH ₄ (%)	Fuente
10Ni/Al ₂ O ₃	Impregnación húmeda	623	1	77	75	[80]
10Ni/Y ₂ O ₃	Impregnación húmeda	548	1	78	78	[80]
10Ni/ZrO ₂	Impregnación húmeda	573	1	76	75	[80]
10Ni/La ₂ O ₃	Impregnación húmeda	723	1	62	54	[80]
10Ni/Ce ₂ O ₂	Impregnación húmeda	623	1	72	72	[80]
10Ni/Sm ₂ O ₃	Impregnación húmeda	573	1	69	68	[80]
Co-Mo/Al ₂ O ₃	Co-precipitación	873	30	45	50*	[127]
Co-Mo-Ce/Al ₂ O ₃	Co-precipitación	833	30	56	48*	[127]
Co-Mo-Mg/Al ₂ O ₃	Co-precipitación	873	30	43	50*	[127]
Co-Mo-Ti/Al ₂ O ₃	Co-precipitación	833	30	45	50*	[127]
Co-Mo-Zr/Al ₂ O ₃	Co-precipitación	873	30	54	47*	[127]
20Ni/Al ₂ O ₃	Impregnación incipiente	873	1	75	60	[123]
20Ni-5Mg/Al ₂ O ₃	Impregnación incipiente	873	1	71	50	[123]
20Ni-5Ca/Al ₂ O ₃	Impregnación incipiente	873	1	71	58	[123]
20Ni-5Sr/Al ₂ O ₃	Impregnación incipiente	623	1	81	81	[123]
20Ni-5Ba/Al ₂ O ₃	Impregnación incipiente	623	1	82	82	[123]
20Ni/rGO	Hummers	623	1	79	78 y 100*	[76]
20Ni-5Ce/rGO	Hummers	623	1	82	82 y 100*	[76]
20Ni/AC	Hummers	623	1	60	57 y 95*	[76]
20Ni-5Ce/AC	Hummers	623	1	77	76 y 100*	[76]
20Ni/Al ₂ O ₃	Hummers	623	1	63	62 y 100*	[76]
20Ni-5Ce/Al ₂ O ₃	Hummers	623	1	79	78 y 100*	[76]

Tabla 1.7.1. Resumen de sistemas catalíticos habituales, recientemente desarrollados. *Selectividad a CH₄.

Sistema catalítico	Método de preparación	Temperatura (K)	Presión (bar)	Conversión de CO ₂ (%)	Rendimiento a CH ₄ (%)	Fuente
13,6Ni-14La/Al ₂ O ₃	Impregnación incipiente	623	1	-	86	[88]
13,6Ni/Al ₂ O ₃	Impregnación incipiente	623	1	-	80	[88]
13Ni/Al ₂ O ₃	Impregnación húmeda	750	10	-	72	[78]
13Ni-1Rh/Al ₂ O ₃	Impregnación húmeda	673	10	-	70	[78]
13Ni-1Ru/Al ₂ O ₃	Impregnación húmeda	703	10	-	67	[78]
13Ni/6Ce-Al ₂ O ₃	Impregnación húmeda	647	10	-	75	[78]
13Ni-1Rh/6Ce-Al ₂ O ₃	Impregnación húmeda	673	10	-	66	[78]
13Ni/3Ce-4Zr-Al ₂ O ₃	Impregnación húmeda	703	10	-	71	[78]

Tabla 1.7.2. Resumen de sistemas catalíticos habituales, recientemente desarrollados (continuación). *Selectividad a CH₄.

1.7.3.6. Desactivación de sistemas catalíticos

Uno de los problemas más importantes de los catalizadores para la metanación de CO₂, es la desactivación que se observa con el tiempo. Esto generalmente implica que los centros activos del catalizador ya no son activos. Las principales causas de desactivación del catalizador son las recogidas a continuación.

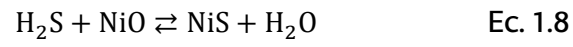
Ensuciamiento por coque: Reacciones secundarias como la de Boudouart (Ec. 1.7), o reacciones de craqueo que puedan tener lugar en el sistema, pueden producir carbono que recubra o encapsule los centros activos del catalizador, desactivándolo. Es un tipo de desactivación física y química (por quimisorción), que puede ser reversible (según sistema) y que aumenta con la temperatura de reacción. La forma más frecuente de eliminación es la gasificación con hidrógeno o mediante combustión [51].

Disgregación y erosión: es especialmente acusado en reactores de lecho móvil y fluidizado con catalizadores heterogéneos, en el caso de la erosión debido a la abrasión, y en el de disgregación, debido al estrés térmico y/o mecánico ocasionados por altas fluctuaciones de temperatura o presión [51].

Sinterizado: es la degradación del catalizador a causa de la temperatura (particularmente por encima de 873 K), siendo frecuente en lecho fijo adiabático, especialmente con la presencia de puntos calientes. Los centros metálicos difunden a través de la superficie del catalizador, hasta alcanzar otro centro activo, formando aglomeraciones y reduciendo significativamente la actividad [51].

Envenenamiento: consiste en la interacción entre los centros activos e impurezas gaseosas como compuestos clorados, partículas, amoníaco, componentes sulfurados o álcalis, causando su desactivación. El envenenamiento por compuestos de azufre es el más común, debido a la alta sensibilidad (de hasta partes por billón) de la mayoría de los metales activos, y en especial la del Ni, a la desactivación en presencia de estos componentes. En el caso del Ni, el envenenamiento se produce por la reacción entre el óxido de níquel (NiO) y el sulfuro de hidrógeno (H₂S), obteniendo sulfuro de níquel (NiS)

y agua (Ec. 1.8), perdiendo toda su actividad para la reacción de metanación. Esta reacción, aunque reversible, es muy costosa y compleja. Es por ello preferible asegurar una completa eliminación de estos componentes de la fuente, que intentar revertir la desactivación del catalizador envenenado con H₂S.



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CAPÍTULO 2



Objetivos

"Hemos modificado tan radicalmente nuestro entorno que ahora debemos modificarnos a nosotros mismos para poder existir dentro de él."

NORBERT WIENER

2.1. Objetivo

El progresivo aumento de la población mundial ha derivado en un aumento de la producción de alimentos, tecnología y energía para satisfacer la creciente demanda. En una sociedad basada en fuentes de energía fósil, el incremento de la demanda de energía ha producido un incremento de las emisiones de gases de efecto invernadero, con sus correspondientes consecuencias. Con el objetivo de reducir las emisiones de dióxido de carbono (CO_2) y satisfacer la demanda energética, se ha desarrollado la tecnología power-to-gas, permitiendo abastecer de energía incluso pequeños núcleos poblacionales más aislados. Sin embargo, uno de los principales retos de esta tecnología, se centra en la transformación de CO_2 procedente de distintas fuentes, e hidrógeno (H_2) obtenido de fuentes renovables, en metano (CH_4) empleando el catalizador adecuado, para conseguir un alto rendimiento y evitando su desactivación a causa de las impurezas que puedan acompañar a los reactivos.

Sobre este planteamiento se enfoca el objetivo de la presente tesis doctoral, siendo éste *el estudio de sistemas catalíticos para la reacción de metanación, con alto rendimiento y selectividad a la producción de CH_4 y con resistencia al envenenamiento por H_2S procedente de la corriente de alimentación de CO_2* . Para cumplir este objetivo general se han planteado varios objetivos específicos, que se recogen a continuación.

2.1.1. Objetivos específicos

- Preparación y estudio de catalizadores de níquel-alúmina que incorporen metales de transición como promotores, para la mejora de la selectividad y el rendimiento a metano en la reacción. Pero, sobre todo, para aumentar la resistencia a la desactivación del catalizador por envenenamiento con H_2S .
- Preparación y estudio de catalizadores de níquel-alúmina, rutenio-alúmina y rutenio-níquel-alúmina que incorporen metales lantánidos y alcalinotérreos como modificadores del soporte, para la mejora de la actividad, selectividad y resistencia al envenenamiento para poder recuperar la actividad tras la desactivación.
- Síntesis de estructuras derivadas de óxido de grafeno, como son el óxido de grafeno reducido, el óxido de grafeno reducido con metilaminoborano, el óxido de grafeno aminado con dodecilamina y el óxido de grafeno aminado con oleilamina, y su estudio como soporte de catalizadores de níquel.
- Preparación y estudio de catalizadores de níquel sobre soportes basados en óxido de grafeno reducido modificado con lantano para la mejora de la selectividad y rendimiento a metano, resistencia a la desactivación y recuperación de la actividad en ausencia de sustancias inhibitoras de la actividad.
- En todos los casos el estudio incluirá una caracterización detallada de los catalizadores, para así profundizar en los efectos de los diferentes elementos empleados y poder establecer propuestas de formulaciones de catalizadores más activas, selectivas y resistentes al envenenamiento.

CAPÍTULO 3



Metodología experimental

"Cuando un hombre de ciencia busca conocimientos, aun no hallándolos en su totalidad, descubre fragmentos muy importantes, que son precisamente los que constituyen la ciencia."

CLAUDE BERNARD

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En el presente capítulo se especifican los diferentes procedimientos que se utilizarán para preparar los sistemas catalíticos planteados, con el fin de justificar los objetivos definidos en esta tesis. De este modo, en primer lugar, se describen los métodos de preparación de catalizadores basados en alúmina, seguido de los métodos de preparación de catalizadores soportados en sistemas basados en grafeno. A continuación, se describen las técnicas empleadas para la caracterización de los catalizadores y finalmente, el procedimiento seguido para determinar la actividad del catalizador en la reacción de metanación.

3.1. Preparación de catalizadores soportados sobre alúmina

Los catalizadores que se han seleccionado para el estudio de la reacción de metanación se basan en el empleo de Ni como metal activo, por su demostrado equilibrio entre eficiencia, actividad y selectividad en esta reacción, y su coste, tal y como se puntualiza en el **capítulo 1**. De igual modo se señalaba el uso de otros metales como promotores (Co, Cr, Fe o Mo) por su estudiado efecto contributivo en la mejora de la actividad, la selectividad y la resistencia al envenenamiento de metales, como el Ni [1]. De este modo se comprobará este efecto en catalizadores para la reacción de metanación. El soporte más comúnmente utilizado para la incorporación de Ni, se ha determinado que es la alúmina por su alta área superficial y estabilidad térmica a las condiciones de operación. En la bibliografía (**capítulo 1**) se observó que la incorporación de metales lantánidos como La o Ce o metales alcalinotérreos como Mg, Ca o Ba, mejoraban la dispersión del metal activo sobre la superficie del soporte, mejorando su actividad catalítica.

La preparación de catalizadores monometálicos: Ni/Al₂O₃ y bimetálicos incorporando promotores: Co-Ni/Al₂O₃, Cr-Ni/Al₂O₃, Fe-Ni/Al₂O₃ y Mo-Ni/Al₂O₃ se preparan siguiendo el método de **impregnación húmeda** que se explicará a continuación, en la **sección 3.1.1**. Por otro lado, la preparación de catalizadores con soporte modificado por lantánidos o alcalinotérreos sigue la metodología de la **impregnación húmeda sucesiva** para la incorporación del metal. El procedimiento seguido se explica adecuadamente en la **sección 3.1.2**.

3.1.1. Catalizadores preparados por co-impregnación

Los catalizadores preparados por el método de impregnación húmeda precisan de los reactivos adecuados, recogidos en la *Tabla 3.1.1*.

Nombre del reactivo	Pureza (%m)	Productor
γ -Aluminio óxido anhidro	100	Merck
Nitrato de níquel (II) hexahidrato	99,999	Sigma Aldrich
Cloruro de rutenio (III) hidrato	99,98	Sigma Aldrich
Cloruro de hierro (III) hexahidrato	97	PRS Panreac Química
Nitrato de cromo (III) nonahidrato	98,5	Alfa Aesar
Cloruro de cobalto (II) hexahidrato	99	Quimivita S.A
Heptamolibdato amonio tetrahidrato	99	Merck

Tabla 3.1.1. Reactivos empleados para la síntesis de catalizadores de metanación mono- y bimetálicos por el método de impregnación húmeda.

La cantidad de reactivos que es necesario emplear para la preparación del catalizador viene determinado por la proporción de metal planteada teóricamente, basada en estudios previos tal y como se determina en la bibliografía (**capítulo 1**). La proporción de Ni como metal activo de la mayoría de los catalizadores preparados, será del 13% en peso, siendo la proporción del promotor del 4% en peso en todos los casos, con excepción del Mo donde se emplean dos proporciones: 4 y 8% en peso. En aquellos catalizadores cuyo metal activo sea el Ru, la proporción del metal noble a incorporar será del 1 % en peso. La cantidad de sales precursoras a emplear para la preparación de los catalizadores se recoge en la *Tabla 3.1.2*, empleando como base de cálculo la masa del soporte, que coincidirá en todos los casos con un valor de 5 g. Los catalizadores preparados se nombran en base a su composición nominal, siendo identificados como sigue a continuación: **13Ni/Al₂O₃**, **1Ru-13Ni/Al₂O₃**, **4Co-13Ni/Al₂O₃**, **4Cr-13Ni/Al₂O₃**, **4Fe-13Ni/Al₂O₃**, **4Mo-13Ni/Al₂O₃** y **8Mo-13Ni/Al₂O₃**.

Catalizador	Masa de sal de Ni (g)	Masa de sal del promotor (g)
13Ni/Al₂O₃	3,70	0,00
1Ru-13Ni/Al₂O₃	3,74	0,12
4Co-13Ni/Al₂O₃	3,88	1,19
4Cr-13Ni/Al₂O₃	3,88	1,19
4Fe-13Ni/Al₂O₃	3,88	1,18
4Mo-13Ni/Al₂O₃	3,88	0,45
8Mo-13Ni/Al₂O₃	4,08	0,94

Tabla 3.1.2. Cantidad determinada de las sales precursoras para la preparación de catalizadores mono- y bimetálicos para metanación, para una masa de soporte de γ -alúmina de 5 g.

La cantidad de los reactivos necesarios para preparar los catalizadores planteados, recogidas en la *Tabla 3.1.2*, se mezclan con el soporte (alúmina) en el interior de un matraz de fondo redondo. En impregnación húmeda, la cantidad de agua necesaria para la preparación de los catalizadores, se corresponde con el volumen total necesario para ocupar el volumen de poro del soporte y un excedente, siendo en este caso para los 5 g de alúmina un volumen de 20 ml. Se incorporan los 20 ml de agua miliQ en el matraz y se agitan para conseguir la completa disolución de las sales precursoras.

La correcta incorporación de los iones metálicos presentes en la disolución sobre el soporte, de manera homogénea, depende del valor de pH. El pH al cual la γ -alúmina presenta un balance de cargas netas cero con el medio (pzc del inglés, potential of zero charge), se corresponde con el valor determinado por el punto isoeléctrico, siendo en el caso de este soporte de 7,5 [2,3]. Por encima de este valor, el soporte permanece cargado negativamente y presenta mayor afinidad por los protones, especialmente a valores altos de pH. Esto se traduce en una mayor afinidad para la incorporación de iones cargados positivamente, como es el caso de los iones

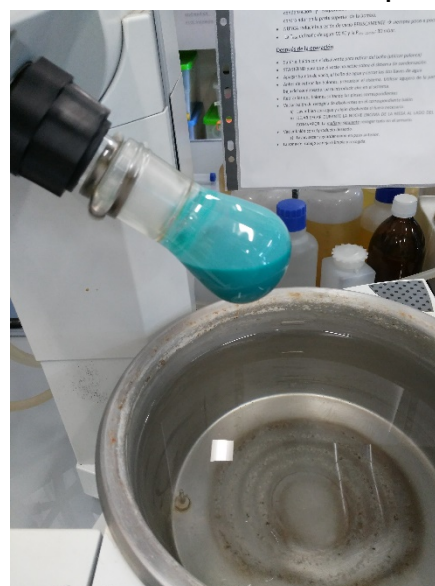


Fig. 3.1. Preparación del catalizador en el rotavapor, en agitación toda la noche

de metal a incorporar. Por este motivo, se controla el pH de la disolución del catalizador hasta alcanzar un valor de pH de 8,5, incorporando amoníaco (Panreac) para elevar el valor del pH o ácido nítrico (Scharlau) en el caso de que sea necesario bajarlo.

La disolución de los metales a pH 8,5 en contacto con el soporte se deja en agitación durante toda la noche, en el interior de un rotavapor (Heidolph Laborota), a 90 RPM, para facilitar el contacto entre todos los componentes (Fig. 3.1). Pasado este tiempo, aún conectado al rotavapor y en agitación se eleva su temperatura hasta los 338 K. Alcanzada esta temperatura, se elimina el disolvente bajo condiciones de vacío (73 mbar) con agitación constante.

Evaporado el disolvente, se introduce el matraz en el interior de una estufa a 373 K para asegurar la completa eliminación del disolvente que pueda quedar adherido al catalizador, durante 2 h. El sólido obtenido se introduce en el interior de un crisol cerámico y se calcina empleando un programa de temperaturas, rampas y tiempos, representados en la Fig. 3.2, todo ello en presencia de aire, para eliminar todas las impurezas presentes y preparar su superficie para su empleo como catalizador.

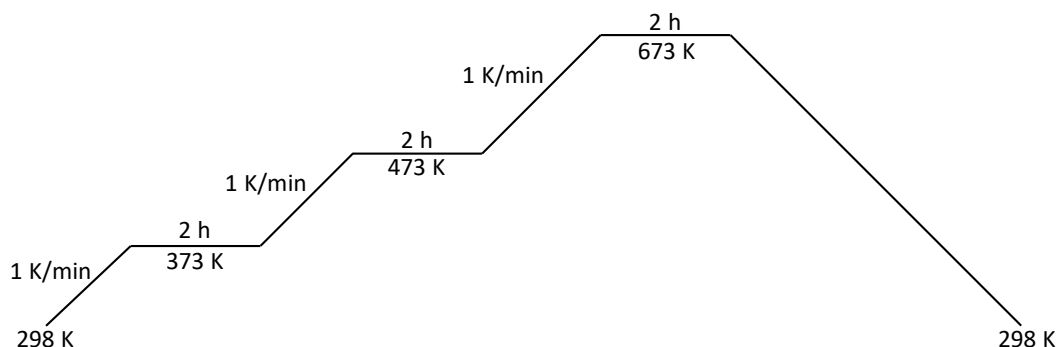


Fig. 3.2. Programa de calcinación del catalizador de metanación en el interior de la mufla

Finalmente, el catalizador calcinado se tamiza y prensa, para obtener un tamaño de partícula de entre 0,42 y 0,50 mm [4].

3.1.2. Catalizadores preparados por impregnación húmeda sucesiva

La incorporación de metales que modifiquen el soporte se realiza por medio del método de impregnación húmeda sucesiva, incorporando los modificadores y el metal activo en dos fases de impregnación húmeda consecutivas. Los reactivos empleados para la preparación de estos catalizadores se recogen en la *Tabla 3.1.3*.

Nombre del reactivo	Pureza (%m.)	Productor
γ -Aluminio óxido anhidro	100	Merck
Nitrato de níquel (II) hexahidrato	99,999	Sigma Aldrich
Cloruro de rutenio (III) hidrato	99,98	Sigma Aldrich
Nitrato de bario	99,999	Sigma Aldrich
Nitrato de calcio tetrahidrato	99	Sigma Aldrich
Nitrato de magnesio hexahidrato	99	Fluka Analytical
Nitrato de lantano (III) hidrato	99,9	Sigma Aldrich
Nitrato de cerio (III) hexahidrato	99,999	Sigma Aldrich

Tabla 3.1.3. Reactivos empleados para la síntesis de catalizadores de metanación mono- y bimetalicos con soportes modificados, por el método de impregnación húmeda sucesiva.

Los catalizadores a preparar se nombran en base a su composición nominal, siendo identificados como sigue a continuación: **13Ni/10Ba-Al₂O₃**, **13Ni/10Ca-Al₂O₃**, **13Ni/10Mg-Al₂O₃**, **13Ni/14La-Al₂O₃**, **13Ni/14Ce-Al₂O₃**, **1Ru-13Ni/14La-Al₂O₃** y **1Ru/14La-Al₂O₃**. Con el fin de incorporar el metal correspondiente, en el soporte modificado, su incorporación se llevará a cabo siguiendo la metodología de impregnación húmeda. Una vez determinada la cantidad de sal del metal necesaria (Tabla 3.1.4) para una cantidad de soporte de 5 g de γ -Al₂O₃, se mezclan, se disuelven, se controla el pH y se elimina el disolvente. Tras la calcinación, al soporte modificado obtenido se le incorpora la sal del metal activo (Ni o Ru, según el catalizador) en la cantidad determinada (Tabla 3.1.4), y se repite el procedimiento de impregnación húmeda, descrito en la sección anterior, cuando el sistema es el bimetalico 1Ru-13Ni, y de este modo se obtienen los catalizadores anteriormente nombrados.

Catalizador	Masa de sal de metal activo (g)		Masa de sal del modificador (g)
	Ni	Ru	Ba, Ca, Mg, La o Ce
13Ni/10Ba-Al₂O₃	4,18	-	2,66
13Ni/10Ca-Al₂O₃	4,18	-	2,66
13Ni/10Mg-Al₂O₃	4,18	-	2,69
13Ni/14La-Al₂O₃	4,41	-	2,25
13Ni/14Ce-Al₂O₃	4,41	-	3,93
1Ru-13Ni/14La-Al₂O₃	4,47	0,14	2,28
1Ru/14La-Al₂O₃	-	0,12	1,93

Tabla 3.1.4. Cantidad determinada de sales precursoras para la preparación de catalizadores mono- y bimetalicos para metanación, para una masa de soporte de γ -alúmina de 5 g.

Los catalizadores ya calcinados, se tamizan y prensan, obteniendo un polvo con tamaño de partícula de entre 0,42 y 0,50 mm. Este tamaño es el más adecuado para facilitar el transporte de materia entre gas y sólido, reduciendo las pérdidas de carga en el reactor.

3.2. Preparación de catalizadores soportados sobre derivados de óxido de grafeno

Los soportes preparados a partir de grafeno se caracterizan por sus propiedades conductoras y su alta porosidad, heredadas de las estructuras de carbono hexagonal del

grafeno. Los derivados de grafeno más relevantes son el **óxido de grafeno** (GO) y el **óxido de grafeno reducido** (rGO), pero según los usos, el **óxido de grafeno aminado** (AGO) también despierta gran interés. Los soportes que se emplean en este estudio presentan dos orígenes diferentes. Por un lado, se emplea GO, rGO y AGO facilitados por la empresa productora especializada Graphenea, suministrados en forma de polvo para su uso directo en la impregnación del metal activo. Por otro lado, los soportes derivados del óxido de grafeno se sintetizan en el laboratorio a partir del GO suministrado por Graphenea. Este es el caso del óxido de grafeno reducido con el agente reductor **metilamina borano** (MeAB), o el óxido de grafeno aminado con **oleilamina**.

La reducción del óxido de grafeno con MeAB, requiere previamente la obtención de este reactivo, tal y como se describe a continuación [5]. Se toma una masa de 11,35 g de borohidruro de sodio (>98,0 %; Sigma Aldrich), que se mezclan con 20,26 g de hidrocloreuro de metilamina (>98,0 %; Sigma Aldrich) y se disuelven con agitación en 600 ml de tetrahidrofurano (THF, >99,9 %; Honeywell) en el interior de un matraz de fondo redondo de tres bocas, conectado a un condensador (**Fig. 3.3**). La reacción tiene lugar en atmósfera inerte de nitrógeno, a temperatura ambiente durante 12 h. Pasado este tiempo, la disolución se filtra en un embudo Büchner con filtro celulósico, por filtración a vacío (**Fig. 3.3**). El producto de la filtración se introduce en el rotavapor (Heidolph Laborota), eliminando el disolvente y concentrando la muestra a temperatura ambiente y bajo condiciones de vacío. Finalmente, el producto obtenido se purifica con metanol (>99,9 %; Sigma Aldrich).

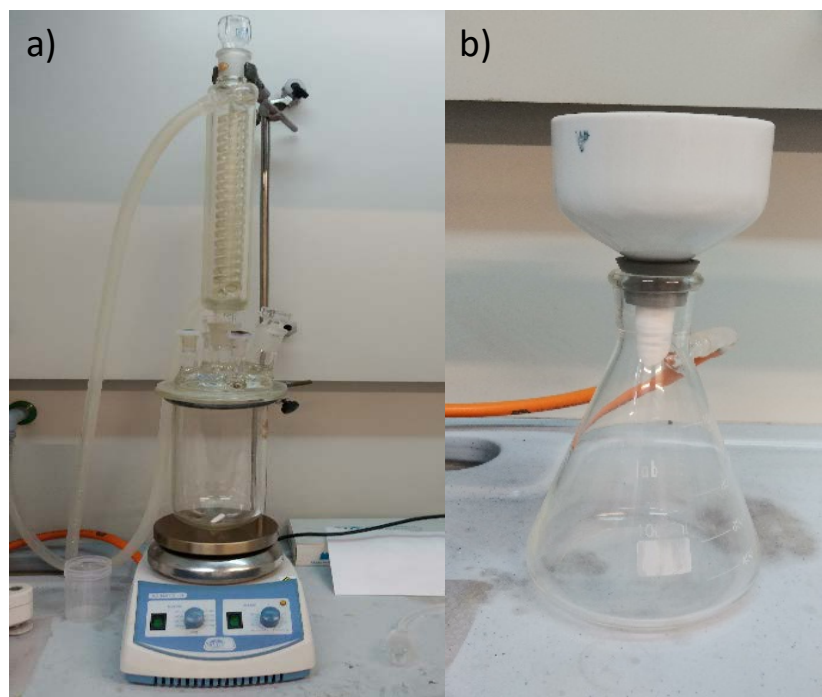


Fig. 3.3. Montaje del sistema a) de síntesis de MeAB y b) de filtrado en la preparación de MeAB.

El procedimiento de obtención del óxido de grafeno reducido con MeAB se aprovecha para la incorporación del metal activo, en este caso el Ni, por el procedimiento descrito a continuación. Se añaden 3 g de GO (Graphenea) en el interior de un matraz de fondo redondo, donde se disuelven con 580 ml de agua miliQ. A la disolución se

incorporan 2,22 g de la sal de níquel (nitrato de níquel (II) hexahidrato, 99,999 %; Sigma Aldrich) y se deja en el interior del equipo de ultrasonidos durante 2 h. Pasado este tiempo, a la disolución anterior se incorpora el agente reductor MeAB, añadiendo 27 g del mismo con 400 ml de agua miliQ y vigorosa agitación. La mezcla anterior se introduce en el rotavapor y se deja en agitación en condiciones ambiente toda la noche. Tras ello, se elimina el disolvente y se concentra la muestra a 313 K y condiciones de vacío. El disolvente se acaba de eliminar en la estufa a 393 K durante 2 h, y el catalizador se acaba de preparar calcinando en el sistema de análisis termogravimétrico (TGA) con el programa de temperaturas descritas en la *Tabla 3.2.1*, en atmósfera inerte de nitrógeno. El catalizador así obtenido se pasa a denominar **13Ni/BGO**.

Pasos	Rango de T ^a	Rampa	Tiempo mantenido
Humedad	273 – 378 K	1 K/min	1h
Calentamiento 1	378 – 453 K	1 K/min	1 h
Calentamiento 2	453 – 493 K	1 K/min	
Calentamiento 3	493 – 673 K	1 K/min	1 h

Tabla 3.2.1. Programa de temperaturas de calcinación para compuestos derivados del óxido de grafeno.

El catalizador basado en la utilización de GO aminado con oleilamina se obtiene por tres procedimientos diferentes, dependiendo del momento en el que se incorpore la sal de níquel y de la incorporación o no de una etapa de purificación en el proceso de obtención, dando lugar a tres catalizadores con características diferentes. El procedimiento general [6] empleado para el primero de los tres catalizadores, comienza mezclando GO (Graphenea) y oleilamina (70 %, Sigma Aldrich) en la misma proporción (3 g) en el interior de un matraz de fondo redondo, mientras se disuelven en 500 ml con agitación durante 30 min. Pasado ese tiempo, se introduce en el equipo de ultrasonidos durante 2h, tras las cuales se introduce en el rotavapor donde se elimina el disolvente por evaporación a 323 K y vacío. La muestra se seca en la estufa a 393 K durante 2 h, se deja enfriar y se purifica con metanol, antes de su calcinación en TGA con el programa de temperaturas de la *Tabla 3.2.1*. Una vez preparado el soporte, se incorpora la sal del metal (Ni) con 500 ml de etanol y se repite el procedimiento descrito para la impregnación incipiente, obteniendo el catalizador **13Ni/OI-GO (Met)**. Eliminando la etapa de purificación del procedimiento anterior, el catalizador obtenido es **13Ni/OI-GO**. Finalmente, el último de los catalizadores se obtiene eliminando la impregnación sucesiva en el proceso de obtención, al introducir la sal de Ni junto con la oleilamina y GO al principio de la preparación. De este modo, el catalizador obtenido se denomina **13Ni-OI/GO**.

Los catalizadores soportados en rGO y AGO suministrados por Graphenea se elaboran siguiendo un protocolo parecido al descrito en las **secciones 3.1.1** y **3.1.2** para catalizadores por impregnación húmeda e impregnación húmeda sucesiva. Los catalizadores preparados con estos soportes serán: **13Ni/AGO**, **13Ni/rGO** y **13Ni/14La-rGO**.

En el caso del catalizador **13Ni/14La-rGO**, el método empleado es el de impregnación húmeda sucesiva. Se mezclan 0,90 g de sal de lantano (Nitrato de lantano (III) hidrato, 99,9 %; Sigma Aldrich) con 2 g de rGO (Graphenea) y 500 ml de etanol en un matraz de fondo redondo. El matraz se introduce en el equipo de ultrasonidos durante 2

h, antes de pasarlo al rotavapor donde se evapora el disolvente en condiciones de vacío a 323 K. El producto obtenido se seca en estufa durante 2h a 393 K, para después calcinarlo en el TGA con el programa de temperaturas de la *Tabla 3.2.1*. Una vez calcinado se incorpora 1,76 g de la sal de níquel al producto anterior con 500 ml de etanol, y tras seguir el mismo procedimiento, el catalizador calcinado se tamiza y prensa para obtener un tamaño de partícula de 0,42 a 0,50 mm. Los catalizadores **13Ni/AGO** y **13Ni/rGO** se obtienen de manera similar, empleando una cantidad de sal de níquel de 1,48 g para la cantidad de 2 g de soporte.

3.3. Caracterización de los catalizadores

La caracterización de los catalizadores es la clave para la determinación de sus propiedades físico-químicas, sus características como catalizador en la reacción de metanación, o de las condiciones de operación óptimas. Los análisis empleados para el completo estudio de los catalizadores son: contenido metálico, propiedades texturales, reducibilidad, acidez y basicidad, composición elemental de la superficie, especies cristalinas, microscopía y análisis elemental.

3.3.1. Contenido metálico

La cantidad de Ru, Ni, Ba, Ca, Mg, La, Ce, Co, Cr, Fe y/o Mo impregnado en los catalizadores frescos se determina por el empleo de la técnica **ICP-OES** (del inglés, Inductively Coupled Plasma-Optical Emission Spectroscopy) con el equipo Perkin-Elmer Optima 330DV (*Fig. 3.6*). Para poder analizar las muestras en este equipo, es necesario preparar las muestras y los patrones previamente.

El primer paso consiste en la digestión de 50 mg de cada catalizador. Para ello se introduce la muestra a analizar en el interior de un vaso de digestión de teflón junto con 6 ml de ácido clorhídrico (HCl) y 2 ml de ácido nítrico (HNO₃). Acondicionadas las mezclas ácidas de todos los catalizadores en el interior de los vasos, se introducen en el equipo de **digestión microondas** Ethos 1 Advanced Microwave Digestion System (*Fig. 3.5*). El programa de temperaturas llevado a cabo durante la digestión se representa en la *Fig. 3.4*.

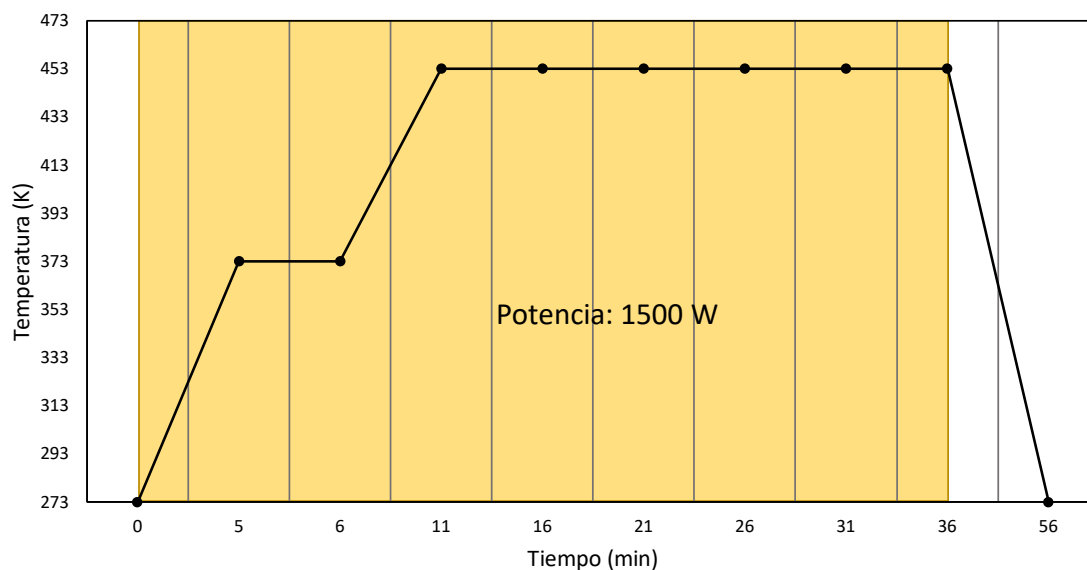


Fig. 3.4. Programa de temperaturas para la digestión de catalizadores en el digestor microondas.

Una vez digeridas las muestras, el contenido de los vasos se filtra y se enrasa en un matraz aforado de 100 ml con agua miliQ, para garantizar que la disolución se encuentra en la concentración adecuada, entre los límites de detección del equipo.

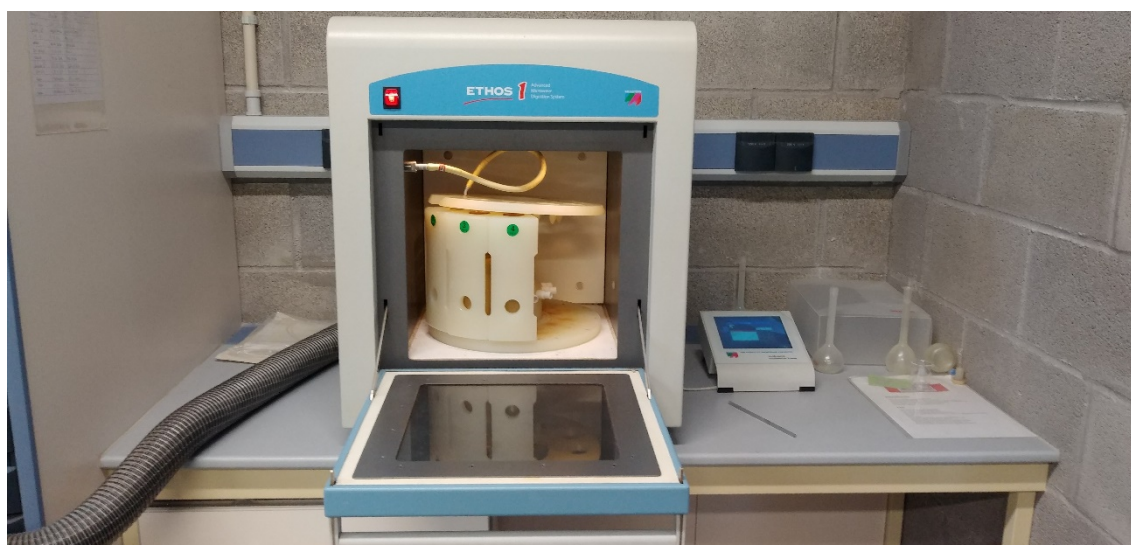


Fig. 3.5. Fotografía del digestor microondas Ethos 1 Advanced Microwave Digestion System.

A continuación, se preparan las **disoluciones patrón** correspondientes a los metales que se vayan a analizar. Se elaboran 4 disoluciones patrón con distintas concentraciones del metal a analizar con el fin de determinar una recta de calibración que abarque las concentraciones teóricas del metal contenido en el catalizador. El enrase de las disoluciones patrón se hace con la disolución **matriz ácida** consistente en un 24% vol de HCl, 8% vol de HNO₃ y el 68 % vol de agua miliQ. A su vez, la matriz ácida se emplea como blanco en la representación de las rectas de calibrado determinadas en el ICP (Fig. 3.6).

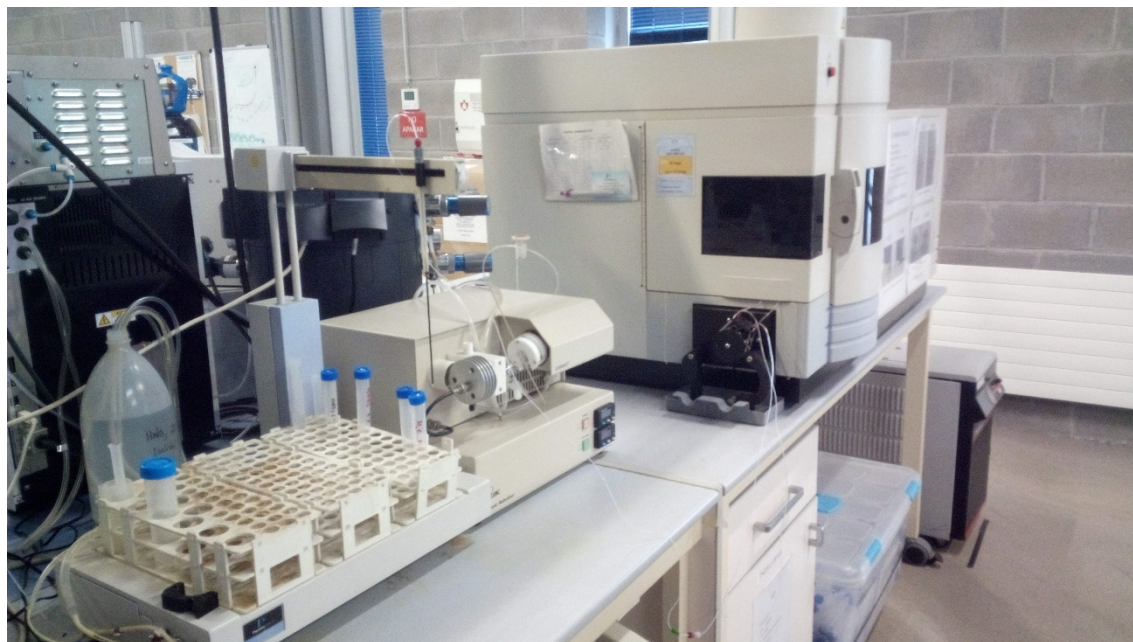


Fig. 3.6. Fotografía del equipo de análisis de muestras ICP-OES Perkin-Elmer Optima 330DV.

Finalmente se representan las rectas de calibrado, y se analizan las muestras de catalizador digeridas y filtradas, determinando el contenido metálico de cada catalizador.

3.3.2. Propiedades texturales

Las principales características texturales (**área superficial, volumen de poro, distribución del tamaño de poro y rango de diámetro de poro**) de los catalizadores frescos se determinan por el análisis en el equipo Autosorb 1C-TCD. Para ello, se introduce una cantidad de muestra de entre 50 a 100 mg en el interior de la celda y se procede a su desgasificación, introduciéndola en la parte correspondiente del equipo, durante 3h a 573K. De esta manera se eliminan todas aquellas moléculas que ocupan el volumen de la muestra y las que puedan estar fisisorbidas en la superficie del catalizador o del soporte a analizar. Pasado ese tiempo, se mide la masa desgasificada, y se introduce la celda en la parte correspondiente del equipo para proceder al análisis. Tras rellenar los dewars con nitrógeno líquido, se introduce la masa de muestra desgasificada en el programa junto con la descripción de la muestra, y se procede con su análisis.

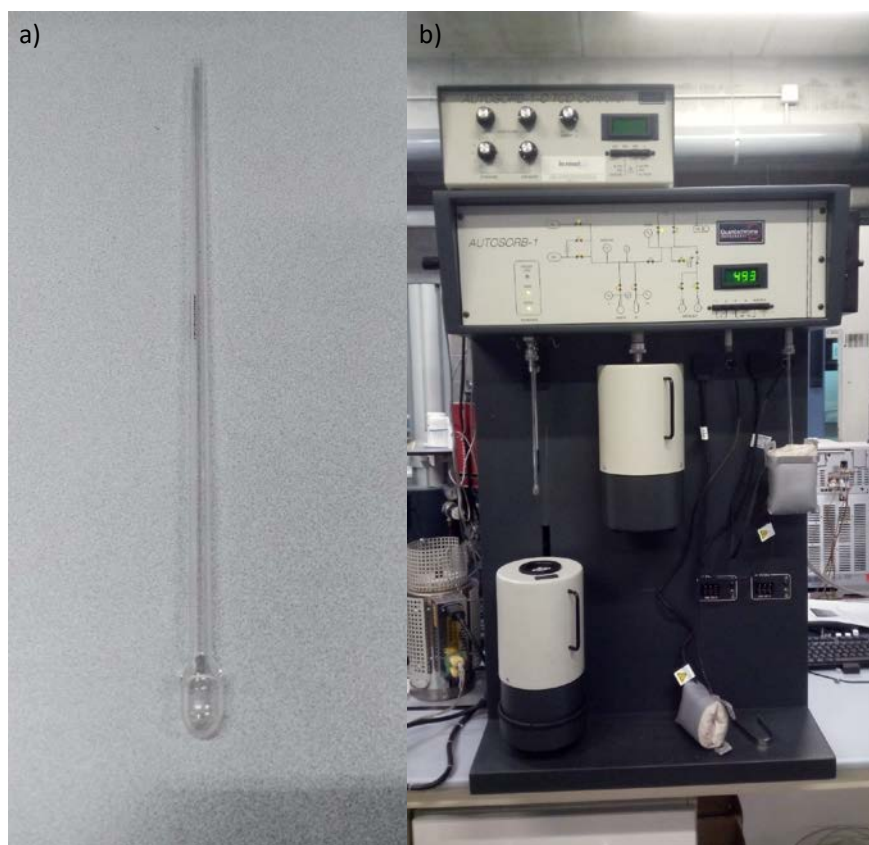


Fig. 3.7. Fotografía de a) celda de análisis del Autosorb y b) equipo Autosorb 1C-TCD.

Durante el análisis, el equipo define las curvas de adsorción-desorción para cada muestra, a 77 K. Con estos resultados, y mediante el empleo del **método Brunauer, Emmett y Teller (BET)** se define el **área superficial** de la muestra. Por otro lado, la aplicación del **método Barret-Joyner-Halenda (BJH)** permite determinar la **distribución del tamaño de poro** y el **rango de diámetro de poro**.

3.3.3. Reducibilidad

La temperatura de reducción y las especies reducibles presentes en los catalizadores se determinan mediante la técnica de **reducción a temperatura programada de hidrógeno o H₂-TPR**, empleando el equipo Micromeritics AutoChem II RS232 (*Fig. 3.8*), equipado con un detector de conductividad térmica (TCD). Los perfiles de reducción se determinan a través de la incorporación de una corriente de 40 ml/min de mezcla H₂/Ar al 5% sobre una masa de aproximadamente 50 mg del catalizador calcinado. La muestra se introduce previamente en una celda de cuarzo con forma de U (*Fig. 3.8*), inmóvil entre dos porciones de lana de cuarzo, que eviten su salida durante el análisis. La celda se introduce en el interior del horno del equipo, mientras que el serpentín del equipo se cubre con un dewar con hielo y agua.

Previo paso al análisis, se acondiciona la muestra, al elevar su temperatura desde la temperatura ambiente hasta los 473 K con un flujo constante de argón de 40 ml/min durante 1h. Pasado ese tiempo se enfría la muestra hasta los 323 K y la corriente de argón se sustituye por la corriente de H₂/nitrógeno. Bajo este ambiente reductor, se eleva la temperatura desde los 323 K hasta los 973 K, mientras se mide en el TCD la variación de

la señal, que es proporcional al hidrógeno que se consume en la reducción de la muestra y a qué temperatura, lo que permite determinar la **temperatura de reducción de la muestra**, pero también las **especies reducibles** y la **fuerza de interacción** con el soporte que posee el catalizador a estudio, mediante su comparación con datos publicados.



Fig. 3.8. Fotografía de a) celda de análisis del AutoChem y b) equipo de análisis Micromeritics AutoChem II RS232.

3.3.4. Acidez y basicidad

El sistema de análisis utilizado para determinar la acidez y basicidad de los catalizadores a evaluación es el mismo empleado en el estudio de la reducibilidad, el equipo Micromeritics AutoChem II RS232 (Fig. 3.8). El estudio de la acidez se asocia con la **desorción de amoníaco a temperatura programada o NH₃-TPD**, mientras que el estudio de la basicidad se asocia con la **desorción de dióxido de carbono a temperatura programada o CO₂-TPD**. Ambos análisis tienen en común la etapa de desorción del compuesto a evaluación, siendo NH₃ o CO₂ según el caso, detectando la cantidad liberada del catalizador con el tiempo/temperatura con ayuda del detector TCD previamente calibrado. A mayor temperatura, mayor fuerza de interacción de la molécula con el catalizador y por tanto más fuertemente ácidas o básicas son las especies que componen el catalizador. Es por ello que esta medida permite determinar la **naturaleza ácida o básica de las especies** presentes en el catalizador.

La preparación de las muestras se realiza de manera similar a lo explicado en la sección 3.3.3 para el estudio de la reducibilidad: 50 mg de muestra (aproximadamente) se introducen en la celda de cuarzo en U (Fig. 3.8) entre lana de cuarzo, introduciendo la celda en el interior del horno. En este caso no es necesario situar el dewar con hielo sobre el serpentín, ya que no pasará por esta sección el flujo.

A continuación, se procede con el análisis, el cual consiste en seis etapas consecutivas. En primer lugar, el catalizador se reduce con una corriente de 5%vol H₂/Ar a 673 K, tras la cual se sustituye la corriente reductora por un inerte, helio, que se emplea para enfriar la muestra hasta los 373 K. Seguidamente se introduce el gas que corresponda, según el tipo de análisis, siendo en el caso de la acidez una corriente 10%vol

NH₃/He y en el caso de la basicidad CO₂ en la misma proporción, y se deja en contacto con la muestra durante 30 min. Se sustituye este gas por He y se eleva la temperatura del sistema en el caso del estudio de acidez, hasta los 423 K. De este modo se eliminan los átomos de amoníaco unidos a la muestra por fisorción, que no resultan de interés en el estudio de la naturaleza química de la muestra. Finalmente, se procede al análisis correspondiente, elevando la temperatura desde los 423 K hasta los 973 K en el caso de la acidez, y desde los 313 K hasta los 873 K en el caso de la basicidad. Acabado el análisis, se enfría la muestra.

3.3.5. Composición elemental de la superficie

Las especies localizadas en la superficie del catalizador se analizan con el sistema de **Espectroscopía Foelectrónica de Rayos X (XPS) SPECS (Fig. 3.9)** equipado con un analizador de energía Phoibos 150 1D-DLD y una fuente de radiación monocromática Focus 500, con ánodo dual Al/Ag, que permite trabajar con potencias de hasta 400 W para el Al y 600 W para la Ag. Esta técnica no sólo permite **identificar las especies** presentes en la superficie y su **estado de oxidación**, sino que además permite su cuantificación posibilitando el cálculo de la **dispersión del metal** de estudio en la superficie del catalizador. Esta técnica permite además comparar el cambio acontecido en las muestras de catalizador activas y tras su uso en la reacción de metanación, con su consecuente desactivación en presencia de H₂S. Previo al análisis, las muestras frescas se reducen en la celda de reacción que incorpora el equipo, emulando las condiciones de reducción llevadas a cabo en el interior del reactor. Se calienta la muestra desde la temperatura ambiente hasta los 673 K con una rampa de 10 K/min y una corriente de H₂/N₂ con un ratio 3:1 (65 Nml/min de H₂) durante 4 h. En el caso de las muestras usadas, se introducen en el equipo donde la atmósfera inerte mantiene las muestras sin alterar, eliminando el disolvente que acompaña las muestras para evitar su oxidación, el iso-octano.



Fig. 3.9. Fotografía del sistema de Espectroscopía Fotoelectrónica de Rayos X (XPS) SPECS.

3.3.6. Especies cristalinas

La medida de las **especies cristalinas** presentes tanto en los catalizadores frescos, como en los usados, y el **tamaño del cristal** medio se determina mediante la **técnica de difracción de rayos X (XRD)**. El equipo empleado para este análisis es el difractómetro de muestra policristalina de geometría theta-theta, PANalytical X'Pert Pro (*Fig. 3.10*), equipado con un monocromador con radiación Cu-K α ($\lambda=1,54 \text{ \AA}$) y un detector del estado sólido PIXcel.

Las muestras, previamente a su análisis, son reducidas en el interior de un horno horizontal con una corriente de H₂/N₂ con ratio 1:3 y elevando la temperatura con una rampa de 10 K/min desde la temperatura ambiente hasta los 673 K, temperatura a la que se mantiene durante 4 h.



Fig. 3.10. Fotografía del difractómetro de muestra policristalina de geometría theta-theta, Panalytical X'Pert Pro.

Los espectros obtenidos tras el análisis de las muestras, permite determinar las **especies cristalinas** que componen la muestra. Su identificación se consigue por el empleo de las bases de datos "The Joint Committee on Powder Diffraction Standards" (JCPDS) [7] o "Power Diffraction File" (PDF) [8], por coincidencia de los picos determinados en los ángulos de difracción correspondientes.

El cálculo del **tamaño de cristal medio** de las especies cristalinas presentes en la muestra, se calcula por el empleo de la ecuación de Scherrer (*Ec. 3.1*):

$$d = K\lambda/B(2\theta)\cos\theta \quad \text{Ec. 3.1}$$

Donde K es el factor de forma (0,89), λ es la longitud de onda de rayos X, $B(2\theta)$ es la ampliación de la línea a la mitad de la intensidad máxima (después de restar la ampliación de la línea instrumental) en radianes y θ es el ángulo de Bragg [9]. De todos los ángulos característicos de la especie a identificar se selecciona el que se encuentre más aislado disponible.

3.3.7. Microscopía

Las técnicas de microscopía empleadas para el estudio morfológico de los catalizadores frescos y usados son tres (*Fig. 3.11*): **microscopía electrónica de transmisión (TEM)**, **microscopía electrónica de barrido (SEM)** y **microscopía electrónica de barrido y transmisión de alta resolución (STEM)**. Los análisis se llevan a cabo en diferentes equipos. Por un lado, las imágenes **TEM** se extraen por medio del microscopio electrónico de transmisión Philips CM200 con resolución de 137 eV. Las imágenes **SEM** se obtienen de un microscopio electrónico de barrido JEOL JSM-7000F con resolución de hasta 1,2 nm (mediante electrones secundarios y 30 kV) y un detector EDX INCA X-sight Serie Si(Li) pentaFET Oxford. Finalmente, las imágenes **STEM** se consiguen por el empleo de un microscopio electrónico de transmisión y barrido Schottky X-FEG (FEI Titan Cubed G2 60-300) con resolución $\leq 0,136$ nm a 300 kV y una energía de resolución de $\leq 0,3$ eV, equipado con un sistema de análisis EDX Super-X para el análisis de las especies químicas presentes.

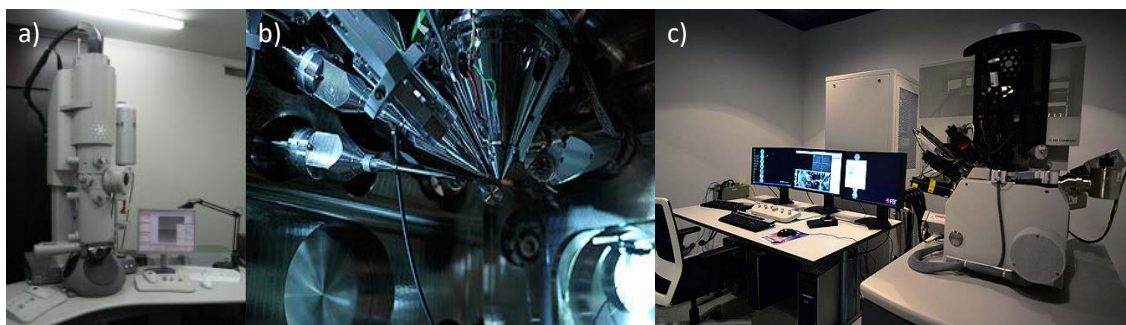


Fig. 3.11. Fotografía de los equipos de microscopía electrónica a) de transmisión Philips CM200, b) de barrido JEOL JSM-7000F y c) de transmisión y barrido de alta precisión Schottky X-FEG (FEI Titan Cubed G2 60-300).

Por medio del estudio de la **morfología** del catalizador con estas técnicas se pueden determinar diferentes parámetros, como el **tamaño de partícula** de los diferentes metales que componen la muestra, su **dispersión, distribución de tamaños, presencia de carbono o azufre, o distribución de los elementos** que componen la muestra (N, O, C, Al, Ni, etc). Al igual que en el estudio de XRD, las muestras frescas deben ser reducidas previamente al análisis bajo las mismas condiciones que tienen lugar en el interior del reactor, para lo que se llevan a cabo los mismos pasos descritos en la **sección 3.3.6**.

3.4. Estudio de la actividad del catalizador

El estudio de la actividad de los catalizadores en la reacción de metanación de CO_2 , se lleva a cabo en el interior de una planta piloto Microactivity Reference (PID Eng&Tech) como la que se muestra en la Fig. 3.12. La planta piloto se puede dividir en varias secciones. La sección de alimentación se compone de todas las conexiones a las botellas de los gases que suministrarán a la planta bien sea como reactivos o como inertes y, seguido, los controladores de flujo (Bronkhorst) que regulan la cantidad de gas que entra al sistema, representados en la Fig. 3.13.

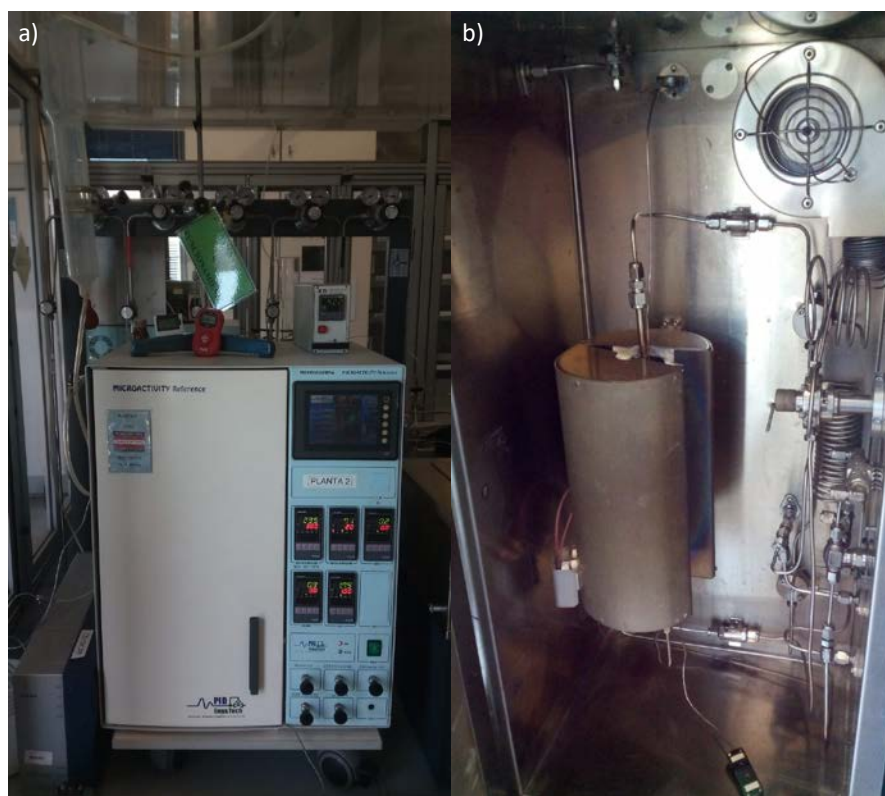


Fig. 3.12. Fotografía de la planta piloto Microactivity Reference (PID Eng&Tech) empleada en el estudio de la actividad catalítica de los catalizadores en la reacción de metanación representando el a) montaje exterior con conexión al sistema de análisis cromatográfico en línea Varian CP-4900 MicroGC y b) montaje interior.

La segunda sección es la de reacción, en la que tras atravesar el transductor de presión el cual indica y controla la presión en el sistema para que sea de 10 bar a la entrada del reactor, y la válvula de 5 vías, los gases de reacción juntos se introducen en el reactor. El reactor (**Fig. 3.14**), de lecho fijo, consiste en un tubo de acero inoxidable de 32 cm con un diámetro exterior de $\frac{1}{4}$ ", en el que se sitúa el catalizador en su interior. La carga de catalizador es de 200, 125 o 60 mg, según el caso analizado, con tamaño de partícula de entre 0,42 y 0,50 mm, conseguido mediante prensado y posterior tamizado, tal y como se describe en la preparación del catalizador (sección 3.1 y 3.2). El catalizador se encuentra diluido con carburo de silicio (SiC) del mismo tamaño de partícula, en una proporción $masa_{catalizador}/masa_{SiC}=1:4,5$, para que el lecho se aproxime al máximo al régimen isoterma. El resto del reactor se rellena con SiC de mayor tamaño, que facilite una homogénea distribución del calor en el interior del reactor.



Fig. 3.13. Fotografías a) de los controladores de flujo de entrada de la planta y b) del condensador de salida acoplado a una placa Peltier para la separación de líquido y gas productos de reacción.

El reactor se encuentra situado en el interior de un horno el cual consta de un termopar, que permite la correcta medida de la temperatura en el interior del mismo. De este modo, se consigue mantener una temperatura constante en la pared del horno, correspondiente a las temperaturas de reacción estudiadas: 498, 523, 548, 573, 623, 673, 723 y 773 K. Para un mayor conocimiento de la temperatura en el interior del sistema, se sitúa un termopar en el interior del lecho catalítico, a la misma altura del termopar controlador de la temperatura, que se encuentra en el exterior en contacto con la pared del reactor. Los otros dos, se sitúan en el exterior, en contacto con el reactor, a la altura del principio y del final del lecho, tal y como se observa en el esquema representado en la Fig. 3.15.



Fig. 3.14. Fotografía del reactor de lecho fijo de 32 cm, $\frac{1}{4}$ " de diámetro exterior, con termopar en el interior del lecho para la lectura de la temperatura en línea.

Previamente a la reacción, el catalizador se activa mediante su reducción empleando una mezcla gaseosa de H_2/N_2 en una proporción 3:1, que corresponde con un flujo de H_2 de 65 Nml/min, a una temperatura de 673 K durante 4 h. Pasado este tiempo, se enfría el sistema con una corriente de N_2 hasta alcanzar la primera temperatura de operación.

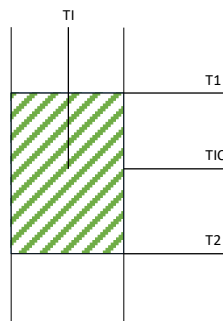


Fig. 3.15. Diagrama de posición de los termopares de control (TIC), medida (TI) y seguimiento (T1 y T2).

Una vez el catalizador está activo, se introduce la mezcla de gases de reacción al sistema, compuesta por H_2/CO_2 en una proporción 4:1, manteniendo una velocidad espacial horaria por peso (WHSV) de catalizador de $38,3 h^{-1}$ para 200 mg de catalizador, $61,0 h^{-1}$ para 125 mg y $125,4 h^{-1}$ para 60 mg. La presión de operación es de 10 bar y las temperaturas de estudio 498, 523, 548, 573, 623, 673, 723 y 773 K, manteniendo cada temperatura 2 h, tiempo suficiente para obtener el estado estacionario.

Los gases se alimentan en la proporción estequiométrica, y en las condiciones de operación adecuadas, para la obtención de la reacción de metanación de CO_2 , evitando de este modo que tengan lugar reacciones secundarias como la reacción de gas de agua inversa (RWGS), la metanación de CO, o la reacción de Boudouard, descritas en el **capítulo 1**.

Finalizada la etapa de reacción, los gases resultantes se dirigen de manera conjunta hacia la sección de salida (Fig. 3.13). En esta sección, los productos de reacción se separan en el interior de un condensador, enfriado con ayuda de una placa Peltier que permite la condensación del agua producida en la reacción, para su medición y evitar su entrada en los equipos de análisis. Los gases separados del agua se canalizan hasta un punto de separación en dos corrientes reguladas por válvulas todo o nada. Por un lado, se conecta con un burbujímetro para la medida del caudal de gas de salida, mientras que por la otra vía se dirige hacia el equipo de análisis cromatográfico en línea Varian CP-4900 MicroGC, equipado con un detector TCD y dos columnas (10 m Molecular Sieve 5, 10 m Poraplot Q) para determinar la composición de la fase gas. Se comprueba así la extensión en que los gases de reacción introducidos se han transformado en los productos de la reacción. Además, se calculan los balances de materia a todos los elementos, siendo una evidencia de que no se producen reacciones secundarias como la coquización.

Un resumen de todas las conexiones, elementos, medidas y parámetros del sistema se recogen de manera esquemática en el diagrama de funcionamiento de la planta (Fig. 3.16), empleada para la reacción de metanación de CO_2 . Los parámetros empleados para la medida de la actividad son principalmente el rendimiento a metano y

la frecuencia de recambio (TOF, del inglés, Turnover frequency), que se definen en las siguientes ecuaciones (Ec. 3.2, Ec. 3.3 y Ec. 3.4).

$$\text{Rendimiento a CH}_4: \eta_{\text{CH}_4} = \text{mol CH}_4^{\text{salida}} / \text{mol CH}_4^{\text{salida}} \text{estequiométrico} \quad \text{Ec. 3.2}$$

$$\text{TOF (h}^{-1}\text{)} = \frac{[\text{CO}_2]_{\text{en}} \cdot X_{\text{CO}_2}}{D \cdot n} \quad \text{Ec. 3.3}$$

$$D = \frac{6 \cdot M_{\text{Ni}}}{d \cdot A_{\text{Ni}} \cdot \rho_{\text{Ni}} \cdot N_{\text{Avogadro}}} \quad \text{Ec. 3.4}$$

Donde $[\text{CO}_2]_{\text{en}}$ se refiere a la corriente de CO_2 medida a la entrada al sistema, X_{CO_2} es la conversión fraccional de CO_2 , n es el número de moles de Ni (determinado por ICP-OES), D es la dispersión de Ni (metal en la superficie por átomos de metal totales) [10], M_{Ni} es la masa del átomo de Ni, d es el diámetro de partícula del Ni (obtenido por las medidas en STEM), A_{Ni} es el área superficial del átomo de Ni, ρ_{Ni} es la densidad del Ni y N_{Avogadro} es el número de Avogadro.

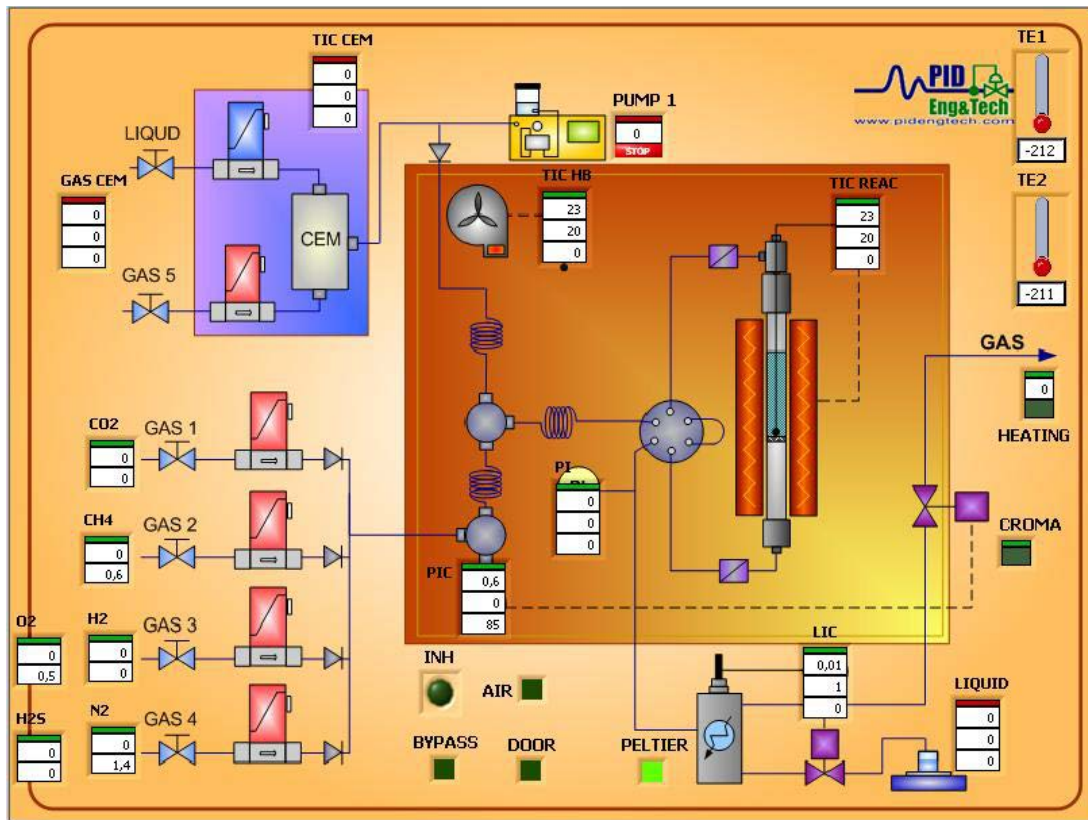


Fig. 3.16. Panel de control del sistema que representa el diagrama de funcionamiento de la planta y todos sus componentes.

Una vez estudiada la actividad de los catalizadores en la reacción de metanación de CO_2 , se debe testear su actividad para una corriente con un contenido de H_2S de 50 ppm. Las condiciones de operación en este caso son 773 K y 10 bar. Bajo estas condiciones, la actividad del catalizador se determina durante 2 h, haciendo medidas de composición y flujo a la salida cada 10 min. Se analiza el efecto del H_2S sobre el catalizador con el tiempo y su efecto según el tipo de catalizador, para poder comparar con la actividad obtenida en ausencia de este componente.

Finalmente, el estudio de la actividad se concluye, determinando la actividad del catalizador tras su desactivación con H_2S por dos vías. En primer lugar, midiendo la actividad del catalizador al eliminar el componente de la fuente a las mismas condiciones de operación (773 K y 10 bar). Y por otro lado, se elimina el componente sulfurado unido al catalizador por una etapa de regeneración con una corriente compuesta por 200 Nml/min de N_2 y 10 Nml/min de O_2 a 773 K durante 4 h; y una etapa de reducción similar a la de activación del catalizador (65 Nml/min de H_2 y 195 Nml/min de N_2 a 673 K durante 4 h). En esta segunda vía, una vez regenerado y reactivado el catalizador, se estudia de nuevo su actividad a las mismas condiciones de operación. Por estas dos vías, se busca determinar la capacidad de recuperación de la actividad del catalizador, tras su envenenamiento con H_2S , según el tipo de catalizador y los metales y/o soporte que los constituyen.

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CAPÍTULO 4



Efecto de la adición de Co, Cr, Fe y Mo al catalizador de Ni/Al₂O₃. Estudio sobre la actividad, resistencia al envenenamiento por H₂S y regeneración

"La ciencia, muchacho, está formada de errores, pero de errores que conviene cometer, porque conduce poco a poco a la verdad"

JULIO VERNE

Extraído del artículo: *A study of deactivation by H₂S and regeneration of Ni catalyst supported on Al₂O₃, during methanation of CO₂. Effect of the promoters Co, Cr, Fe and Mo.*

Autores: David Méndez-Mateos, V. Laura Barrio, Jesús M. Requies, José F. Cambra.

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Abstract

Energy storage from renewable sources is possible by chemical procedures, being Power to Gas technology a possible solution for the long-term storage. In this work, CO₂ methanation from a sulphur containing gas was studied, taking into account deactivation of the catalysts and a regeneration process. In order to improve the sulphur resistance of a standard nickel (13%) catalyst supported on alumina, transition metals like molybdenum (Mo), iron (Fe), cobalt (Co) or chromium (Cr), in different proportions (from 4 to 8 wt. %) were added to the catalyst formulation. The catalysts activity, between 573 and 773K, at 10 bar, increased when transition metals were added except for Mo in the highest proportion. These bimetallic catalysts presented a similar deactivation resistance than the monometallic catalyst when sulphur was present in the feed. Once H₂S was removed from the feed, and catalysts regenerated with oxygen, only the catalyst containing cobalt recovered up to a 13% of methane yield.

4.1. Introduction

Energy strategies in the EU have faced very important transformations after the decision about the 2030 climate and energy package [1]. Some of the energetic strategies of this program are the emissions reduction from fossil fuels, replace from conventional to renewable energy sources and search for new and more efficient processes to harness the available sources, reducing the greenhouse gases in Earth's atmosphere [2]. Renewable systems produce clean energy from sun, wind or water which are available natural resources [3]. However, the energy production depends of the availability and quantity of the natural resources, and may cause temporal and spatial energy fluctuations in the grid. That could be solved by energy storing when the supply exceeds the demand and using it when the demand is larger than the supply. Nowadays the energy storage systems are varied, with different advantages and disadvantages. Depending on the application the requirement about efficiency, self-discharge rate, rapid-response, lifetime, life cycle, capital cost, technology maturity or resources decide the appropriate system [4–6]. On the other hand what is clear is that in this transition to a system based on renewable energies a combination of all them would be necessary. In the case of the long-term energy storage the power-to-gas technology present some advantages converting renewable power to fuel or chemicals. Some of the main advantages of Power-to-Gas (PtG) technology are: continuously decreasing production cost due to the advances in electrolysis technology, availability of low-cost electricity, long-term energy storage, recycled or captured CO₂ is needed and large amount of energy/electricity is stored.

Power-to-gas is a technology which converts the excess electricity into a gaseous fuel, such as hydrogen or methane in two steps (*Fig. 4.1*), and it is supporting the penetration of the renewable sources [7].

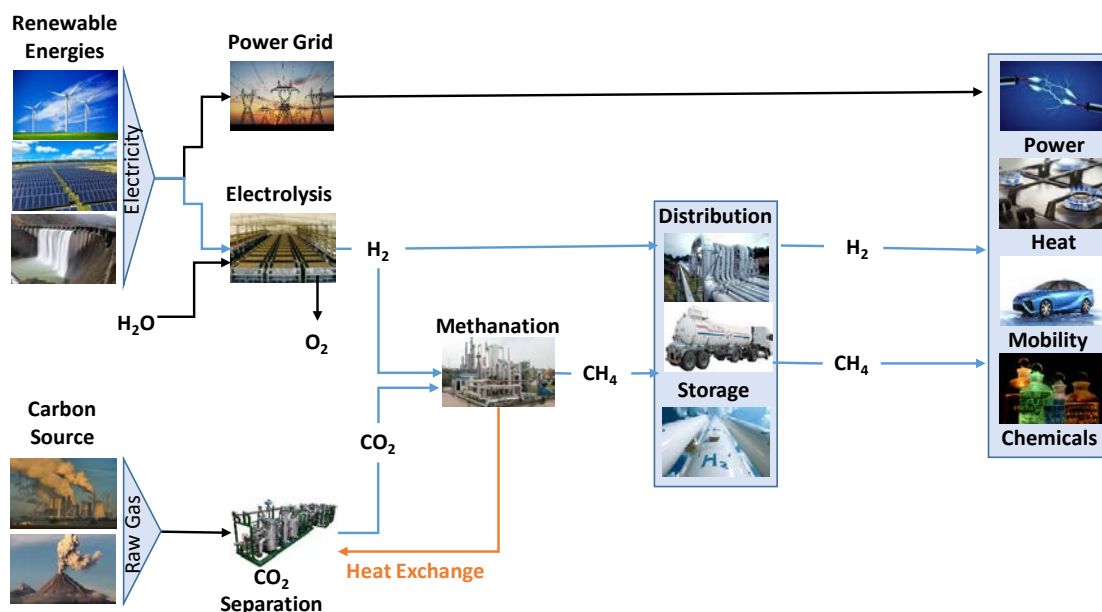
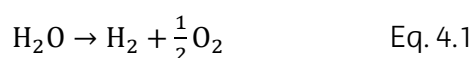


Fig. 4.1. Scheme of Power-to-Gas technology.

In the first step, hydrogen and oxygen are produced via water electrolysis (*Eq. 4.1*). Oxygen can be released to the atmosphere or used as raw material in industrial production process, but the main product of this transformation is hydrogen like fuel (whose burn product is water) [8]; then it can be transported or stored either in a dedicated distribution grid or mixed in the existing natural gas infrastructure [9].



In a second step, methane is produced via carbon dioxide hydrogenation (methanation), using the hydrogen from the first step, process known as Sabatier reaction (*Eq. 4.2*). This reaction has been extensively studied and applied industrially since 1900s, using catalysts based on nickel, ruthenium, rhodium and cobalt as active metals and alumina as support for the catalyst, being Ru-Al₂O₃ catalyst one of the most active systems [8]. The carbon dioxide could be obtained from exhaust or process gases of industrial processes or fossil power plants, biogas plants or from the atmosphere. The methane produced can be stored, burned or injected into the existing natural gas grid, being cheaper and easier than for the hydrogen [10].



The carbon dioxide from biogas industry is a good source and when biogas is produced large amounts of carbon dioxide are generated but with the problem of the presence of other compounds, that are deleterious for the catalyst performance. The usual biogas composition is 50-75% CH₄, 50-25% CO₂, 0-10% N₂ and 0-3% H₂S [11]. One of the major challenges in utilizing biogas is the presence of H₂S as the catalyst deactivates by sulphur poisoning [12,13].

This research was planned to improve the methanation step of the PtG process, based on Sabatier reaction, employing renewable H₂ and CO₂ from biogas, which contains hydrogen sulphide. The nickel, ruthenium, rhodium, platinum and palladium catalysts have been wide reported as active catalyst in Sabatier reaction, supported on different metal oxides (CeO₂ or Al₂O₃, among others) due to the high available area [14–

18]. The high surface, stability, activity and selectivity improved on metallic catalyst due to γ -Al₂O₃ structure, specially, at operation conditions, marking this support how most suitable [13,19]. Moon et al. [14] combined Ni, Ce and Zr to store oxygen achieving 82% CO₂ conversion at 573 K and atmospheric pressure.

The low price and the good activity of the nickel with respect to noble metals, implied all of the catalysts prepared were based on nickel as active metal [20–22]. Addition of transition metals increased the dispersion and the reducibility of the nickel species, same effect than using noble metals but with significantly lower price [20,21]. The nickel species provide high activity in Sabatier reaction, but high sulphur sensitivity, it was necessary the addition of modifier that doped the metal surface. The transition metals used were VIII B metals, mainly Co, Cr, Mo or Fe because of contribute the H₂S resistance of the catalyst [23–27].

There are limited reports that investigate the H₂S effect in the catalyst deactivation in methanation reaction, being studied in other processes like the steam reforming or water gas shift (WGS). Zhang et al., [28] studied the deactivation in the WGS reaction to design Fe-based sulphur tolerant catalyst in which sulphur-related phases were not observed. In this work, the authors explained that the tolerance of H₂S to metal, thus chemical bonding, block or inhibit active sites and this could cause a marked activity loss specially for the Cu samples. Generally the deactivation of transition metal catalysts in the presence of H₂S is an exponential function of time, described by Appari et al. [11], and takes from 5 to 20 h in the case of the steam reforming system to complete deactivation. Ni catalyst supported on γ -Al₂O₃ was studied in this work for the deactivation and regeneration as a function of concentration of H₂S and the temperature. The sulphur removal and Ni-based catalyst regeneration was widely studied by Li et al. [29], focused on sulphur removal in the form of SO₂ from a biomass derived syngas. Feng et al. [30] studied the regeneration of the catalyst removing the catalyst poison over iron oxide employing N₂-diluted air (6 vol% O₂) achieving high desulphurization and regeneration yield after many sulphidation-regeneration cycles.

In the present work, Ni was chosen as the active metal due to its low price with respect to platinum group metals, while maintaining a good activity [11]. In order to improve the catalyst performance, the effect of transition metals such as Co, Cr, Fe and Mo was studied to increase active metal dispersion, reducibility and, probably, catalyst resistance to H₂S poisoning [23,25,26,31–33]. The catalysts were supported on γ -Al₂O₃ and prepared by the incipient impregnation method, which facilitates the dispersion of the metals on the support, and their interaction [27,34]. The H₂S effect and resistance over catalyst activity and the regeneration capability by different ways.

4.2. Experimental details

4.2.1. Catalyst preparation

The bimetallic catalyst supported on γ -Al₂O₃ (Alfa-Aesar) were synthesized by wetness impregnation method. The metallic precursors employed for catalysts preparation were the following:

- Nickel (II) nitrate hexahydrate (99.999 wt%, Sigma Aldrich).
- Iron (III) chloride hexahydrate (97 wt%, PRS Panreac Química).
- Chromium (III) nitrate nonahydrate (98.5 wt%, Alfa Aesar).
- Cobalt (II) chloride hexahydrate (99 wt%, Quimivita S.A.).

- Ammonium heptamolybdate tetrahydrate (99 wt%, Merck).

Measured quantities of support γ -Al₂O₃ (5 g) and metal precursors in order to achieve the desired metal loading (13 wt% Ni and 4 wt% Co, 4 wt% Cr, 4 wt% Fe, 4 wt% Mo or 8 wt% Mo) were mixed and then dissolved in distilled water. A volume equal to or slightly in excess of the total pore volume calculated for the support was used, being 20 ml in the case of alumina. The optimal pH value was related with the isoelectric point (pI), when the zeta potential is zero (pzc), achieving that when the net charge on the surface is zero. The pzc of gamma alumina powder was found to be pH 7.5. For the pH value over pzc, the support has high affinity for protons and thus remains positively charged up to high pH values [19,35]. The solution was stirred continuously measuring the pH, to achieve a pH of 8.5 adding ammonium (Panreac) to increase the pH or nitric acid (Scharlau) to decrease the pH value. At pH 8.5, the solution was stirred overnight, in order to ensure homogeneous mixture during the impregnation process and to avoid the formation and precipitation of metal hydroxides of [36], not detected during the preparation process of the catalysts in this work. In a rotary evaporator (Heidolph Laborota 4000) was evaporated the solvent to dryness, helped for a vacuum pump that reduce the boiling point of the solution. The solvent evaporation was attained, heating at 338 K, and reducing slowly the pressure until 40-100 mbar.

Once the solvent was evaporated, the solid so obtained was introduced in an oven at 373 K during 2 h in order to ensure a complete drying. After that, the sample was calcined at 673 K (to ensure the stability of the γ -Al₂O₃) in presence of air for 2 h, with a ramp of 1 K/min. Finally, the calcined catalysts were pressed and sieved to the desired particle size: $0.42 \text{ mm} < d_p < 0.50 \text{ mm}$. It was chosen this particle size (d_p) in order to avoid reagents bypassing near the wall according to an internal pipe diameter-to-particle size ratio higher than 10 [37].

The catalysts prepared were named, according to their nominal composition, as follows: 4Co-13Ni/Al₂O₃, 4Cr-13Ni/Al₂O₃, 4Fe-13Ni/Al₂O₃, 4Mo-13Ni/Al₂O₃ and 8Mo-13Ni/Al₂O₃.

4.2.2. Catalyst characterization

The main techniques employed to determine the physicochemical properties of the catalysts were: temperature-programmed reduction (TPR), inductively coupled plasma-optical emission spectroscopy (ICP-OES), N₂ adsorption-desorption isotherms at 77 K, X-ray photoelectron spectroscopy and X-ray diffraction.

TPR: reducible species present in the catalysts and their reduction temperatures were determined. The equipment used was an Autochem, equipped with a thermal conductivity detector. It was loaded with approximately 0.05 g of fresh catalysts powder an U shaped quartz tube and heated from room temperature to 473 K for 1 h in Ar stream (30 ml/min). The samples were then cooled down to 323 K and the Ar was replaced by 5 vol%, H₂/Ar (45 ml/min) stream. The samples were heated from 323 K to 973 K, at a ramp rate of 10 K/min.

TPD: the NH₃-TPD and CO₂-TPD profiles were determined employing the Autochem, the acid and basic centres of the catalysts were analysed according to the NH₃ or CO₂ desorbed per unit time and catalyst mass. Depending on the quantity of NH₃ or CO₂ desorbed and the temperature of desorption, the acid strength and concentration were determined.

ICP-OES: the equipment employed for this analysis was a Perkin–Elmer Optima 3300DV. The Ni, Co, Cr, Fe and Mo contents in the catalysts were measured. The solid samples were firstly disaggregated in acid solution (mixture of 3:1 HCl and HNO₃ respectively), and then analysed.

N₂ adsorption–desorption isotherms: the textural properties (BET surface area, pore size distribution and average pore diameter) of the catalysts were determined using an Autosorb 1C-TCD. In order to remove the moisture and any adsorbed gases, the samples were degassed under vacuum at 573 K during 3 h.

XPS: to determine the elemental composition at the surface of the catalysts. The equipment employed was a SPECS (Berlin, Germany) system equipped with a Phoibos 150 1D-DLD analyser and an Al K α (1486.6 eV) monochromatic radiation source with electrons output angle of 90° to obtain XPS patterns of reduced and used catalyst. XPS is a technique that allows the study of the species present on the surface of the catalyst and their chemical state.

XRD: the analysis was conducted for catalyst samples between $2\theta = 20^\circ$ to 90° using CuK α radiation ($\lambda = 0.15418$ nm) at 40 kV and 30 mA, calculating crystalline species and an approximation of the average crystal size. X-ray diffraction patterns were obtained using a PANalytical X'Pert Pro diffractometer. Preceding the analysis, samples were reduced at 1,073 K during 4 h. XRD technique can measure at about 1–2 μ m depth of the sample. It was used Scherrer equation (4.3) to calculate the average particle size of the crystalline species.

$$d = K\lambda/B(2\theta)\cos\theta \quad \text{Eq. 4.3}$$

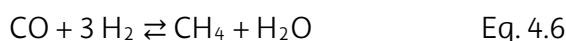
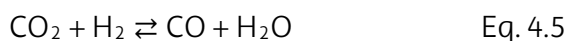
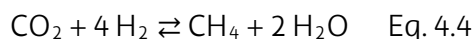
Where K is the shape factor (0.89), λ is the X-ray wavelength, $B(2\theta)$ is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle [38].

SEM and TEM: the fresh and used samples were analysed by TEM (Transmission Electron Microscopy) and by SEM (Scanning Electron Microscopy), determining the morphology of the active phase of fresh and used with H₂S catalysts. The measurements were carried out employing a Philips CM200 transmission electron microscopy with resolution of 137 eV and the JEOL JSM-7000F scanning electron microscopy with resolution until 1.2 nm (mode secondary electrons and 30 KV) and detector EDX INCA X-sight Serie Si(Li) pentaFET Oxford.

4.2.3. Activity test

To study the catalyst activity a bench-scale plant was used (PID Eng&Tech), where 0.2 g of catalyst were introduced in a stainless steel fixed bed reactor. The catalyst was diluted with inert SiC, in order to minimize thermal gradients in the catalytic bed ($\text{weight}_{\text{catalyst}}/\text{weight}_{\text{SiC}} = 1:4.5$). The reactor employed had 0.635 cm inner diameter and 32 cm of length, placing the catalyst in the central zone to an effective heating in an electrical furnace. Furnace temperature was adjusted to maintain the catalyst bed under isothermal condition, using two thermocouples: the first one inside the catalytic bed to measure the reactor temperature, and the second one before the catalytic bed in order to control the inlet temperature accurate. The first step was the catalyst activation, reducing the catalyst with a mixture of N₂ (99.999%) and H₂ (99.999%) with a ratio of H₂/N₂ equal to 3:1 (65 NmL/min of H₂) at 673 K during 4 h. Once the catalyst was activated, the reaction gasses, H₂ and CO₂, were fed in a ratio H₂/CO₂ of 4:1. Thus is the stoichiometry

proportion for the methanation reaction to obtain biogas (Eq. 4.4). The methanation reaction is the combination of equations 4.5 and 4.6, in which the CO could be generated as an intermediate product, or as a final product in combination with methane, in case the reactions of equations 4.4 and 4.5 run parallel to each other [21]. The weight hourly space velocity of the flow fed was $33.5 \text{ g}_{\text{feed}}/(\text{g}_{\text{cat}} \cdot \text{h})$.



A schematic representation of the system is shown in Fig. 4.2. The reactor was heated to the desired temperature at a rate of 10 K/min under N_2 flow and the catalyst activity was studied at different temperatures, between 573 K and 773 K, and at 10 bar of pressure, separating the reaction products in a partial condenser: condensed water and gas products. Each 10 min the output massflow and composition of the gases were analysed, maintaining each temperature 60 min, corresponding with 6 points, collecting the water produced, weighing and measuring in this time. The gas phase composition was on-line analysed using a Varian CP-4900 MicroGC equipped with a high sensitivity TCD and two columns (10 m Molecular Sieve 5, 10 m Poraplot Q).

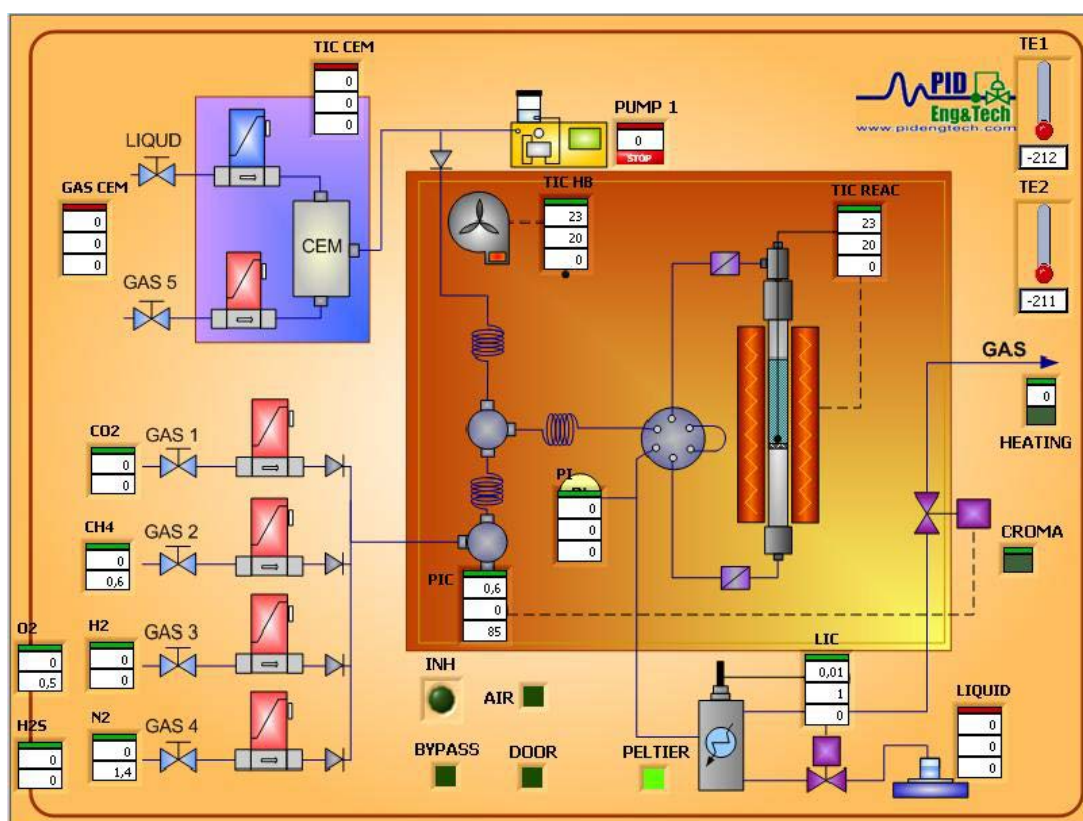


Fig. 4.2. A schematic representation of control panel used for experiments. The abbreviations used are as follows: Pressure Indicator Controller (PIC), Pressure Indicator (PI), Temperature Indicator Controller (TIC).

For a better understanding of the process, the parameter used in the calculations were calculated, which are defined below:

$$\text{CH}_4 \text{ yield: } \eta_{\text{CH}_4} = \frac{\text{mol CH}_4^{\text{out}}}{\text{mol CH}_4^{\text{out stoichiometric}}} \cdot 100 \quad \text{Eq. 4.7}$$

$$\text{TOF (h}^{-1}\text{)} = \frac{[\text{CO}_2]_{\text{in}} \cdot X_{\text{CO}_2}}{D \cdot n} \quad \text{Eq. 4.8}$$

$$D_{\text{Ni}} = \frac{6 \cdot M_{\text{Ni}}}{d_{\text{Ni}} \cdot A_{\text{Ni}} \cdot \rho_{\text{Ni}} \cdot N_{\text{Avogadro}}} \quad \text{Eq. 4.9}$$

Where $[\text{CO}_2]_{\text{in}}$ refer to inlet CO_2 stream, X_{CO_2} is the CO_2 fractional conversion, n is the molar Ni (as determined by ICP), D is the Ni dispersion (surface metal per total metal atoms) [39], M_{Ni} is the Ni atom mass, d is the Ni particle diameter (obtained from STEM measurements), A_{Ni} is the Ni atom surface area, ρ_{Ni} is the Ni density and N_{Avogadro} is the Avogadro number.

Once the activity of the bimetallic catalyst was tested in the methanation reaction from biogas flow, the next step was the reaction with a sulphur containing biogas (50 ppm H_2S , 20 vol% CO_2 and 80 vol% H_2). The methanation reactions were continued in the presence of H_2S until catalyst deactivation. Two different techniques have been explored for catalyst regeneration:

- removal of H_2S from feed stream
- catalyst treatment with an O_2 mixture flow (200 Nml/min N_2 and 10 Nml/min O_2) at 773 K during 4 h, and reducing the catalyst with a mixture of N_2 and H_2 in a 3:1 (65:195 Nml/min) ratio at 673 K during 4 h

The active catalyst, regenerated, was used again in methanation reaction of H_2 and CO_2 with 4:1 ratio at 773 K and 10 bar to measure the regeneration effectiveness and the H_2S resistance of the catalyst.

All the experiments were repeated to ensure reproducibility.

4.3. Results and discussion

4.3.1. Catalyst characterization

4.3.1.1. ICP analysis

The metal composition of the catalyst was measured by ICP-OES analysis, determining the iron, cobalt, chromium, molybdenum and nickel content. All catalysts were prepared to obtain a nominal content of 13 wt.% of Ni and 4 wt.% of promoter metal. An additional sample containing an 8 wt.% of Mo was also prepared. As shown in *Table 4.1*, the actual metal content of the catalysts were close to the theoretical, being the highest deviations present in the Ni and Co-Ni catalysts.

Sample	Composition (wt%)		S_{BET}^b (m^2/g)	V_{P}^c (m^3/g)	D_{P}^d (nm)	D_{XRD}^{e1} (nm)	D_{XRD}^{e2} (nm)	TOF CO_2^f (h^{-1})
	X ^a	Ni						
Al_2O_3	-	-	202	0.81	7.7	-	-	-
13Ni/ Al_2O_3	-	13.9	180	0.55	7.2	5	10	2951
4Co-13Ni/ Al_2O_3	4.5	12.5	187	0.22	5.1	5	10	784
4Cr-13Ni/ Al_2O_3	3.8	13.2	179	0.26	6.2	5	10	1676
4Fe-13Ni/ Al_2O_3	4.0	13.0	115	0.17	6.3	5	10	2958
4Mo-13Ni/ Al_2O_3	4.2	12.8	101	0.15	6.2	5	10	2745
8Mo-13Ni/ Al_2O_3	8.2	12.8	108	0.16	6.4	5	10	2301
Commercial	-	12.4	22	0.09	16.9	-	-	-

Table 4.1. Summary of the contents of Ni and promoter, specific area, the particle size of Ni and turnover frequency.

^aMetal promoter (Co, Cr, Fe or Mo) according to the corresponding catalyst;

^bThe surface area was calculated by the BET equation;

^cBJH desorption pore volume;

^dBJH desorption average pore diameter;

^e D_{XRD}^{e1} (after reduction) and D_{XRD}^{e2} (after reaction) are an approximation calculated from Ni (111) plane using Scherrer equation;

^fTOF_{CO₂} were calculated from Eq. 4.8 reaction conditions: GHSV=36,000 h⁻¹, T=683 K, at 1 atm.

4.3.1.2. BET measurements

The textural properties of supports and prepared catalysts were analysed in an Autosorb 1C-TCD, measuring the N₂ adsorption and desorption isotherms obtain summarized in *Table 4.1*. The isotherms obtained are type-IV, exhibiting H2 hysteresis loops, due to the presence of "ink-bottle" mesoporous structure [40]. The main textural properties studied were surface area, average pore diameter and pore volume (*Table 4.1*). These properties were compared for the different calcined catalyst with respect to the calcined support ($\gamma\text{-Al}_2\text{O}_3$) to determine the effect of the metal addition over the support. The surface area of the support (202 m²/g) was reduced slightly with the nickel addition (180 m²/g) due to the nickel deposition into the support channels, attached inside the mesopore, and partially blocking its internal pore volume during the impregnation step [41]. The addition of a second metal resulted in lower surface area and pore volume, as after the metal incorporation channels and pores of the support can be blocked. But for the cobalt-nickel bimetallic catalyst, the surface area slightly increased in relation to nickel monometallic catalyst. In the case of Fe, this decrease can be attributed to the destruction of mesopores structure or pore blockage [42]. And similar trend for the Mo, as a higher amount of metal was incorporated, was observed [43].

4.3.1.3. H₂-TPR studies

The H₂-TPR profiles of the different Ni catalysts in Al₂O₃ supported and calcined at 673 K, are collected in *Fig. 4.3*. According to the bibliography [44], a correlation is established between temperature and nature of reduction peaks. Usually, peaks under 873 K are assigned to NiO species with low to moderate interaction with the support and over

these values, with non-stoichiometric and stoichiometric nickel aluminate, not being detected in the analysed catalysts. This is due to an interesting outcome of this work is that the addition of the second metal decreased the reduction temperature under 750 K, lower than the maximum temperature in activity tests. Depending of the metal, the number and the position of the reduction peaks are different, corresponding to the reduction of different species (NiO-Al, NiAl_xO_y, ...). In the work of Rynkowski et al. [44] the effect of Ru and Ni in systems supported over Al₂O₃ in the different characterization analysis was studied. The addition of a second metal, in this case a noble metal, leads to decrease the reduction temperature, approaching the Ni reduction peak to Ru reduction peak, splitting in two peaks for proportions of Ru higher than 15%, effect of the higher contribution of RuO than NiO, as the effect observed in these experiments.

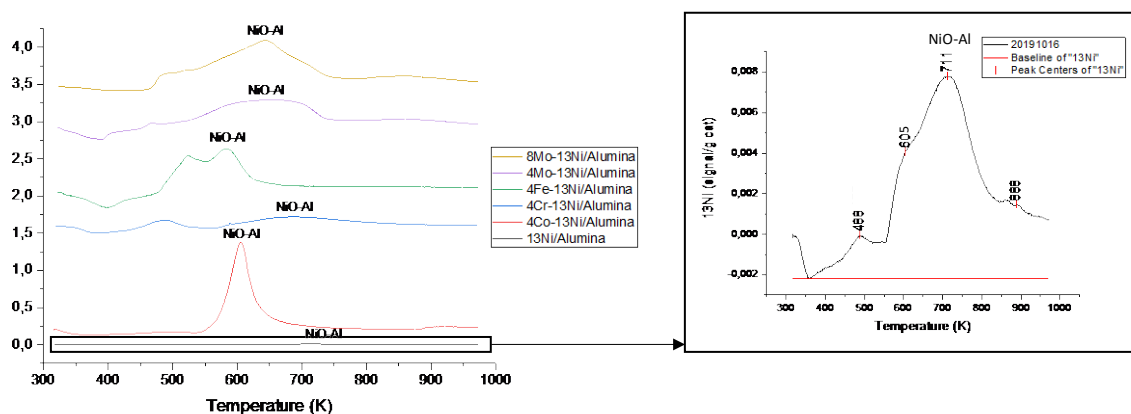


Fig. 4.3. H₂-TPR profiles of the prepared catalysts in 4% H₂/Ar atmosphere and 10 K/min heating rate.

In the case of Co, the peak appeared at around 605 K; and for the Fe catalyst, two similar peaks were measured at 520 K and at 582 K, all of them attributed to nickel oxide species with a weak interaction with the support. In the case of the iron, some Fe₂O₃ was measured by XRD, as the reduction of Fe₂O₃ to Fe₃O₄ normally occurs between 533–643 K, some reduction of Fe₂O₃ could happen overlapped by the nickel oxide reduction [45]. Thus, by the addition of Co and Fe, the reduction peaks clearly shifted to lower temperature indicating a weaker interaction of Ni with the support.

The addition of Cr showed a small and narrow peak at a low temperature (486 K) and another wider from 550 K until 750 K approximately. But there is not a significant peak for the nickel reduction and this profile can be attributed to NiO species with low interactions. For the Mo-Ni catalysts with content 4:13 and 8:13, a peak at 660 K and two shoulders (at 500 K and 720 K approximately) were observed.

For the Mo catalyst, the reduction of Mo⁶⁺ to Mo⁴⁺ appeared at temperatures around 748 K as the peaks appeared in the range between 600 K and 700 K only the reduction of NiO species are observed with weak interaction at the lower temperature (623 K) and with stronger interaction at the higher temperature (880 K) [46]. But for all the bimetallic catalysts the presence of nickel aluminate species was not measured as they appear at temperatures higher than 1173 K, and this peak was not detected.

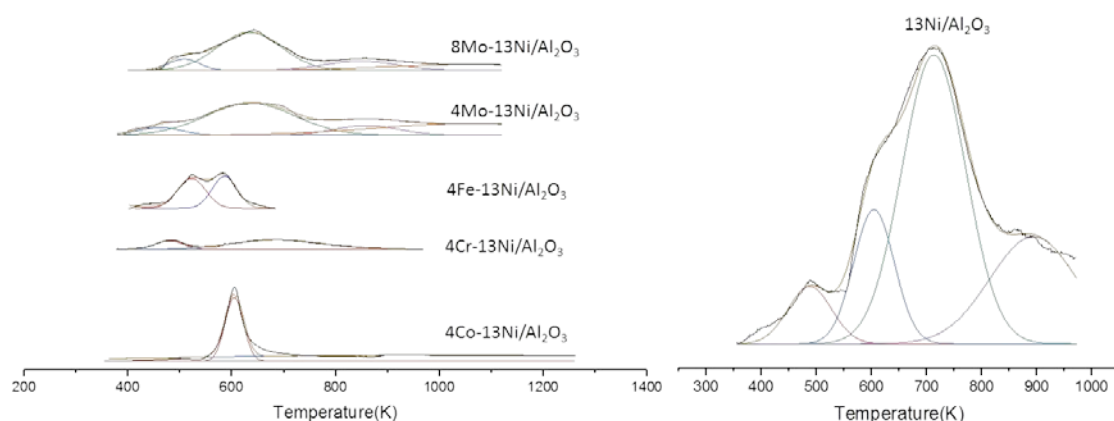


Fig. 4.4. Gaussian fitted curves of H_2 -TPR patterns for the prepared catalysts

In general, the addition of metal promoters (Co, Cr, Fe and Mo) facilitates the reducibility of the nickel catalyst. The promoters interact with the metal (Ni) achieving a higher degree of reducibility that could promote the NiO dispersion and decrease their particle size.

4.3.1.4. TPD studies

In order to determine the quantity and strength of catalyst acid and basic sites, the NH_3 and CO_2 previously bonded to acid and basic centres respectively were desorbed. Desorption temperature determines the strength of the bond, so that higher desorption temperature means stronger bond.

The NH_3 -TPD profiles are slightly different according to metal added to nickel-alumina, increasing or decreasing the desorption temperature to which weak and strong acid centres desorbed NH_3 . These profiles are shown in Fig. 4.5. The main peaks are shown at ca. 547 K, 597 K, 808 K and 1.073 K, corresponding to weak acid sites the first and second one and to strong acid sites the other two [47,48]. The amount of acid centres, and their distribution, related to ammonia desorption, are presented in Table 4.2 for the studied range. The medium acid sites of alumina are coordinated with NH_3 , due to the electron deficiency of trivalent aluminium atoms, presenting a maximum centred at 548 K [48]. Furthermore, the peak centred at 1.073 K, in strong acid region, could correspond with Brønsted acid sites by the hydrogen atoms that may act as proton donor [49], presenting more amount for all the catalysts studied.

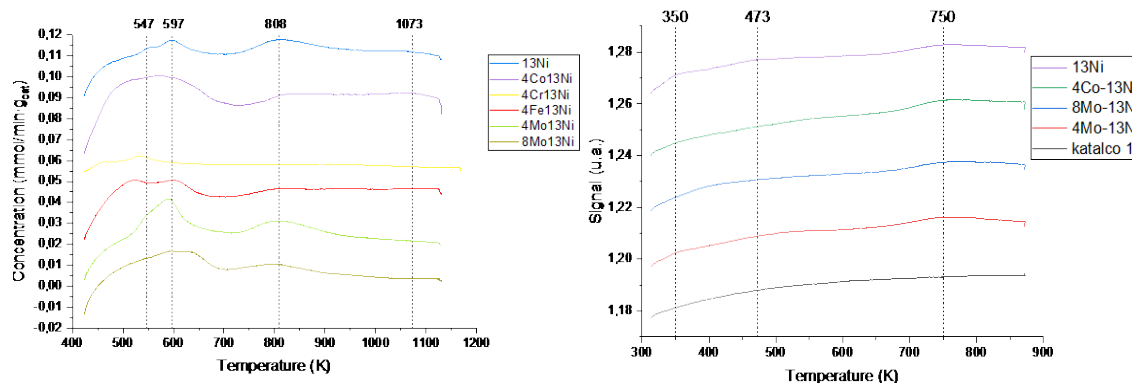


Fig. 4.5. NH₃-TPD and CO₂-TPD profiles of the prepared catalysts in 4% H₂/Ar atmosphere and 10K/min heating rate.

As can be observed in *Table 4.2*, all the bimetallic catalysts presented a higher acidity than the base catalyst, especially for medium acid sites. Only the catalyst with Cr as promoter presented qualitatively a lower acidity, probably due to CrO₃ partial reduction to Cr₂O₃. However, the different oxidation states that Cr can be present (with valences from 2 to 6), and facilitate a higher incorporation of acid centres, especially with strong character, than the rest of promoters (with valences of 2 to 3, except to Mo), giving rise to a greater quantitative acidity of this catalyst. Molybdenum exhibits a lower reducibility, which resulted in a lower incorporation of acid centres, and therefore a lower total acidity. The increase in acidity in the remaining bimetallic catalysts may be due to the incorporation of metal atoms in the support structure [50].

The CO₂-TPD profiles are shown in *Fig. 4.5*, while the amount and strength of basic centres, related to moles of CO₂ desorbed per gram of catalyst, are shown in *Table 4.2*. According to the force of interaction of CO₂ with the basic centres of the catalyst, determined by the temperature that is necessary to release the CO₂, three regions are identified. Weak basic centres between 313 K and 423 K, moderate basic centres between 423 and 723 K and strong basic centres between 723 and 873 K. It is possible to identify three peaks in the TPD profiles, corresponding on the one hand with weak bonds corresponding to bicarbonate species formed by the CO₂ molecules on the surface of the catalyst in the low temperature region. On the other hand, at higher temperatures, in the temperature region corresponding to moderate interaction with the basic centres, the peak found is associated with bicarbonate species and bicarbonate monodentate species give rise to the peak observed at higher temperatures (associated with strong interactions) [51]. All the catalysts analysed have a similar interaction with CO₂ being the commercial catalyst the most basic one, due to the support of commercial catalyst is different from that used in this work. It is also remarkable that the number of strong basic centres. This demonstrates the strong character of the interactions of these catalysts with CO₂, interacting with the monodentate species of the bicarbonate species.

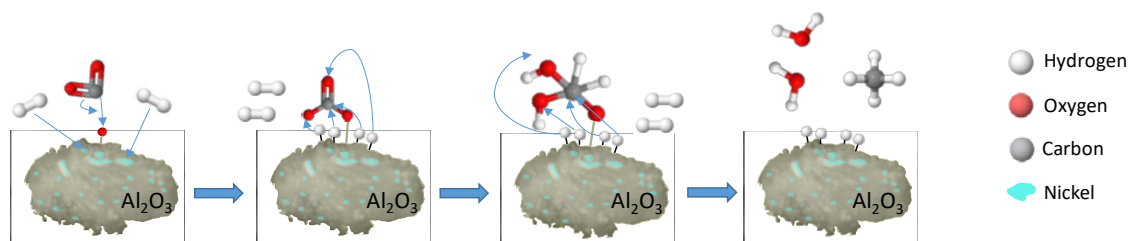


Fig. 4.6. Scheme of CO₂ methanation mechanism on Ni/Al₂O₃ catalyst.

Furthermore, the similar spectrum obtained for all the catalysts supported by alumina and with different promoters, suggests that the binding of CO₂ is done on the alumina, while the H₂ binds to the metal, as justified in the TPR analyses. According to this, and as it has been analysed in other works [52–55], the mechanism of the methanation reaction in these catalysts could follow a model similar to that represented in Fig. 4.6.

Catalyst	Acidity (μmol NH ₃ /g _{cat})			Basicity (μmol CO ₂ /g _{cat})		
	Weak	Medium	Strong	Weak	Medium	Strong
Temperature (K)	< 523	523 < T < 673	>673	< 423	423 < T < 723	>723
Commercial				12.64	61.19	115.64
13Ni/Al ₂ O ₃	145.89	346.79	1,118.73	10.95	56.97	100.82
4Co-13Ni/Al ₂ O ₃	244.20	512.97	1,338.98	8.17	54.26	108.78
4Cr-13Ni/Al ₂ O ₃	237.11	732.28	1,809.12	11.56	60.78	110.05
4Fe-13Ni/Al ₂ O ₃	192.20	389.72	1,172.34	8.60	55.64	106.59
4Mo-13Ni/Al ₂ O ₃	149.83	454.23	1,097.76	8.67	52.80	94.72
8Mo-13Ni/Al ₂ O ₃	176.83	420.23	987.5	9.45	52.28	95.74

Table 4.2. Distribution of the strength of acidity by NH₃-TPD and basicity by CO₂-TPD of the catalysts.

4.3.1.5. SEM, TEM and STEM

The morphology of the different catalysts was studied employing the techniques SEM, TEM and STEM. These micrographs show few morphological differences between fresh and deactivated, after reaction, catalysts. Applying EDX analysis to metal and sulphur atoms, presence of sulphur in the used catalysts after regeneration was detected, being remarkable in the 4Cr-13Ni/Alumina catalyst. Pictures showing the results are shown in Fig. 4.7-13.

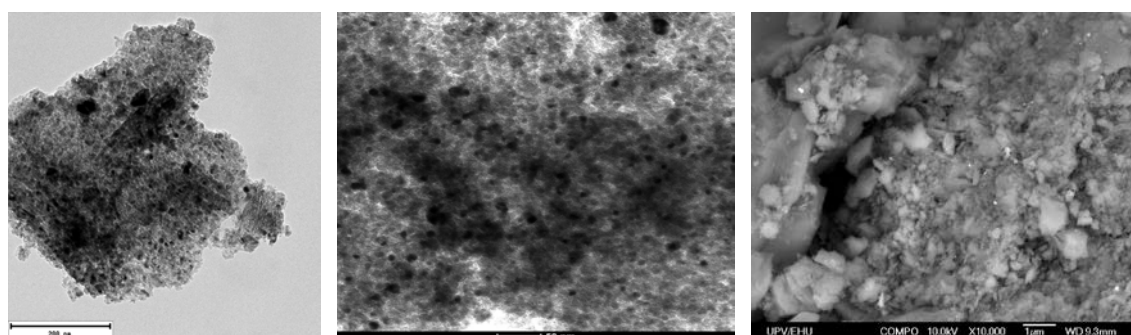


Fig. 4.7. TEM micrographs of fresh and used catalyst, and SEM micrograph of deactivated catalyst of 13Ni/Al₂O₃.

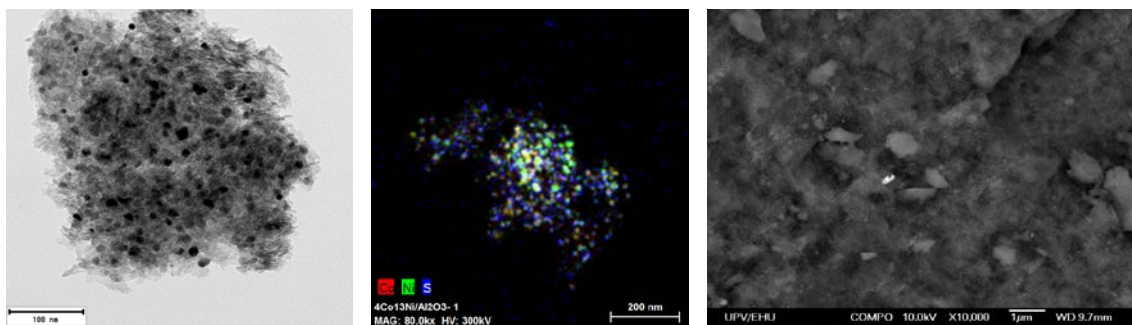


Fig. 4.8. TEM and STEM micrographs of fresh and used catalyst and SEM micrograph of deactivated catalyst of 4Co-13Ni/Al₂O₃.

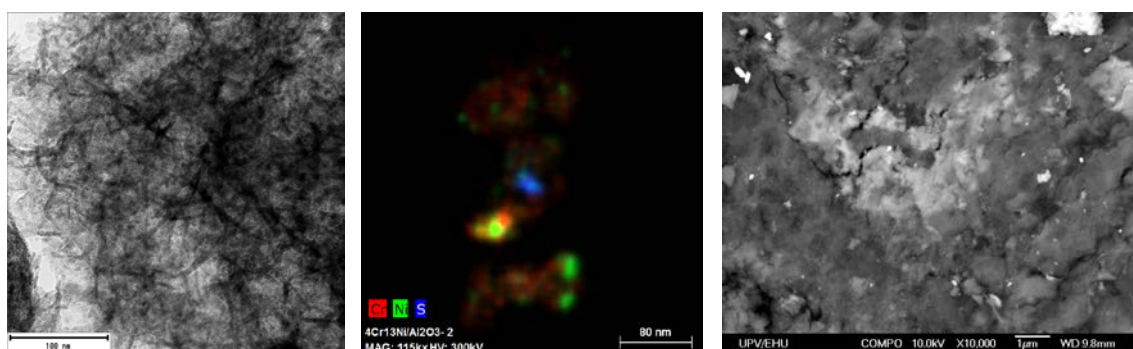


Fig. 4.9. TEM and STEM micrographs of fresh and used catalyst and SEM micrograph of deactivated catalyst of 4Cr-13Ni/Al₂O₃.

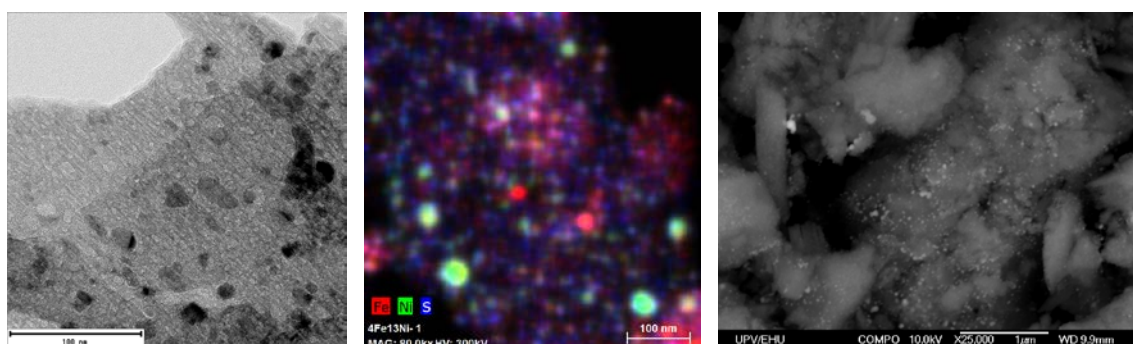


Fig. 4.10. TEM and STEM micrographs of fresh and used catalyst and SEM micrograph of deactivated catalyst of 4Fe-13Ni/Al₂O₃.

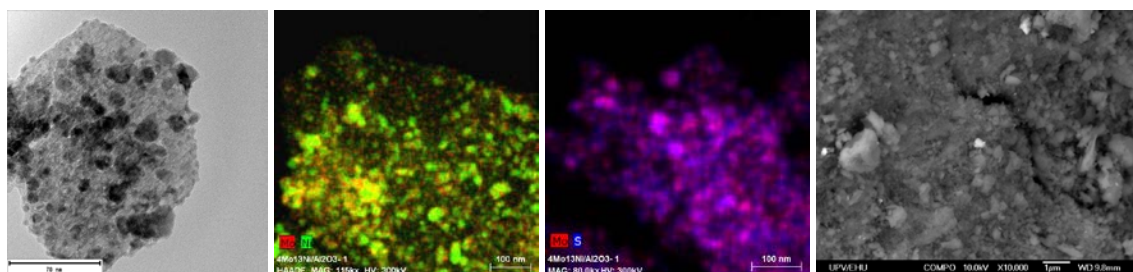


Fig. 4.11. TEM and STEM micrographs of fresh and used catalyst and SEM micrograph of deactivated catalyst of 4Mo-13Ni/Al₂O₃.

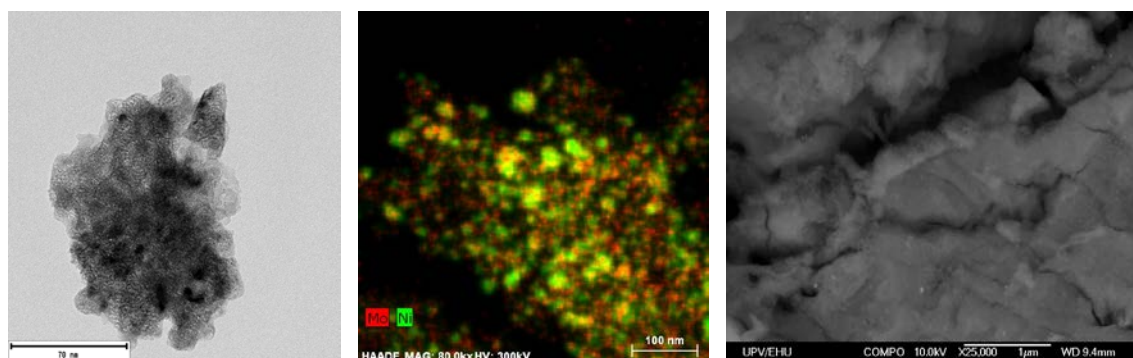


Fig. 4.12. TEM and STEM micrographs of fresh and used catalyst and SEM micrograph of deactivated catalyst of 8Mo-13Ni/Al₂O₃.

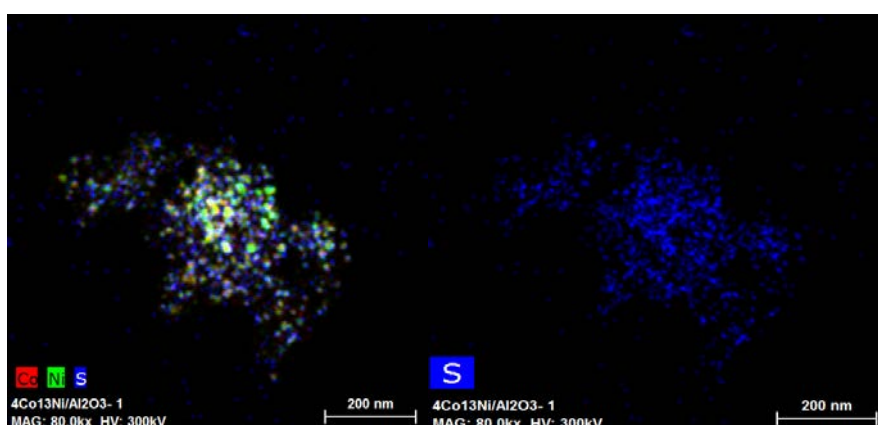


Fig. 4.13. STEM micrographs of used 4Co-13Ni/Al₂O₃ catalyst.

Regarding the SEM pictures, they do not allow any meaningful conclusion. As the atomic weight of the metal atoms involved are quite close, it is difficult to distinguish if there are interaction between Ni and promoter [56]. Thus, STEM-EDX images of used catalysts were analysed. They suggest that only in the catalysts containing cobalt (Fig. 4.8) [57] and molybdenum as second metal (Fig. 4.11 and Fig. 4.12) there is a significant interaction between the promoter metal and nickel species, which could indicate that they really are bimetallic catalysts. However, in iron (Fig. 4.10) or chromium (Fig. 4.9) catalysts, Ni with little interaction with promoters is observed. The promoter metals are located in the pore structure of the catalyst along with the Ni species.

In the catalysts 13Ni/Al₂O₃ and 4Co-13Ni/Al₂O₃ (Fig. 4.7 and Fig. 4.8) a high dispersion of the metallic centres was observed throughout the surface of the porous support. The dispersion was calculated with Eq. 4.9 from the nickel particle size values determined from the measurements made in STEM. The metal particles present in these catalysts have an average size value between 4.41 and 10.03 nm, as summarized in Table 4.3, as a result of the size measurement of more than 200 metal particles in each case. On the contrary, catalysts 4Cr-13Ni/Al₂O₃, 4Fe-13Ni/Al₂O₃, 4Mo-13Ni/Al₂O₃ and 8Mo-13Ni/Al₂O₃ (Fig. 4.9-12) exhibit a larger size of metal particles, between approximately 5.33 and 16.5 nm, due in part to the accumulation of these atoms in the form of agglomerates. This resulted in a smaller dispersion of the metallic atoms onto the alumina surface, as it was checked by EDX.

In addition, as explained below by the XRD and showed in Table 4.1, the metal crystal size is close in all cases to 5 nm. This implies that from a morphological point of

view, in those cases in which a larger particle size is determined, the sintering of several of these crystals. This phenomenon is remarkable in the case of nickel, where a higher metal content results in a greater extent of accumulation of these atoms, giving rise to metallic agglomerates. This may involve a decrease in the activity of the catalyst.

Regarding the formation of metal sulphides, in *Fig. 4.13* a significant amount of sulphur in all catalysts is detected. Even taking into account that a regeneration procedure with oxygen was applied.

	Particle size (nm)		Ni dispersion
	Ni	Promoter metal	
13Ni/Al ₂ O ₃	10.03	-	0.10
4Co-13Ni/Al ₂ O ₃	4.41	8.36	0.23
4Cr-13Ni/Al ₂ O ₃	6.72	5.33	0.15
4Fe-13Ni/Al ₂ O ₃	11.12	7.59	0.09
4Mo-13Ni/Al ₂ O ₃	12.31	10.20	0.08
8Mo-13Ni/Al ₂ O ₃	16.50	8.47	0.06

Table 4.3. Average metal particle size and Ni dispersion of the catalysts determined by STEM measurements.

4.3.1.6. XPS

The surface species of the catalyst were analysed by XPS, identifying the main metals and their oxidation states. The catalysts studied, based on Ni, showed three peaks at 852.9, 857 and 862.3 eV according to Ni⁰, Ni²⁺ from NiAl₂O₄, and Ni²⁺ satellite respectively for fresh catalyst [58], as observed in *Fig. 4.14*. Used catalyst showed also three peaks, at 854, 857 and 862.3 eV, corresponding to Ni²⁺ from NiO, Ni²⁺ from NiAl₂O₄, and Ni²⁺ satellite respectively, as observed in *Fig. 4.15*. It is observed that the Ni forming the NiAl₂O₄ is not reducible. Its value does not change in the monometallic catalyst after its use in the reaction. In bimetallic catalysts a significant increase in nickel aluminate is observed due to the effect of the temperature and the sintering of the catalyst. This transformation causes the disappearance of metallic nickel, which produces the oxidation of the remaining Ni, as observed in *Table 4.4*. This justifies the loss of activity that takes place in the catalysts after their use in the reaction, especially at high temperatures and after the use of a stream of gases containing H₂S.

	Fresh catalyst		Used catalyst	
	Ni ⁰	Ni ²⁺ (NiAl ₂ O ₄)	Ni ²⁺ (NiO)	Ni ²⁺ (NiAl ₂ O ₄)
13Ni/Al ₂ O ₃	0.94	0.63	0.65	0.61
4Co-13Ni/Al ₂ O ₃	0.34	0.22	0.27	0.31
4Cr-13Ni/Al ₂ O ₃	0.44	0.34	0.92	0.46
4Fe-13Ni/Al ₂ O ₃	0.63	0.30	0.46	0.58
4Mo-13Ni/Al ₂ O ₃	1.09	0.48	0.53	0.93
8Mo-13Ni/Al ₂ O ₃	1.90	0.52	0.74	1.34

Table 4.4. Concentration percentage of metallic Ni⁰, Ni²⁺ from NiO and Ni²⁺ from NiAl₂O₄, with respect to the total.

The presence of the secondary metal was detected by XPS, however it was not possible to quantify it due to the superposition with the Auger LMM line of Ni in the case of the catalyst 4Co-13Ni/Al₂O₃ and 4Fe-13Ni/Al₂O₃. However, chromium and molybdenum could be analysed by this technique, appearing in the positions 577.7 and 586.3 eV for the Cr oxides 2p (3/2 and 1/2 respectively); 228.1 and 231.1 eV for the metallic

Mo (3d 5/2) and 232 and 235 eV for the MoO₃ (3d 5/2). It is observed that the amount of quantified Cr does not vary after its use in the reaction (from 1.3% to 1.4%). However, in the case of Mo, the amount of oxide does not vary after the use of the catalyst, but the amount of Mo metal does, which is considerably reduced (from 8.8% to 1.7% for 8Mo and from 1% to 0.34% for 4Mo). This reduction is due to sintering of the metal, which produces an agglomeration in deeper layers of the catalyst.

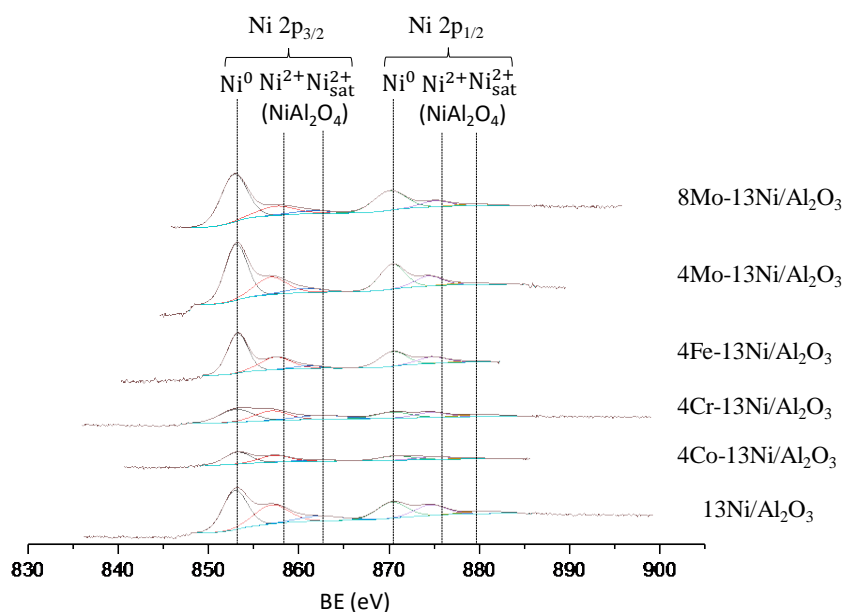


Fig. 4.14. XPS spectra of Ni 2p_{3/2} and 2p_{1/2} regions of fresh mono- and bimetallic catalysts.

The analyses have detected the presence of carbon in the catalysts, due to the formation and deposition in the reaction process. The proportions of metal to aluminium in the catalysts analysed was collected in *Table 4.5*, for the results obtained in the XPS analyses. The incorporation of the promoter reduces the proportion of Ni/Al considerably in all catalysts, with the exception of catalysts with Mo, in which it increases, with molybdenum being part of the catalyst bulk coordinating with the Ni on the surface. The use of the catalyst in the reaction reduces the ratio of the secondary metal to Al, increasing that of Ni/Al, especially in the catalysts promoted by Mo. This justifies that the wear of the catalyst with the high temperature and the poisoning with H₂S not only produces the oxidation of the Ni, but it also the NiS formation, during the reaction, that could increase the sintering of the catalyst [59]. After removing the H₂S stream and the corresponding regeneration step, the sulphur containing compounds in the catalyst are removed, not being detected in the XPS analyses. However, it does result in loss of activity and the disability to recover activity.

	Fresh catalyst		Used catalyst	
	M/Al	Ni/Al	M/Al	Ni/Al
13Ni/Al ₂ O ₃		0.067		0.069
4Co-13Ni/Al ₂ O ₃		0.023		0.040
4Cr-13Ni/Al ₂ O ₃	0.033	0.038	0.040	0.054
4Fe-13Ni/Al ₂ O ₃		0.038		0.059
4Mo-13Ni/Al ₂ O ₃	0.048	0.069	0.035	0.112
8Mo-13Ni/Al ₂ O ₃	0.363	0.127	0.126	0.203

Table 4.5. Metal/Al ratio obtained by XPS analysis of the different catalysts studied (M= Cr or Mo).

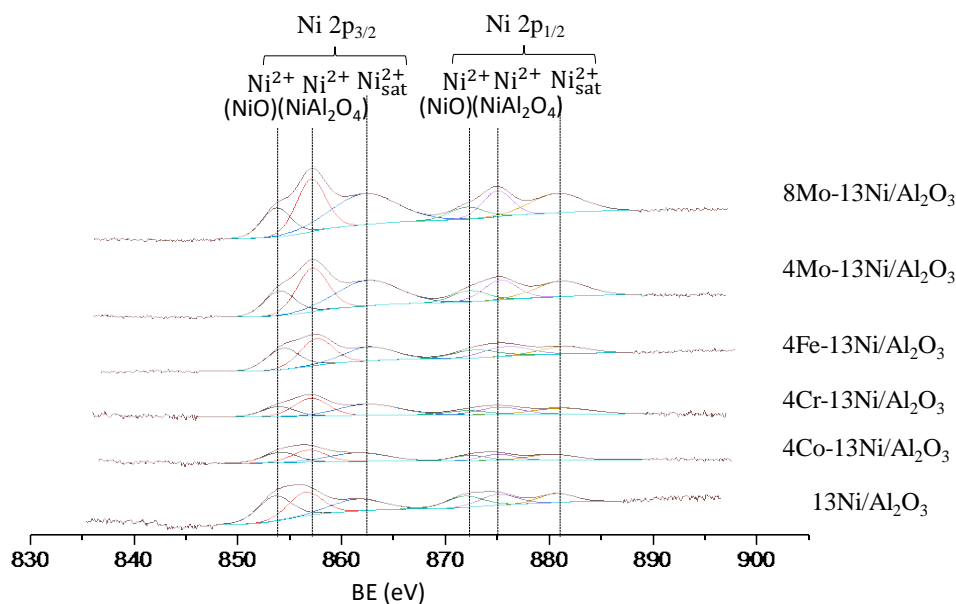


Fig. 4.15. XPS spectra of Ni 2p_{3/2} and 2p_{1/2} regions of used mono- and bimetallic catalysts.

4.3.1.7. XRD

The X-Ray Diffraction (XRD) is an analysis used for phase identification of a crystalline material of the catalyst and the determination of the dimensions of crystal size. The XRD patterns of the bimetallic and monometallic fresh-reduced catalysts supported over Al₂O₃, are shown in Fig. 4.16. This figure report the pattern from 20° to 90°, being located the highest peaks between 30° and 70°. The XRD pattern of the 13Ni/Al₂O₃ showed the characteristics peaks of Ni metallic and Al₂O₃ support. In comparison with the XRD patterns of the other catalysts, the significant peaks measured in all the cases coincided in Ni peaks (44.8° and 52°) and Al₂O₃ peaks (32.2°, 37.7°, 39.5°, 46.4° and 67.3°). According to these analyses, the Al₂O₃ support and metallic Ni were the main phases detected. The low crystallinity of the samples and the overlap of nickel peak with the second metallic species, as shown in Table 4.6, make difficult a clear identification of the phases present in each sample.

The analysis of the XRD pattern revealed the effect of adding a second metal, widening the Ni and Al₂O₃ characteristic peaks, reducing the intensity of the signal and moving slightly the 2θ position of these peaks. The XRD pattern of the catalysts used, presented in the Fig. 4.17 showed, in general, a lower amount of elements in a reduced state, as observed specially in the 4Co-13Ni/Al₂O₃ spectrum, due to the sintering process at high temperature and the presence of H₂S.

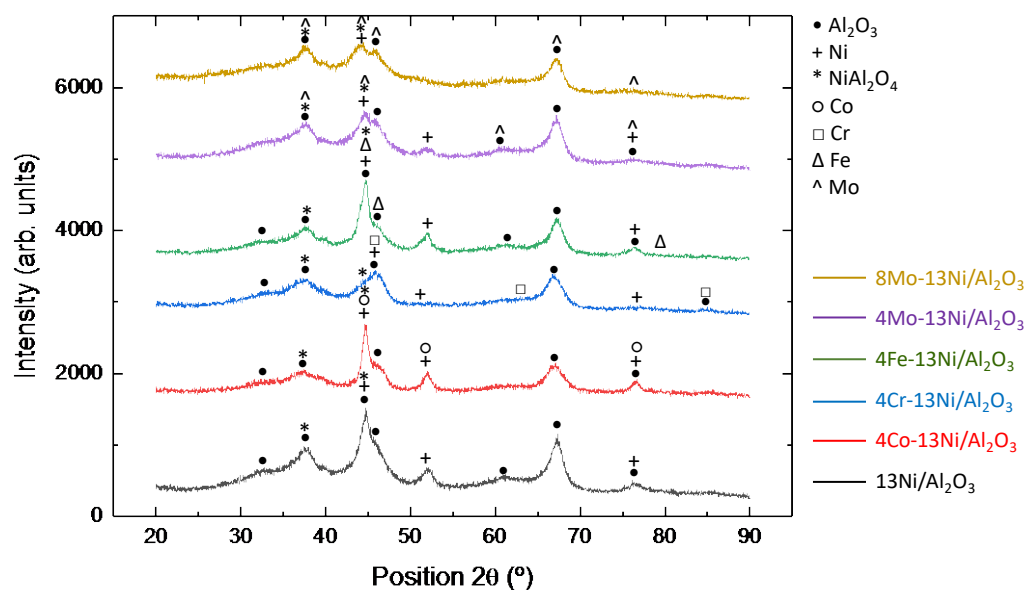


Fig. 4.16. XRD patterns of bi- and monometallic fresh-reduced catalysts supported over Al_2O_3 .

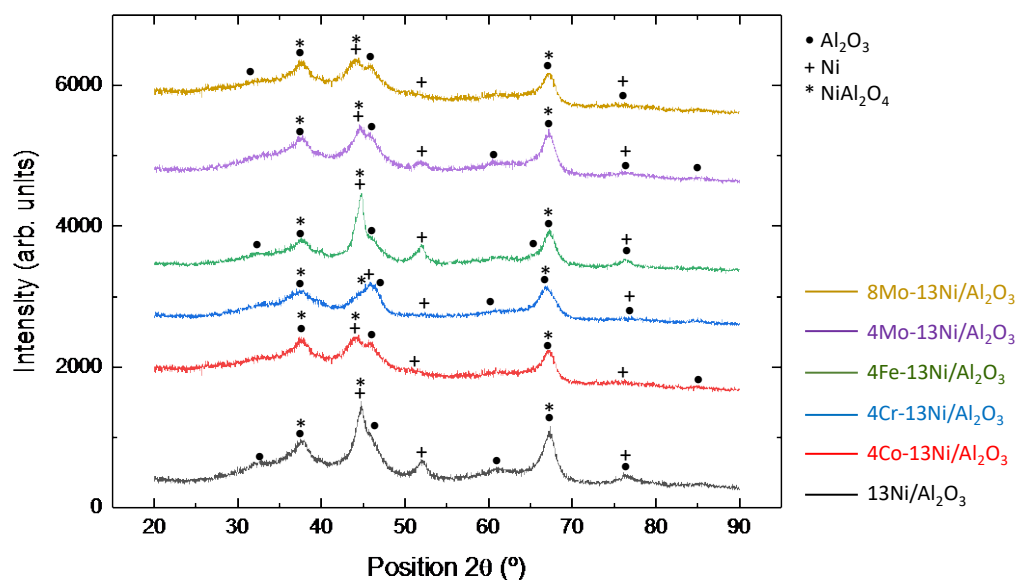


Fig. 4.17. XRD patterns of bi- and monometallic used-reduced catalysts supported over Al_2O_3 .

The 2θ position of the crystalline phases determined from Joint Committee on Powder Diffraction Standards (JCPDS) database, are represented on the *Fig. 4.16* and *Fig. 4.17* for the different species of the catalysts. These results are collected in the *Table 4.6*, contrasted with the bibliography [60–63].

Phase	JCPDS code	Value (°)
Ni fcc structure	087-0712	44.5, 51.6, 76.7
Al ₂ O ₃	077-0396	32.2, 37.7, 39.5, 46.4, 67.3
NiAl ₂ O ₄	073-0239	37.2, 44.2, 64.3
Metallic -Co	015-0806	44.7, 52, 76.6
Cr	001-1250	43.8, 64, 82
Fe	088-2324	44.8, 46, 79
Mo	088-2331	37.6, 44.2, 45.8, 65, 79, 83.8

Table 4.6. XRD crystalline phases for the catalysts.

The crystallite size was determined from XRD technique by applying the Scherrer equation, and collected in *Table 4.1*. The crystallite sizes were calculated using the most representative XRD peak that does not overlap those of other crystals. Values around 5 nm for all the catalysts analysed were obtained, and in contrast with higher values measured by TEM, SEM and STEM for the nickel particles. The XRD analysis showed the low value of crystallinity of the samples. For the Co sample, NiCo₂O₄ was formed due to the interaction between Ni and Co [45]. For the Fe sample, XRD corroborated that NiFe alloy was not formed and only small amounts of Fe₂O₃. The main peaks mentioned in *Table 4.6* for the Mo revealed the presence of MoO₃ but no separated signals were detected for metal nickel and MoO₃ [64].

4.3.2. Activity tests

Nickel is a metal commonly used in CO₂ methanation for the high yields to methane achieved [65]. Therefore, the catalysts employed in this work, are based on nickel as active metal, supported on alumina due to high surface area. In order to improve the catalytic activity and H₂S resistance of the nickel-alumina system (13Ni/Al₂O₃), a second metal was added modifying the physical and chemical properties. The metals employed are transition metals in a quantity of 4 wt.% in all the cases (4Cr-13Ni/Al₂O₃, 4Co-13Ni/Al₂O₃, 4Fe-13Ni/Al₂O₃ and 4Mo-13Ni/Al₂O₃) and 8 wt.% (8Mo-13Ni/Al₂O₃) also in the case of the molybdenum, as was indicated and justified in the introduction.

The activity was measured as CH₄ yield obtained at each temperature analysed for the different mono and bimetallic nickel-alumina catalysts. The results obtained for the activity tests are shown in Fig. 4.18 (zoom of the graphic between 220-500 K has been included in Fig. 4.19).

In the tests without presence of H₂S, 4Mo-13Ni/Al₂O₃, 8Mo-13Ni/Al₂O₃, 4Fe-13Ni/Al₂O₃ and 4Co-13Ni/Al₂O₃ presented lower yields at low temperatures than the monometallic. It was necessary to increase the reaction temperature above 623K to reach the highest yields. At 723K, the catalysts reached the maximum methane yields in the temperature range studied, reaching in all cases a maximum value close to the thermodynamic equilibrium, except for the 8Mo-13Ni/Al₂O₃ catalyst that did not reached this maximum at the temperatures studied. Once the temperature of this maximum has been exceeded, the yield falls parallel to the trend of thermodynamic equilibrium, with the methane yield remaining in all cases around 80% for the maximum temperatures analysed, except for molybdenum catalysts. The iron catalyst exhibits the highest yield values together with the commercial catalyst. Subsequently, the trajectory of the methane yield curve of these catalysts, as the temperature increases, is similar in the range studied.

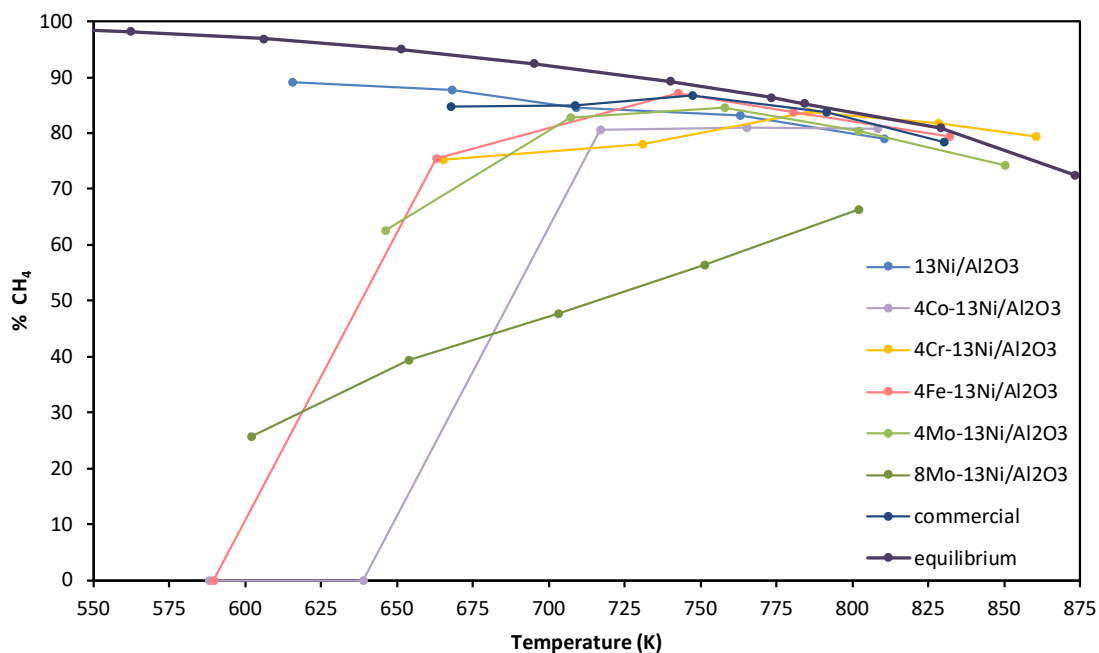


Fig. 4.18. Methane yield obtained for the catalysts supported on alumina.

According to Rönsch's et al. work [66], the activity should be greater for Fe than for Ni, followed by Co and finally by Mo. In the case of selectivity, it is mentioned that the monometallic Ni catalyst is the one with the highest yield to methane, followed by the bimetallic with Co and finally with Fe. In the case of Frontera et al. [67] according to the calculated activity from Volcano curve and economic considerations, the catalysts with Ni-Fe alloys can be considered good candidates for CO₂ methanation. Thus, this is accordance with the highest yield achieved for the Fe bimetallic catalyst. For the Mo bimetallic catalyst, the one with the lower activity, it appeared with the lower theoretical activity, but it was used in order to improve the sulphur resistance.

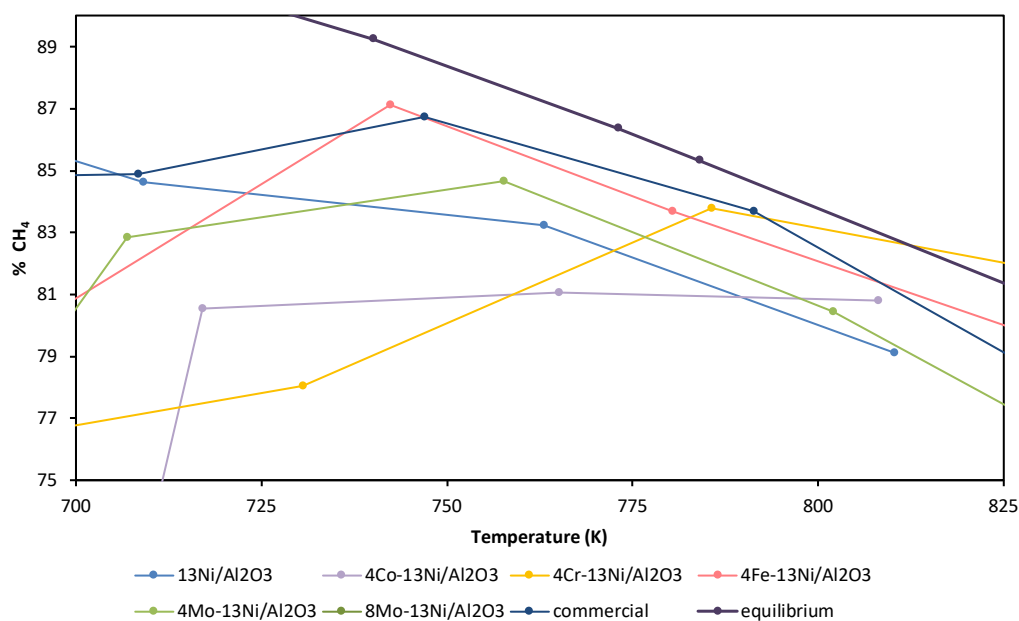


Fig. 4.19. Extension of methane activity curves obtained for alumina supported catalysts.

The methanation tests continued in the presence of H₂S until catalyst deactivation Fig. 4.20. The addition of 50 ppm of H₂S to the reaction feed rapidly reduced the activity of 4Co-13Ni/Al₂O₃ and 4Fe-13Ni/Al₂O₃ catalysts, until their complete deactivation in approximately 50 min. The catalysts 4Cr-13Ni/Al₂O₃, 4Mo-13Ni/Al₂O₃ and the monometallic (13Ni/Al₂O₃) showed a higher resistance, than the previous ones, to the action of H₂S, being completely deactivated after 80 min. The greatest resistance to the inhibitory action of H₂S among the prepared catalysts was the 8Mo-13Ni/Al₂O₃ catalyst, which was not deactivated until 100 min. However, the most stable catalyst in the presence of H₂S is the commercial catalyst, which maintains its catalytic activity until 120 min, before starting its deactivation, which was completed at 170 min.

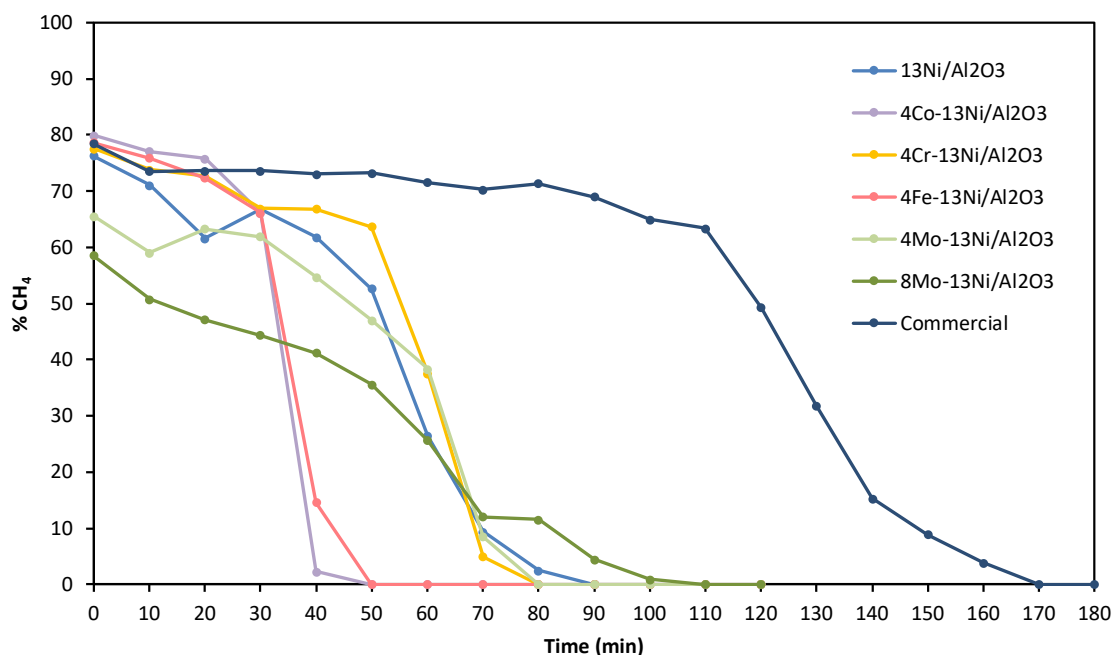


Fig. 4.20. Catalysts deactivation due to 50 ppm of H₂S at 773K.

After deactivation of the catalysts in the presence of H₂S, the auto-regeneration capacity of the catalysts was studied eliminating this gas from the feed at 500 °C. In all the cases analysed, the catalysts did not recover the activity.

Finally, the catalysts were regenerated, employing a mixture of 3% O₂ in N₂, in order to eliminate the NiS species and carbon depositions (increased by Ni-S presence), blocking the catalyst's active centres [59]. Afterwards, the catalysts were reactivated reducing with H₂. The recovered catalyst was used in a reaction stage, at 500 °C. It was observed that the catalysts activity as methane yield was not recovered, with the exception of the 4Co-13Ni/Al₂O₃ catalyst that recovers a methane yield of about 13%. During the reaction, deactivation, and after regeneration stage, the presence of CO was not detected as it can be produced as a by-product due to the reverse water gas shift reaction.

4.3.3. Discussion

Nickel has proved to be the catalyst with the best characteristics in the methanation reaction, reaching a high yield (89.05%) to methane at low temperatures (615.2 K), in accordance with the work of Muroyama et al. [22] for a 10Ni/Al₂O₃ catalyst calcined at 873 K.

However, the work of García et al. [13] and Garbarino et al. [21], done at temperatures around 673 K, obtained methane yields significantly lower (approximately 50%). This shows that the temperature has great influence on the start of the reaction, so that there is an interval, characteristic for each catalyst, below which the reaction does not occur (or with low performance), with a higher temperature being necessary to overcome the activation energy of that system. This fact was observed by comparison with other catalysts, such as 4Co-13Ni/Al₂O₃ or 4Fe-13Ni/Al₂O₃. The addition of a suitable metal promoter produces the modification of reaction ignition temperature of the nickel catalyst.

The high performance of this monometallic catalyst can be justified by its particular characteristics observed in the characterization: the high specific area, determined by BET, indicates a high dispersion of the metallic sites, which are reduced at operating temperature as demonstrated in the H₂-TPR profiles. The metallic centres were observed by SEM and TEM, which present a small size, without the formation of agglomerates and well distributed over the entire surface. The nickel, as indicated by the XPS and XRD analysis, is mainly reduced and/or NiAl₂O₄.

This catalyst has similarities with the 4Co-13Ni/Al₂O₃, sharing the characteristic of being composed of metallic centres of small size with high dispersion, as can be deduced from the analysis of SEM and TEM. These active centres are dispersed on the surface of the catalyst, which has a larger surface area than the rest of the catalysts (as analysed in BET). This coincides with that observed by Wang et al. [68] for Co and Mo catalysts. In this work, the use of these catalysts is also justified by the inhibition in the formation of S²⁻. This may justify the greater resistance that the catalysts of Mo have to the deactivation with H₂S and the capacity of recovery of the catalytic activity of the Co catalyst, recovering the yield up to 13%. The performance values of the Co catalyst are consistent with what Alrafi et al. [69] demonstrated in his work, where they studied how the proportion of Co and Ni affects the reaction of CO₂ methanation. According to this work, Co is an active metal in this reaction. However, the lower activity in methanation of this metal indicates the blocking of some active centres, as observed in the reduction of the metal/Al ratio in the 4Co-13Ni/Al₂O₃ catalyst with respect to 13Ni/Al₂O₃.

The addition of Mo improves the resistance of the Ni catalyst to H₂S, as justified above. However, the added amount of this promoter affects the catalytic capacity of Ni, so that as the Mo ratio increases (from 4 to 8), the greater the resistance to H₂S but the catalyst yield is lower. This phenomenon was reported Maluf's et al. [70] work, where they used a Ni:Al molar ratio of 3, with different proportions of Mo (0.05, 0.5, 1.0 and 2.0 wt.%) as a promoter and Ni (60 wt.%) for steam reforming. They observed that using the optimal amount of Mo as a promoter, improves the yield, avoiding the formation of CO. This effect occurs due to the blocking of the active centres of the Ni by the Mo, verified by the reduction of the specific surface in BET and the greater presence of this metal than the Ni in the analysis in XPS. At low amounts of Mo, the activity improves as a result of the transfer of electrons from the MoOx of the surface to Ni, increasing the electronic density of the metallic Ni [70].

The 4Fe-13Ni/Al₂O₃ catalyst needs to reach a temperature of 663 K for the methanation reaction to take place, needing a lower temperature than the 4Co-13Ni/Al₂O₃ catalyst. This is in contrast to Lu's et al. [26] work, where Co addition on ZrO₂ modified mesoporous clays had a similar contribution to Fe on CO₂ conversion. Although it explains the similarity in methane yield of both catalysts at higher temperatures.

Furthermore, in the SEM analysis, a similar morphology was observed between the Co and Fe catalyst, although there is a lower dispersion of the metal centres when agglomerates appear in fibrous structures, which are distinguished in TEM.

The low specific surface area and the smaller micropore surface determined in BET justify a greater exposure of the active centres. It is verified by observing the metal/Al ratio of the XPS analysis and the metal distribution in SEM. Due to the arrangement of these metal centres (in a similar way to the iron catalyst) with homogeneously dispersed agglomerated particles, they are more accessible. Therefore, the reaction is initiated with high methane yield. This is also why the amount of Cr that is added to the system has a great influence, as demonstrated by Liu et al. [71] for the CO methanation with OMA as support, with a 10 wt.% of Ni and different proportion of Cr as promoter. So that, the adequate amount of promoter has a positive effect on the catalyst, while high amounts can block the active centres of the other metal (Ni in this case) and low amounts do not bring any benefit to the system. In this case, the amount used is among the most favourable values for the methanation reaction, according to this work.

Finally, other interesting method used to measure the catalyst activity is the turnover frequency (TOF). In this work turnover frequency of CO₂ (h⁻¹) is employed to compare the quality of available active centres, based on the Ni particles sizes and their dispersion, with respect to the total amount of Ni atoms. TOF values obtained for the catalysts analysed are shown in *Table 4.1*. As expected, catalysts with smaller particle size have a higher dispersion, as in the 4Co-13Ni/Al₂O₃ and 4Cr-13Ni/Al₂O₃ catalysts (*Table 4.3*). Similar results were reported by Aziz et al. [72], showing that a balance between the Ni dispersion and basic site concentration led to the optimum CO₂ conversion over the 5wt.% Ni/SiO₂ catalyst. In the present work, this comparison is more complicated due to the fact that catalyst included a second promoter.

As an example, the catalysts 4Mo-13Ni/Al₂O₃, 8Mo-13Ni/Al₂O₃, and 4Fe-13Ni/Al₂O₃, follow the general rule of a higher dispersion (*Table 4.3*) results and a higher CO₂ conversion and, in this case, a higher value of TOF. However, when compared this catalysts with 4Fe-13Ni/Al₂O₃, the tendency is different, this catalyst presented the highest dispersion, but a low activity, and then a low TOF. One possible explanation of this effect is the interaction of Ni with the promoter. As it can be seen comparing *Fig. 4.7-10*, the catalyst presenting the highest interaction between Ni and promoter (yellow areas) is the 4Co-13Ni/Al₂O₃, and this is the catalyst with the highest dispersion (lowest Ni particle size) and the lowest activity. This result is in agreement with the conclusion presented by Italiano et al. [51]. They stated that CO₂ hydrogenation was affected by the nature of active centres rather than the number of active sites available to perform methanation reaction. In this case, this close interaction hinders the Ni activity. Nevertheless, also this close interaction has a beneficial effect when sulphur is present in the reaction media, as the 4Co-13Ni/Al₂O₃ is the catalyst that revealed the best deactivation tolerance.

Regarding the relationship between TOF and basicity, there is not a clear correlation. In this case, it seems that the interaction with the metallic active centers is the most important parameter.

Finally, the regeneration procedure employed to recover initial activity of the catalysts was not successful as sulphur was detected by STEM. This seems to be responsible for the loss of catalytic activity. In *Fig. 4.13*, for the 4Co-13Ni/Al₂O₃ catalyst, it

can be observed the presence of S interacting with both the active metal and the promoter.

4.4. Conclusions

The CO₂ methanation was studied over a 13Ni/Al₂O₃, and 4Co-13Ni/Al₂O₃, 4Cr-13Ni/Al₂O₃, 4Fe-13Ni/Al₂O₃, 4Mo-13Ni/Al₂O₃ and 8Mo-13Ni/Al₂O₃ modified catalysts. The promoter was integrated in the catalyst attached to the Ni metal centres, reducing the dispersion and forming agglomerates, with the exception of the catalyst of 4Co-13Ni/Al₂O₃, as observed by SEM and EDX, and as it was verified by XPS. The catalytic activity of the Ni modified catalysts is improved being positive between 700 and 800 K for all the catalysts except for 8Mo-13Ni/Al₂O₃. Mo in small quantities improves the methanation reaction, but at high concentration levels it blocks the Ni active centres, reducing the activity of the catalyst. The best catalytic system to operate above 700 K was the promoted by iron, reaching the highest methane yield (87%) at 742 K.

The second objective of adding a promoter to the Ni catalyst was the improvement of its resistance to H₂S poisoning, achieved in the 8Mo-13Ni/Al₂O₃ catalyst. The resistance to 50 ppm of H₂S in the reaction gases was increased from 90 to 120 min. The addition of Cr increased the stability of the catalytic activity before starting to deactivate from 10 to 60 min.

Finally, the third objective of the use of promoters consisted in the improvement of the recovery capacity of the catalyst to the deactivation by poisoning with H₂S. The only catalyst able to recover the catalytic activity up to a 13% of CH₄ yield, after a stage of regeneration and reactivation, was the 4Co-13Ni/Al₂O₃ catalyst, by inhibiting the formation of the S²⁻ bond on the metal surface.

Upgrading promoters to nickel catalyst has benefited the performance of the catalyst system in several ways, depending on the metal used. Improving performance is related to an increase in metal dispersion in some cases, an improvement in the interaction between metals that can reduce the effect of temperature compared to deactivation by sintering in other cases, or finally an improvement in resistance to H₂S poisoning. In future works, a larger study of the metal charge would be interesting to improve its positive effect on the catalyst, with different catalyst concentrations that allow a better comparison between the study catalyst systems.

4.5. Acknowledgements

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CAPÍTULO 5



**Efecto de la adición de alcalinotérreos y
lantánidos como modificadores del soporte de
alúmina en catalizadores de Ni y Ru**

*"En la investigación es incluso más importante el proceso
que el logro mismo".*

EMILIO MUÑOZ

Extraído del artículo: *Effect of the addition of alkaline earth and lanthanide metals for the modification of the alumina support in Ni and Ru catalysts in CO₂ methanation.*

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Abstract

In order to reduce greenhouse gas emissions, which reach alarming levels in the atmosphere; the capture, transformation and recovery of carbon dioxide emitted to methane is considered. This transformation, known as methanation, is a catalytic reaction that has mainly used catalysts based on noble metals such as Ru and although with less efficiency on transition metals such as Ni. In order to improve the reaction efficiency, the effect of adding alkaline earth metals (Ba, Ca or Mg at 10 wt%) and lanthanides (La or Ce at 14 wt%) to nickel (13 wt%), ruthenium (1 wt%) or both-based catalysts has been studied; at temperatures between 498 and 773 K and 10 bar pressure. The deactivation resistance in presence of H₂S was also studied.

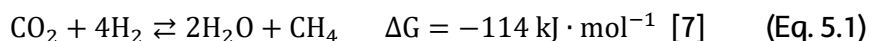
The incorporation of La into the catalyst structure changes interactions between active metal of Ni, Ru or bimetallic Ru-Ni and support of alumina, as determined by the characterization. This results in an improvement in the catalytic activity of the 13Ni/Al₂O₃ catalyst, which achieves a methane yield of 82% at 680 K for 13Ni/14La-Al₂O₃ in addition to an increase in H₂S deactivation resistance. Furthermore, 89% was achieved for 1Ru-13Ni/14La-Al₂O₃ at 651 K, but more vulnerable to H₂S.

5.1. Introduction

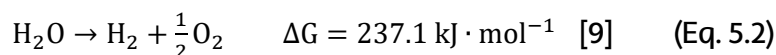
Greenhouse gases (GHGs) constitute part of the Earth's atmosphere naturally, maintaining the optimal conditions for life [1]. The ability of GHG to conserve part of the energy from solar radiation allows the planet's temperature to be moderate (17°C global average) [2]. However, with the advent of the industrial revolution, new energy sources based on the combustion of fossil fuels appeared. The increasing industrialization of the last century and a half, energy demand has been going up to gratify the growing food demand caused by the increase in the world's population. Moreover, large-scale agriculture has increased, this entails great deforestation to enlarge arable land. All this has produced that GHGs levels have reached levels never seen before. Carbon dioxide (CO₂) is especially important in composing two-thirds of GHGs and whose emission is related in three quarters with the combustion of fossil fuels [3].

In the recent climatic summit of the United Nations of 2019, member countries have been instigated to mobilize the implementation of several of the sustainable development goals for 2030, complying with the measures established by the 2015 Paris agreement. The objectives set include the reduction of greenhouse gas emissions up to 45% in 2030 and up to 0% in 2050 to limit global warming below 2 °C [4]. The strategies established by the European Union (EU) to achieve the agreed objectives consist of betting on energy efficiency, renewable energy, reducing emissions in transport and industry and carbon capture and storage [5]. In order to achieve the objectives in reducing GHGs emissions there are several possible ways. The first way is the minimization of emissions: from the capture and storage of gases, greater use of waste materials, improvement of the efficiency of combustion systems, implementation of more biomass-based energy systems, replacing traditional fuels with biofuels, or proper management of arable land and cultivation techniques. However, it is now strongly believed that the best way to achieve these objectives is the capture, transformation and recovery of emitted gases, especially carbon dioxide. These gases would become other compounds that can be used to obtain fuels (methane, ethane), plastics (ethylene), medicines (formaldehyde), solvents (methanol, ethanol) or other uses (carbon monoxide,

formic acid) [6]. The methanation of CO₂, studied by Sabatier (Eq. 5.1), proposes a sustainable way to transform residual CO₂ and obtain methane as a biofuel.



This reaction constitutes the second stage of a broader process known as power-to-gas. In this process, hydrogen is obtained from water electrolysis (Eq. 5.2) using energy from renewable sources, whose intermittent production would cause problems in the operability of the electricity grid [8].



Obtaining methane by the Sabatier reaction is a favourable process from a thermodynamic point of view, but with kinetic limitations for the complete reduction of CO₂ to methane, due to its exothermic nature [9]. For this reason, various catalysts have been studied in order to overcome these limitations for methane production. Some of the metals that have proven to be active in methane production are noble metals such as Ruthenium (Ru), Rhodium (Rh) and Palladium (Pd), but also Nickel (Ni) and its combination [9–22]. The most commonly used supports in the literature for the dispersion of these metals are metal oxides as Al₂O₃, SiO₂, TiO₂, CeO₂, zeolites (among others) and even, in recent works, start using reduced graphene oxide (rGO) [12]–[22]. Nickel-based catalysts are common in the literature due to their competitive activity and low price, which proposes them as a viable alternative to noble metals [9,12,16–18,20,22]. However, in order to verify the effect that the noble metal has on Ni, Mihet M. and Lazar M.D. [22] have studied the addition of small amounts (0.5 wt.%) of Pd, Platinum (Pt) and Rh on Ni (10 wt.%) in the methanation reaction. They demonstrated that doping Ni with Pd or Pt improves activity at lower temperatures, contrary to what happens when Rh is added. In view of these results and those corresponding to Ru catalysts, which show their high activity in the methane reaction, in this work the activity of 13 wt.% Ni, 1 wt.% Ru and 13 wt.% Ni doped with 1 wt.% Ru was compared, based on the high activity in methanation of Ru and noble metals with Ni.

The most common support is the alumina due to the high surface area observed which increased the dispersion of the metal, facilitating the access of reaction gases to the active centre [12–14,18–22]. The high surface, stability, activity and selectivity improved on metallic catalyst due to γ -Al₂O₃ structure, marking this support how most suitable [23]. It has been shown in recent works that modification of the alumina support in Ni catalysts for the methane reaction increases activity, especially at low temperatures [18,24,25]. Liang et al. described an increase in the conversion of CO₂ at low temperatures after the addition of Magnesium (Mg), Calcium (Ca), Strontium (Sr) and Barium (Ba) to the Ni/alumina catalysts, specially the last two [24]. Also García-García et al. showed that the addition of Cerium (Ce) increased the capacity in obtaining methane at lower temperatures with modified alumina with 4 and 6 wt. % of Ce and 3 wt. % Zirconium (Zr) [18]. However, a smaller amount of Ce (4 wt.%) and a small amount of Zr (3 wt.%) was not enough to improve the activity of the catalyst. Furthermore, the effect of modifying alumina support with different amounts of La (0, 4, 14 and 37 wt.%) has also been studied [25]. Garbarino et al. concluded that the methane yield increases at lower temperature, as the amount of added increases to a maximum of 14 wt.%. Finally, the modification of alumina supports with alkaline earth metals or lanthanides has been studied in other reactions (Fischer-Tropsch or dry reforming), showing an improvement in reaction performance [26–28].

In the present work, it was studied the effect of modifying the support of the 13Ni/ γ -Al₂O₃ catalyst with alkaline earth metals (Ba, Ca and Mg) and lanthanides (La and Ce) and the effect of Ru, Ni and Ni-Ru as active metal and its modification of the support with La, on the CO₂ methanation reaction.

5.2. Experimental details

5.2.1. Catalyst preparation

The modified catalysts were prepared by wetness impregnation method in two successive stages. Determined amounts of γ -Al₂O₃ (Merck) and support modifying metals (Table 5.1), were mixed in appropriate proportions (10 wt.% Ba, Ca or Mg; or 14 wt.% La or Ce). 20 ml distilled water was added to the mixed salt supports and the pH value of γ -Al₂O₃ (7.5) was fitted over point of zero charge (pzc) at 8.5 [23,29]. The pH was adjusted adding ammonium (Panreac) to increase the pH or nitric acid (Scharlau) to decrease the pH value. The solution was stirred overnight, in a rotary evaporator (Heidolph Laborota 4000) and the solvent was evaporated, heating at 338 K, and reducing slowly the pressure until 40-100 mbar helped for a vacuum pump. The support obtained was dried in an oven at 373 K during 2 h, and calcined at 673 K in presence of air for 2 h, with a ramp of 1 K/min.

Product name	Purity Grade	Producer
Barium nitrate	99.999%	Sigma Aldrich
Calcium nitrate tetrahydrate	99%	Sigma-Aldrich
Magnesium nitrate hexahydrate	99%	Fluka Analytical
Lanthanum (III) nitrate hydrate	99.9%	Sigma-Aldrich
Cerium (III) nitrate hexahydrate	99.999%	Sigma-Aldrich

Table 5.1. Support salts to prepare the catalysts, purity grade and producer.

The catalysts were prepared by adding the metal salt of nickel (II) nitrate hexahydrate 99.999% (Sigma Aldrich) and/or ruthenium (III) chloride hydrate 99.98% (Sigma-Aldrich) to the prepared support and mixing with 20 ml of distilled water to obtain catalysts with 13 wt% of nickel, 1 wt% Ru or both. The procedure was like the support preparation, using the wetness impregnation method: pH control at 8.5, overnight stirring, solvent evaporation, drying and calcining.

Finally, the calcined catalysts were pressed and sieved to the desired particle size: $0.42 \text{ mm} < d_p < 0.50 \text{ mm}$. This particle size (d_p) was chosen in order to avoid reagents bypassing near the wall, according to keep an internal pipe diameter-to-particle size ratio higher than 10 [30].

The catalysts prepared were named, according to their nominal composition, as follows: 13Ni/10Ba-Al₂O₃, 13Ni/10Ca-Al₂O₃, 13Ni/10Mg-Al₂O₃, 13Ni/14Ce-Al₂O₃, 13Ni/14La-Al₂O₃, 1Ru/14La-Al₂O₃, 1Ru-13Ni/14La-Al₂O₃, 1Ru-13Ni/Al₂O₃ and 1Ru/Al₂O₃.

5.2.2. Catalyst characterisation

The N₂ adsorption-desorption method was employed to evaluate the textural properties of the catalysts in the Autosorb 1C-TCD, after outgassing the samples at 573 K for 3 h. The specific surface area was calculated using Brunauer-Emmett-Teller (BET) equation and pore volume and pore sizes were calculated by Barrett-Joyner-Halenda (BJH) method.

The real composition of the catalysts was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on a Perkin–Elmer Optima 3300DV. Moreover, after disaggregating the catalyst in acid solution (mixture of HCl 3:1 and HNO₃ respectively), the composition and chemical element were identified by a characteristic wavelength emission intensity.

The crystalline species and an approximation of the average crystal size (estimated by XRD patterns and Scherrer equation [31]) of the catalysts were carried out on a PANalytical X'Pert Pro diffractometer using a CuK_α radiation ($\lambda=0.15418$ nm) at 40 kV and 30 mA and a scanning angle (2θ) of 20° to 90°.

The Temperature Programmed Reduction with H₂ (H₂-TPR) and Temperature Programmed Desorption of ammonia (NH₃-TPD) or of CO₂ (CO₂-TPD) were carried out in a Micromeritics AutoChem II RS232, equipped with a thermal conductivity detector (TCD). The TPR profiles were recorded heating 50 mg of the sample from 323 K to 973 K, at a ramp rate of 10 K/min. Previously, the sample was heated from room temperature to 473 K for 1 h in Ar stream (30 Nml/min). Later, the sample was cooled down to 323 K and the Ar was replaced by 5 vol%, H₂/Ar (45 Nml/min) stream and analysed. The TPD profiles were recorded after pretrating the sample reducing with 5 vol%, H₂/Ar (45 Nml/min) stream, heating to 723 K. Then, the sample was cooled with He, replacing this stream for 10 vol% NH₃/He or pure CO₂ stream during 30 min. Recovering the He stream, NH₃ or CO₂ desorbed per unit time and catalyst mass was determined heating the sample from 423 K to 1173 K, at a ramp rate of 10 K/min.

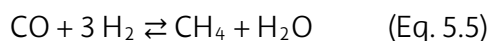
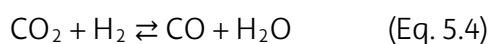
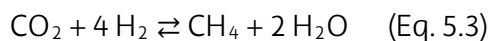
X-ray Photoelectron Spectroscopy (XPS) was obtained on a SPECS (Berlin, Germany) system equipped with a Phoibos 150 1D-DLD analyser and an Al K_α (1486.6 eV) monochromatic radiation source with electrons output angle of 90°. XPS is a technique that allows the study of the species present on the surface of the catalyst and their chemical state.

5.2.3. Activity test

The CO₂ methanation was carried out in a stainless steel fixed bed reactor of 32 cm of length, with an outside diameter of 1/4" inside a bench-scale plant (PID Eng&Tech) at 10 bar and temperature range of 498 – 773 K. The reactor was loaded with 60 mg of catalyst, diluted with inert SiC, in order to minimize thermal gradients in the catalytic bed ($\text{weight}_{\text{catalyst}}/\text{weight}_{\text{SiC}}=1:4.5$). Furnace temperature was adjusted to maintain the catalyst bed under isothermal condition using four thermocouples: the first one, inside the catalytic bed to measure the reactor temperature; the second one, on the catalytic bed; the third one, outside the catalytic bed in order to control the inlet temperature accurate; the last one, under the catalytic bed. The first step was the catalyst activation, reducing the catalyst with a mixture of N₂ (99.999%, Air Liquide) and H₂ (99.999%, Air Liquide) with a ratio of H₂/N₂ equal to 3:1 (65 Nml/min of H₂) at 673 K during 4 h. Once the catalyst was activated, the reaction gasses, H₂ and CO₂ (99.98%, Air Liquide), were fed in a ratio H₂/CO₂ of 4:1. Such that the weight hourly space velocity (WHSV) of the flow fed was 38.30, 60.80 or 128.75 $\text{g}_{\text{feed}}/(\text{g}_{\text{cat}}\cdot\text{h})$, depending on the amount of catalyst used 200, 125 or 60 mg respectively.

The stoichiometry proportion for the methanation reaction was employed to obtain biogas (Eq. 5.3). The methanation reaction is the combination of Eq. 5.4 and 5.5, where CO could be generated as an intermediate product, or as a final product in

combination with methane, in case the reactions of *Eq. 5.3* and *Eq. 5.4* run parallel to each other [20].



The reactor was heated until the reaction temperature at a rate of 10 K/min under N₂ flow, studying the catalyst activity. The reaction temperatures studied were from 498 K to 573 K each 25 K and from 573 K to 773 K each 50 K. The products were separated and were analysed in a partial condenser (separating condensed water and gas products). The reaction was stabilized at each temperature for 120 min, analysing the output massflow and composition of the gases each 10 min. The water produced was collected and weight in this time. The gas phase composition was on-line analysed using a Varian CP-4900 MicroGC equipped with a high sensitivity TCD and two columns (10 m Molecular Sieve 5, 10 m Poraplot Q). The CH₄ yield was calculated using the following equation:

$$\eta_{\text{CH}_4} = \text{mol CH}_4^{\text{out}} / \text{mol CH}_4^{\text{out stoichiometric}} \cdot 100 \quad (\text{Eq. 5.6})$$

In the *Eq. 5.6*, η_{CH_4} represent the methane yield, $\text{mol CH}_4^{\text{out}}$ represent the flow rate of the methane out of the reactor and $\text{mol CH}_4^{\text{out stoichiometric}}$ represent the theoretical flow rate of the methane out of the reactor, based on stoichiometric of reaction. Thus, if all CO₂ is converted to CH₄, the value of η_{CH_4} would be 100 %.

All the experiments were repeated to ensure reproducibility.

5.3. Results and discussion

5.3.1. Catalyst characterisation

5.3.1.1. Chemical composition

The chemical composition of the catalysts employed in the CO₂ methanation was measured by ICP-OES analyses. The catalysts were prepared to have a target nominal content of 13 wt.% for the Ni, 1 wt.% for Ru, 10 wt.% for the alkaline earth Ba, Ca and Mg and 14 wt.% for the lanthanides La and Ce. Catalysts that only contain Ni showed a Ni content slightly higher compared to the target. However, the experimental nominal content of Ni was higher or lower than the target composition depending on the metal modifying the support. In the presence of La, the amount of Ni determined was greater than expected, as it was observed experimentally and confirmed in the literature [33,34]. In the case of Ca and Mg, a considerable decrease in its value was observed with respect to 13Ni/Al₂O₃. Contrary, a decrease in the proportion of Ni with respect to Ba was produced by the presence of Ba modifying the support. The catalyst whose support was modified with Ce, slightly reduces the Ni content. In contrast, the catalyst 1Ru-13Ni/Al₂O₃ showed slightly more nickel and less of Ru respect to the expected values. The chemical composition measured by ICP of the prepared catalysts and their target nominal values (in brackets) are shown in the *Table 5.2*.

Catalyst	Composition (wt%)			$S_{\text{BET}}^{\text{b}}$ (m^2/g)	V_{P}^{c} (cm^3/g)	d_{P}^{d} (nm)	$d_{\text{XRD}}^{\text{e1}}$ (nm)	$d_{\text{XRD}}^{\text{e2}}$ (nm)
	Ni	Ru	χ^{a}					
$\gamma\text{-Al}_2\text{O}_3$	0	0	0	202	0.81	7.7	-	-
13Ni/Al ₂ O ₃	13.9	0	0	180	0.55	7.2	5	10
13Ni/10Ba-Al ₂ O ₃	8.83	0	14.17	93	0.12	6.9	5	15
13Ni/10Ca-Al ₂ O ₃	15.73	0	7.27	74	0.08	6.1	10	25
13Ni/10Mg-Al ₂ O ₃	17.52	0	5.48	109	0.15	7.3	5	15
13Ni/14Ce-Al ₂ O ₃	12.16	0	14.84	86	0.12	7.2	5	15
13Ni/14La-Al ₂ O ₃	15.41	0	11.59	79	0.11	6.5	5	15
1Ru/14La-Al ₂ O ₃	0	1.19	13.81	129	0.17	7.2	5	15
1Ru-13Ni/14La-Al ₂ O ₃	14.79	0.52	12.69	93	0.12	7.1	5	15
1Ru-13Ni/Al ₂ O ₃	13.73	0.27	0	163	0.22	7.5	5	15

Table 5.2. Summary of the contents of Ni, Ru and modifier metal (M), textural properties, the crystal size of Ni and turnover frequency of the samples.

^aMetal modifier of support (Ba, Ca, Mg, La or Ce) according to the corresponding catalyst;

^bThe surface area was calculated by the BET equation;

^cBJH desorption pore volume;

^dBJH desorption average pore diameter;

^e $S_{\text{XRD}}^{\text{e1}}$ (after reduction) and $S_{\text{XRD}}^{\text{e2}}$ (after reaction) are an approximation calculated from Ni (111) plane using Scherrer equation.

5.3.1.2. BET measurements

In Table 5.2 are represented the surface area, pore volume and pore size, determined measuring the N₂ adsorption and desorption isotherm, in order to analyse the textural properties of supports and prepared catalysts. The isotherms obtained for the supports and catalysts prepared are IV-type curves, with a remarkable H₂ hysteresis loop, representative of mesoporous structure and due to the presence of "ink-bottle" or cylindrical channels [35].

The addition of Ru barely reduces the surface area of the alumina support (202 m^2/g), due to its small amount added. Contrary to what happens with the addition of Ni causing a significant reduction of the surface area and pore volume, by the partial blockage of the small pores of the supports [36]. The addition of a second metal contributed to the nickel blocking effect depending on the metal and its interaction with the support. In the case of Mg, the surface area (and pore volume and size) reduction is lower than in the cases of Ca and Ba by promoting the creation of porous structures during the catalyst calcination stage [24]. The addition of Ba in amounts greater than 5 wt.% produces the occupation of the pores by the metal, causing the reduction of the total surface area [24]. Ca causes the union of smaller pores to obtain larger pores during the calcination stage, being increased with the amount of metal added [24]. The incorporation of La or Ce as support modifiers has a similar effect that the observed for alkaline earths. So that as metal is added to the catalyst, the blocking of the pores (specially the smallest) of the support was increased and also the pore sizes via merge of the catalysts.

5.3.1.3. Temperature programmed reduction (H₂-TPR)

It was evaluated the effect of the alkaline earth and lanthanides on the reducibility and the metal-support interaction of the catalysts using the H₂-TPR. Measurements and results are collected in the Figure (Fig. 5.1). According to the reducibility and the strength of interaction that the Ni had with the support, the peaks represented in the H₂-TPR show four species of nickel oxides. In the range of 523 to 623 K, species reducible correspond to metallic nickel with weak interaction with the support. The NiO with weak-medium interaction with the support corresponds to the reducible species between 623K and 773 K. Stronger interaction (medium-strong) with the support for the Ni²⁺ occurs in the range of 773 to 1023 K for the non-stoichiometric nickel aluminate (NiO-Al₂O₃), being the stoichiometric nickel aluminate species (NiAl₂O₄) harder to reduce. These are reducible from 1,073 K having a strong interaction with the support [24,37–40].

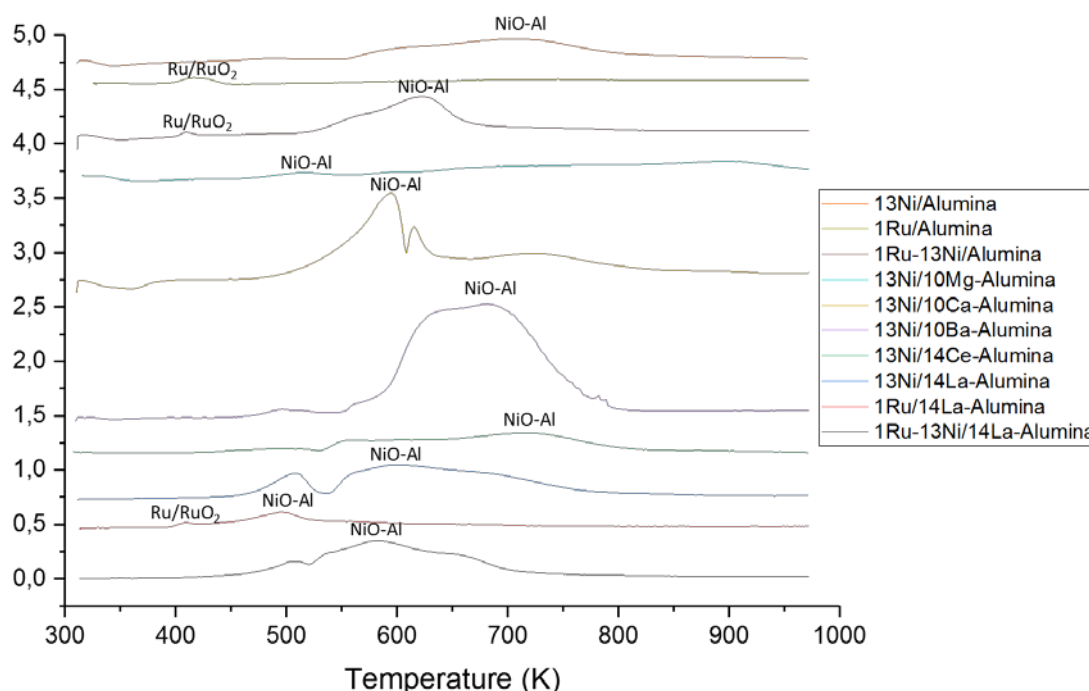


Fig. 5.1. H₂-TPR profiles of the prepared catalysts in 5% H₂/Ar atmosphere and 10°C/min heating rate.

The addition of noble metals, such as Ru, changes the reduction profiles of the Ni-catalyst as was reported in the literature [18,41,42]. The reduction profile of the Ru catalyst showed a maximum located at 416 K corresponding to the reduction of supported RuO₂ into metallic Ru and a shoulder at 348 K according to the reduction of well dispersed RuO_x species [42]. The bimetallic catalyst of Ru and Ni exhibit mainly two peaks at 410 and 623 K and two shoulders at 376 and 562 K respectively. The peak and shoulder reported at 410 and 376 K correspond to those determined for the monometallic catalyst of Ru. The main reduction peak reported at 623 K represent NiO reduction, and the shoulder at 562 K represent the reduction of RuO₂ and NiO on the alumina surface, mainly forming Ni-Ru bimetallic particles [41].

TPR patterns of La modified supports, shown a splitting of the peaks at temperatures between 500 and 700 K. The new peak appears at 505 K and corresponds to the free NiO species in the alumina support, which increases as the La content of the catalyst increases [25,37,43]. Based on the results and the literature observations, the

stable La-alumina structure weakens the interaction between NiO and support of Al₂O₃ with La increasing, by destroying partially metastable Ni-Al mixed oxide phase [37,43].

The low reducibility of the alumina support could be improved with the addition of Ce, as it was observed in the literature [44]. The reduction peaks were found at 598, 798 and 993 K corresponding to non-stoichiometric CeO₂, surface reducible metal centres of CeO₂ and bulk reducible metal centres of CeO₂, respectively [44]. Attending to the TPR profile obtained, the participation of the support in the reducibility of the nickel catalyst was observed at low reduction temperatures (561 K), corresponding the reduction peak at medium temperature (715 K) with the interaction of NiO with the support. At low temperature, the reduction peak represents the contribution in the reduction of Ni and Ce⁴⁺ at the surface of CeO₂ [44].

The TPR profiles of the supports of Ni catalysts modified with alkaline earth define a different spectrum, depending on the metal. Barium in contact with the alumina support produces reducible species as BaAl₂O₄ that at 763 K show a reduction peak. In combination with nickel, the greatest contribution in the TPR profile corresponds to the reduction of nickel and barium-alumina species (with reduction peaks at 583, 903 and 1053 K), being facilitated the interaction of Ni and alumina by the presence of Ba. The contribution of Ba was mainly observed in the increase of the first two catalyst reduction peaks and decrease in the third, due to the interaction of BaO with the support, forming other structures (as spinel) [45]. The experimental profile presented three peaks and one shoulder at 498, 650, 682 and 561 K respectively, as the literature shows [24,45]. The contribution of Ca is due to the presence of CaO in the catalyst, which is related to the reduction at low temperatures but it strengthens the interaction with NiO, making it difficult to reduce NiO [24]. This produces a splitting of the low temperature reduction peak corresponding with the reduction of NiO, obtaining two peaks at 595 and 615 K. The first one increases with respect to the second one, as the amount of Ca added increases [46]. It was observed that the addition of Mg (presented in form of MgO) decreased the reduction peaks corresponding to NiO and Ni aluminate [47]. In the TPR profile obtained for Ni/Mg-Alumina three peaks at 513, 600 and 890 K were determined, with lower hydrogen consumption regarding to other catalysts analysed. Some causes attributed by Tan et al. [47] are the effect of coverage of MgO on the NiO species; a strong interaction between NiO and MgO; a formation of larger Ni(Mg)O; or the combination of some of them [24]. NiO-MgO catalysts usually form NiO-MgO solid solution, which makes it very difficult to reduce, but when reduced at high temperatures; they usually give very dispersed crystals, as observed in the Requies work [48]. In general, according to the above, the addition of Ba facilitates the reduction of the catalyst against the use of Ca and Mg that makes it difficult.

Based on the results obtained and the literature, the catalysts activated by the reduction at 673 K must be completely reduced for the reaction conditions between 498 and 773 K for CO₂ methanation.

5.3.1.4. NH₃-TPD and CO₂-TPD studies

The acidity and basicity of the catalysts was studied by NH₃-TPD and CO₂-TPD desorption profiles, determining the quantity and strength of catalyst acid and basic sites, respectively. Desorption temperature determines the strength of the bonds, so that higher desorption temperature means stronger bonds.

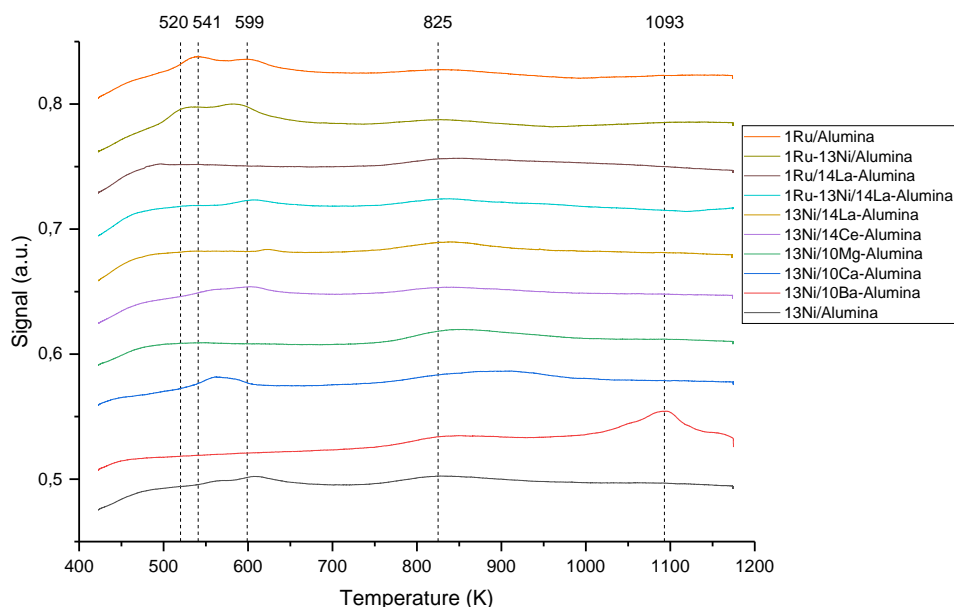


Fig. 5.2. NH_3 -TPD profiles of the prepared catalysts.

According to their nature, strength acid centres and adsorbed NH_3 react towards NO_x formation, define three regions: up to 523 K, weak acids (Lewis acid sites), from 523 to 673 K middle acids (Lewis acid sites) and from 673 K strong acids (Bronsted acid sites) [33,41,48]. Depending on the metal modifying the alumina support of the catalyst and according to the metal, the NH_3 -TPD profiles will be different. These profiles are shown in Fig. 5.2. The main peaks are shown at around 520 K, 541 K corresponding to Lewis acid sites (middle acids) and 599 K, 825 K, 1.093 K conforming to Bronsted acid (strong acids). The total amount of acid centres, and their distribution, related to ammonia desorption, was presented in Table 4.2 for the studied range, calculating as the area under the concentration-time curve of the TPD profiles, according to regions. The Lewis acid sites of alumina are coordinated with NH_3 , due to the electron deficiency of trivalent aluminium atoms, presenting a maximum centred at 548 K [48]. Furthermore, the peak centred at 1.073 K (in strong acid region) was the most significant in the catalysts studied and corresponds with Bronsted acid sites by the hydrogen atoms that may act as proton donor [49].

The 13Ni/ Al_2O_3 catalyst is characterized by having a small peak at 460 K in weak acid region; two peaks in the medium acid region, with a main peak at 599 K and a weaker peak at 552 K; and another two wider peaks in the strong acid region at 825 K and 1093 K. In the case of 1Ru/ Al_2O_3 catalyst, the peaks present in the region of medium centres are more significant, taking into account the spectrum of Fig. 5.2. These peaks appear at 542 and 599 K. This catalyst shows a quantitatively greater number of weak and medium acid centres than 13Ni/ Al_2O_3 catalyst. However, the peak present in strong acid regions is significantly lower for ruthenium. Therefore, the combination of both metals, Ru and Ni, produces an additive effect on the number of weak and medium acid centres. Thus, a significant increase in these centres is observed with respect to the Ni catalyst (and that of Ru), exhibiting two peaks similar to those of Ru, slightly displaced at lower temperatures. These peaks appear at 520 K and at 485 K.

Ba produces a significant decrease in the number of weak and medium acid centres, compared to the sharp increase in strong acid centres, quantitatively. Also qualitatively, due to the presence of two peaks, one smaller at 825 K and the other more noticeable at 1093K. It is observed in 13Ni/10Ca-Al₂O₃ catalyst, that the presence of Ca produces a migration of the density of active centres towards a medium interaction strength, close to a low interaction, at 558 K and to the region of strong centres at 915 K. However, despite its concentration, the density of acid centres in this case is decreased for all strength. Something similar happens to 13Ni/Mg-Al₂O₃ catalyst, concentrating the centres mainly in the region of strong acid centres with a wide peak at 845 K and with a significant reduction in the density of centres of medium strength. The Ce-incorporating catalyst shows little significant difference from 13Ni/Al₂O₃ spectrum, except for a slight increase in the density of active centres in all regions.

Finally, the addition of La to the catalysts formed by Ru, Ni or both demonstrates its contribution to the significant increase in the density of acid centres of higher strength. This effect is justified in the literature, referring to an interaction that takes place between La³⁺ - O²⁻ pairs with the strongest acid and basic centres of alumina. This results in the reduction of Lewis acidity, as was more easily observed in 1Ru/Al₂O₃ catalyst, but providing strongest acid-basic couples [33].

Furthermore, the similar spectrum in TPD-CO₂ obtained for all the catalysts supported by alumina and modified with different metals, suggests that the binding of CO₂ was done on the alumina, while the H₂ binds to the promoter metal, as justified in the TPR analyses. According to this, and as it has been analysed in other works [50–53], the mechanism of the methanation reaction in these catalysts could follow a model similar to that represented in Fig. 5.3.

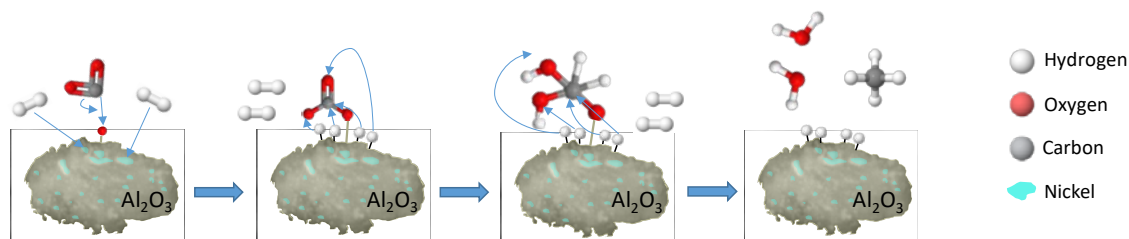


Fig. 5.3. Scheme of CO₂ methanation mechanism on Ni/Al₂O₃ catalyst.

Fig. 5.4 shows the representation of the CO₂-TPD profiles defined by the catalysts studied. The curves defined in this analysis define the distribution of basic catalyst centres as a function of temperature. In this way, as temperature increases, interaction between CO₂ and catalyst is stronger and, therefore, stronger are the basic centres. According to the strength of the basic centres of the catalyst, three regions of the curve are distinguished: the region of weak basic centres (between 313 and 423 K), moderate basic centres (between 423 and 723 K) and strong basic centres (between 723 and 823 K). The total sum of all the basic centres in each region are shown in Table 5.3.

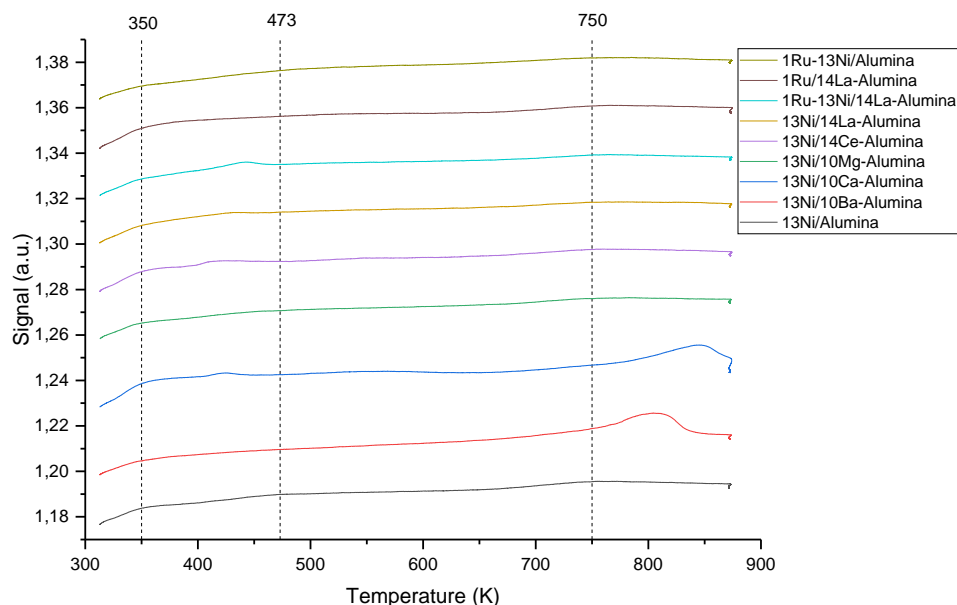


Fig. 5.4. CO₂-TPD profiles of the prepared catalysts.

The incorporation of alkaline earth elements and lanthanides to the catalyst structure, contributes the incorporation of basic centres that facilitate the union of CO₂ for its reaction with H₂. The low electronegativity of these metals results in the metal oxide formed having a base behaviour [50]. In this way, the presence of these metals increases the number of basic centres of 13Ni/Al₂O₃ catalyst, as observed in the table for the three regions, especially for 13Ni/10Mg-Al₂O₃ catalyst.

The CO₂-TPD profiles are similar in the catalysts analysed, having in common the presence of three peaks that appear at temperatures of 350, 473 and 750 K. The first, in the region of weak centres, corresponds to the formation of carbonates on the catalyst surface at the CO₂ bond. Second, the peak appearing in the moderate centre region, at 473 K, is due to bicarbonate formation on the catalyst surface. Finally, when the interaction between CO₂ and catalyst is greater (750 K), the formation of monodentate bicarbonate species takes place [51]. In the 1Ru-13Ni/14La-Al₂O₃, 13Ni/14Ce-Al₂O₃ and 13Ni/10Ca-Al₂O₃ catalysts, the formation of bicarbonate species is facilitated at lower temperatures, with the corresponding peak appearing at a temperature of approximately 423 K. The incorporation of Ba and Ca to the 13Ni/Al₂O₃ catalyst produces an increase in strong basic centres (although without reaching the one that produces 13Ni/10Mg-Al₂O₃), shifting the peak corresponding to the formation of monodentate bicarbonate species to 808 and 846 K respectively. It is also remarkable that the number of strong basic centres. This demonstrates the strong character of the interactions of these catalysts with CO₂, interacting with the monodentate species of the bicarbonate species.

Catalyst	Acidity amount $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$			Basicity amount $\mu\text{mol CO}_2/\text{g}_{\text{cat}}$		
	Weak	Media	Strong	Weak	Media	Strong
Temperature	< 523	523<T<673	>673	< 423	423<T<723	>723
13Ni/Al ₂ O ₃	127.31	337.94	1,146.17	10.95	56.97	100.82
13Ni/10Ba-Al ₂ O ₃	85.74	197.30	1,407.31	12.67	64.60	127.37
13Ni/10Ca-Al ₂ O ₃	83.68	260.24	1,091.13	18.07	70.63	124.51
13Ni/10Mg-Al ₂ O ₃	119.63	251.15	1,116.46	15.59	79.26	143.03
13Ni/14Ce-Al ₂ O ₃	143.10	383.18	1,274.84	14.23	61.96	105.21
13Ni/14La-Al ₂ O ₃	166.78	345.32	1,268.69	15.18	70.77	118.48
1Ru-13Ni/14La-Al ₂ O ₃	167.41	378.84	1,253.09	13.43	65.75	108.45
1Ru/14La-Al ₂ O ₃	165.51	316.19	1,180.72	10.80	64.95	112.27
1Ru-13Ni/Al ₂ O ₃	169.09	470.66	1,167.03	12.73	55.78	91.98
1Ru/Al ₂ O ₃	153.60	411.25	974.57			

Table 5.3. Distribution of the strength of acidity by NH₃-TPD and CO₂-TPD respectively of the different catalysts.

5.3.1.5. XPS

The XPS technique has allowed us to determine the species present on the catalytic surface, their oxidation state and their quantification. The main species identified on the surface correspond to the support, identifying Al 2p at 74.2 and O 1s at 531.0-531.8 that make up the alumina and the oxides of the rest of the metals. Nickel is the main active metal of the catalysts studied, showing a multiplet split at 854-854.5, 855.7-857.2 and 860.8-862.6 eV [54] according to Ni⁰, Ni²⁺ from NiAl₂O₄, and Ni²⁺ satellite respectively for fresh catalyst [54], as observed in Fig. 5.5 and Fig. 5.6. Used catalyst showed also three peaks in 13Ni/14La-Al₂O₃ and 1Ru-13Ni/14La-Al₂O₃, at 855.1, 857.5 and 862.8 eV, corresponding to Ni²⁺ from NiO, Ni²⁺ from NiAl₂O₄, and Ni²⁺ satellite respectively, and only two in the others at 855.8-856.6 and 862.0-863.0 eV, corresponding to Ni²⁺ from NiAl₂O₄, and Ni²⁺ satellite respectively, as observed in Fig. 5.7 and Fig. 5.8. Specifically, in fresh catalysts a greater intensity of the metallic nickel peak than of the oxide is observed, due to the in situ reduction stage in the reduction cell incorporated in the analysis equipment. However, in the case of the used catalysts, without reducing treatment, and due to the aggressive effect of temperature, the effect of hydrogen sulfide poisoning and sintering, only the presence of nickel aluminate is determined in most catalysts, identifying nickel oxide only in catalysts composed of Ni-La. The disappearance of metallic nickel in its transformation into nickel oxide or nickel aluminate can cause loss of activity of the catalyst.

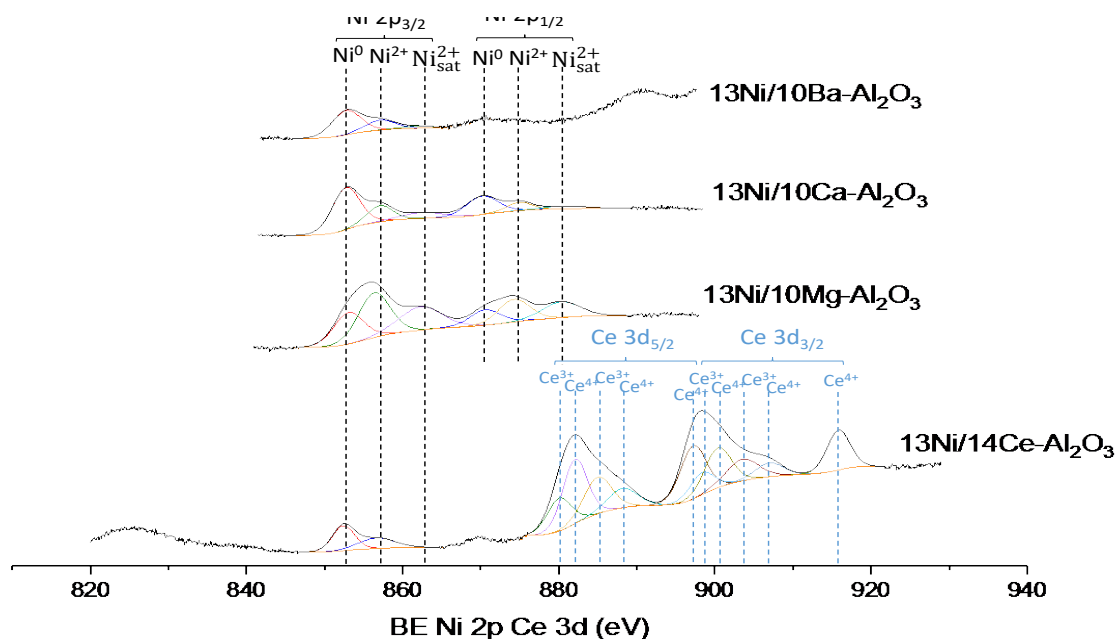


Fig. 5.5. XPS spectra of Ni 2p_{3/2}, Ni 2p_{1/2}, Ce 3d_{5/2} and Ce 3d_{3/2} regions of fresh catalysts.

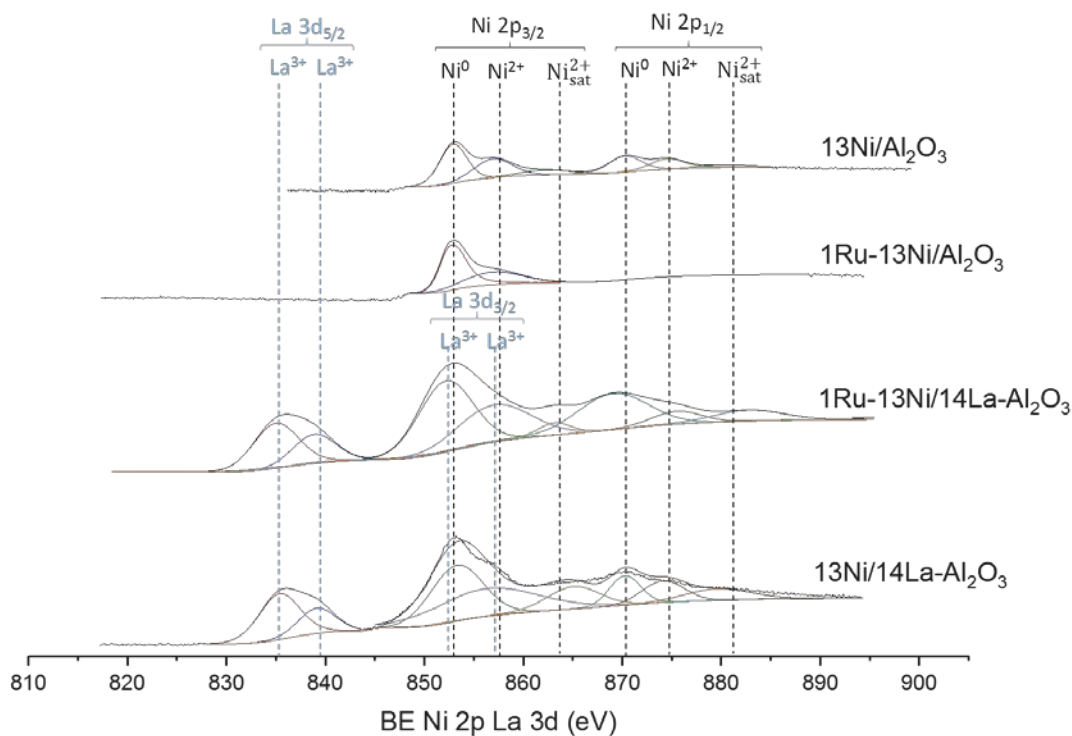


Fig. 5.6. XPS spectra of La 3d_{5/2}, La 3d_{3/2}, Ni 2p_{3/2} and Ni 2p_{1/2}, regions of fresh catalysts.

Ru 3p_{3/2} at 459.5–461.9, used as an active metal or mainly as a promoter, is difficult to identify in some of the catalysts due to its low concentration, which approximates its spectrum to that of noise. The rest of the metals incorporated in the support are also identified. Ba 3d_{5/2} with doublet at 781.1–781.9 and 796.4–797.2 eV with overlap in the Auger Ba MNN line that can lead to an underestimation of %Ni. Ca 2p at 346.7–347.5 eV. Mg 2p at 49.5–49.6 eV. Ce with quintuplet 3d_{5/2} and 3d_{3/2} in positions 880.0–880.6 and

885.0-885.5 eV for Ce^{3+} duplicated at 898.3-898.9 and 903.5-904.1 eV. In addition, at 882.1-882.9, 888.1-889.0 and 897.2-898.2 eV for Ce^{4+} duplicated at 900.4-901.2, 906.9-907.6 and 915.8-916.5 eV. Thus, in the less energetic positions, there is a slight inclusion of the Ce spectrum in that of Ni, which hinders the identification of nickel $2p_{1/2}$ and underestimate %Ni.

Finally, La $3d_{5/2}$ and its satellite were located at 834.9-836 and 838.5-839.7 eV, and $3d_{3/2}$ and its satellite at 852.5-853 and 856.5-856.9 eV. However, it was not possible to identify La $3d_{3/2}$ in those catalysts whose active metal is Ni, in the same way that the Ni content cannot be quantified. This is due to the superposition with the Auger LMM line of Ni $2p_{3/2}$ and La $3d_{3/2}$ in the case of the catalyst $13\text{Ni}/14\text{La-Al}_2\text{O}_3$ and $1\text{Ru}-13\text{Ni}/14\text{La-Al}_2\text{O}_3$. Nonetheless, the Ni $2p_{3/2}$ corresponding triplet moves toward lower bond energy, while the La $3d_{3/2}$ doublet increases its bond energy, producing the overlapping of the corresponding peaks, confirming the interaction that occurs between La^{3+} and Ni^{2+} [25].

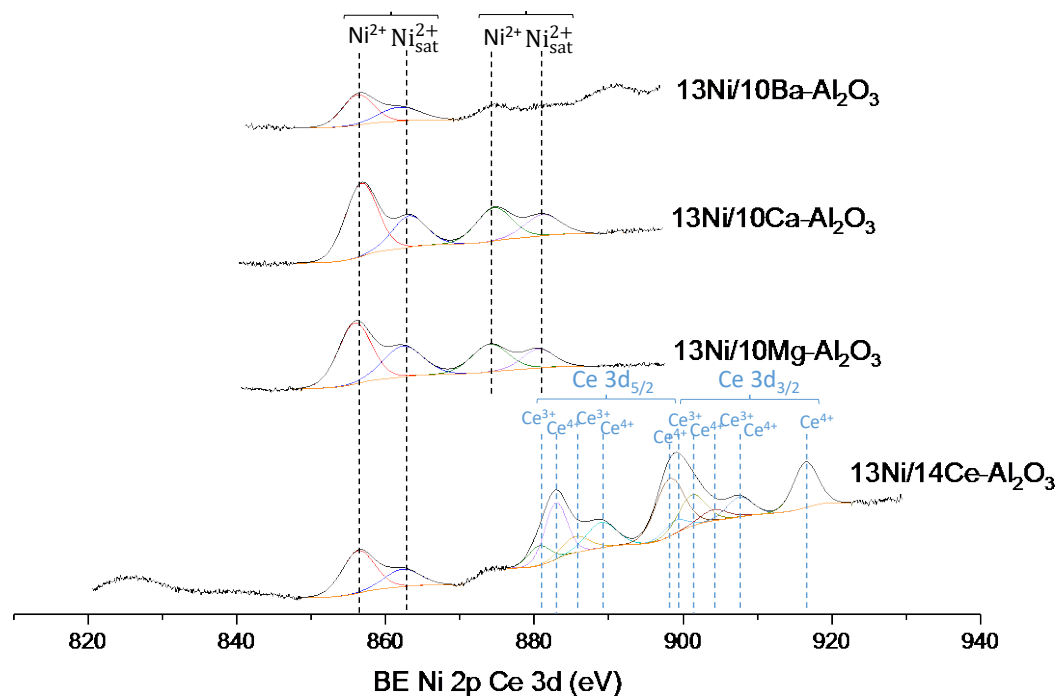


Fig. 5.7. XPS spectra of Ni $2p_{3/2}$, Ni $2p_{1/2}$, Ce $3d_{5/2}$ and Ce $3d_{3/2}$ regions of used catalysts.

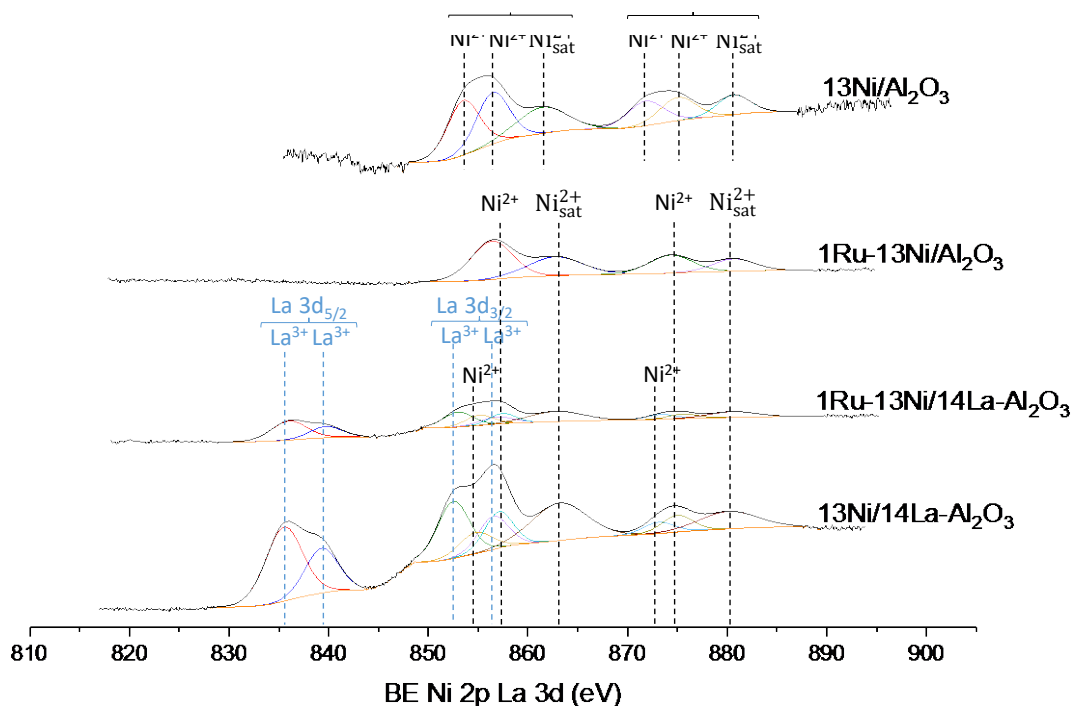


Fig. 5.8. XPS spectra of La $3d_{5/2}$, La $3d_{3/2}$, Ni $2p_{3/2}$ and Ni $2p_{1/2}$ regions of used catalysts.

According to the results shown in the spectra represented in Fig. 5.5, a lower proportion of Ni^0 than of NiO is observed in $13\text{Ni}/10\text{Mg}-\text{Al}_2\text{O}_3$ catalyst, after being reduced in situ. This can be justified by a higher ease for the oxidation of this catalyst, compared to the rest of the catalysts analysed. The magnesium introduced interacts with the nickel forming a solid solution difficult to reduce, as observed in the work of Requies [48]. After use in the reaction, the complete oxidation of the nickel present in the catalysts is observed, raising the proportion of oxygen present, as shown in Table 5.4. This increase is especially significant in catalysts with Ca and Ru-La in their composition, assuming an increase of more than 10%. This increase in the amount of oxygen is compensated by a decrease in the same proportion of the Al content in $1\text{Ru}-13\text{Ni}/14\text{La}-\text{Al}_2\text{O}_3$ and $1\text{Ru}/14\text{La}-\text{Al}_2\text{O}_3$ catalysts and a significant reduction in the proportion of the secondary metal in $13\text{Ni}/10\text{Ca}-\text{Al}_2\text{O}_3$ and $1\text{Ru}-13\text{Ni}/14\text{La}-\text{Al}_2\text{O}_3$ catalysts. This is due to sintering of the metal, which produces an agglomeration in deeper layers of the catalyst. On the other hand, although the increase in the proportion of oxygen is not as marked in $13\text{Ni}/14\text{Ce}-\text{Al}_2\text{O}_3$ and $13\text{Ni}/14\text{La}-\text{Al}_2\text{O}_3$ catalysts, the reduction in the proportion of Al is up to 9%. Finally, it is necessary to highlight the increase that occurs in the proportion of Ni after its use in the reaction, in $13\text{Ni}/14\text{Ce}-\text{Al}_2\text{O}_3$ and $13\text{Ni}/10\text{Ca}-\text{Al}_2\text{O}_3$ catalysts, raising the proportion to double its value. Something similar to what happens with Ru in $1\text{Ru}/\text{Al}_2\text{O}_3$ catalyst.

	Fresh catalyst					Used catalyst				
	Al (%)	O (%)	Ni (%)	Ru (%)	M (%)	Al (%)	O (%)	Ni (%)	Ru (%)	M (%)
13Ni/Al₂O₃	40.4	56.5	2.7	-	-	37.7	59.1	2.6	-	-
1Ru-13Ni/Al₂O₃	36.9	58.3	3.2	-	-	35.9	60.6	2.7	0.3	-
1Ru-13Ni/14La-Al₂O₃	38.6	57.0	*	-	4.4	24.5	69.8	3.9	-	1.8
13Ni/14La-Al₂O₃	35.7	60.3	*	-	3.4	26.7	64.9	5.3	-	3.1
13Ni/10Ba-Al₂O₃	32.7	59.2	2.1	-	6.0	28.9	62.9	2.9	-	5.3
13Ni/10Ca-Al₂O₃	27.7	55.2	3.8	-	13.4	21.2	65.5	6.5	-	6.8
13Ni/10Mg-Al₂O₃	33.3	55.6	4.8	-	6.3	30.6	58.1	5.2	-	6.1
13Ni/14Ce-Al₂O₃	32.3	60.8	1.9	-	5.1	23.7	67.5	4.2	-	4.5
1Ru/14La-Al₂O₃	38.1	57.3	-	0.6	3.5	28.5	67.0	-	0.7	3.1
1Ru/Al₂O₃	42.1	55.9	-	0.5	-	40.2	58.2	-	1.1	-

Table 5.4. Surface atomic values obtained by XPS analysis of the different catalysts studied *presence of Ni, but cannot be quantified (2p line of Ni overlapped with 3d line of La).

The XPS results show that the Al present in used catalysts is found primarily as aluminate. The aluminate is attached to the active metal in its oxidized form, giving rise to a strong interaction. Due to the effect of high temperature and the action of H₂S, it is possible that the migration of the strongly oxygen-bound metal from the aluminate to the surface occur. Despite the increased exposure of the metal, its interaction with the support is likely to block its catalytic capacity, disabling the catalyst. Due to the strong structural change, despite the removal of the H₂S, the catalyst will probably not recover its activity.

5.3.1.6. X-ray diffraction

The identification of the main crystalline species was possible through the study of the XRD patterns presented in **Fig. 5.9** and **Fig. 5.10**, corresponding to the XRD patterns of the fresh and used catalysts studied. **Fig. 5.9** shows the crystalline species in a reduced state, prior to the use of the catalysts in reaction. The γ -Al₂O₃ support exhibits its diffraction peaks at 37.5°, 44.5° and 67.4° mainly, corresponding to the crystal plane of (331), (400) and (440) respectively [55,56]. Peaks at 19.7° (111), 34° (220), 57° (422), 61° (511) and 85° (444) can also be used for the identification of the alumina, although they are more difficult to detect specially in the presence of other metals [55,56]. The diffraction peaks of the support observed in the XRD pattern after using the catalysts in the methane reaction up to 773 K, with a current containing H₂S, do not show significant variations.

The diffraction peaks obtained before and after the reaction stage coincide in the same position and without variation of the determined crystal size. In the case of metal promoters, Ni and Ru are in their metallic form both in the reduced fresh and used catalysts, their oxidized form not being detected. Ni peaks are observed at 44.5° (111), 51.6° (200) and 76.7° (220) [16]. In the case of Ru, the main peak is shown at 44.2° (101), the peaks of positions 38.5° (100), 42.3° (002), 78.6° (103) and 84.9° (004) also being part of its pattern [57,58]. Due to the low amount of Ru added to the catalysts the peaks of this metal disappear [59] in the presence of other promoters, such as Ni in this case. In the presence of the support it is possible to identify some peaks, which even being overlapped

by those of the support can be identified, especially at 44.2° . This is the only peak located in the presence of La as a support modifier. The lanthanum detected in the XRD pattern is the one associated with the support, in the form of $\text{Al}_{22}\text{La}_2\text{O}_{36}$ and La_3Al , the La_2O_3 phase cannot be identified, which implies its high dispersion on the surface of the support [28]. After the reaction step, the La_2O_3 dispersed into the $13\text{Ni}/14\text{La}-\text{Al}_2\text{O}_3$ catalyst is transformed into the $\text{La}_2\text{O}_2\text{CO}_3$ species. In the rest of the catalysts no compound of La is identified, accusing its release of the link with the support and remaining as La_2O_3 dispersed in the support.

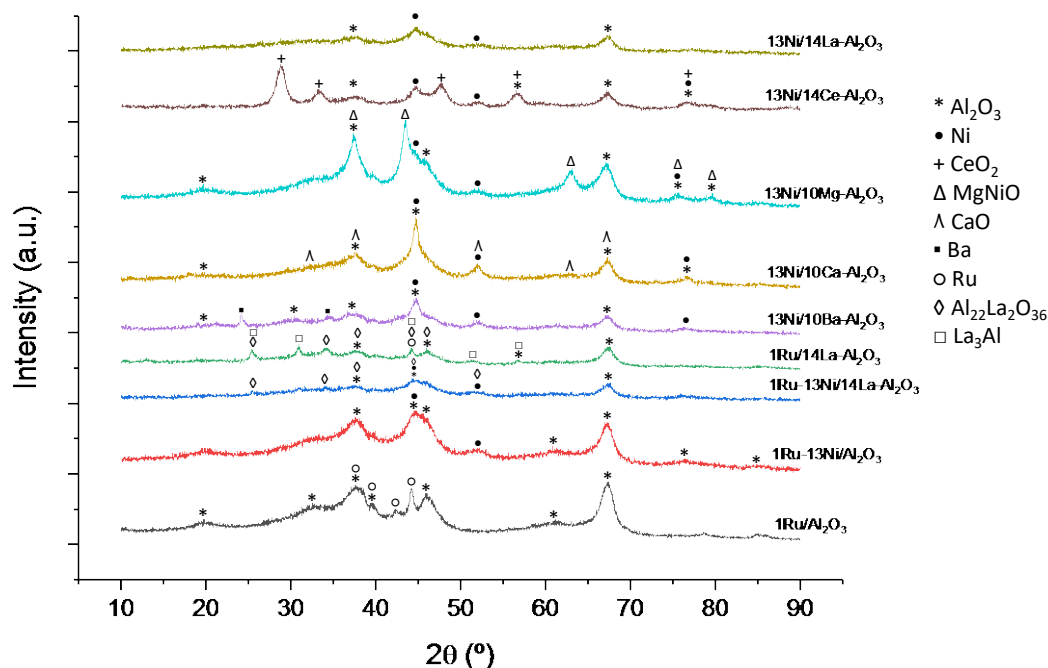


Fig. 5.9. XRD patterns of bi- and monometallic fresh-reduced catalysts supported over Al_2O_3 .

The addition of La, Ce and Ba to the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts produces the damping of the Ni reflection peaks, due to the dispersion of the metal in the support [16,24,25]. The catalyst with Ce has a similar XRD pattern before and after participating in the reaction, identifying the diffraction peaks of CeO_2 in both spectra.

The XRD patterns of the alkaline earth metals studied in the reduced catalysts were shown in their metallic or oxidized form: Ba, CaO and MgNiO . After the reaction, the spectrum of the Mg hardly changes, identifying the $\text{Mg}_{0.4}\text{Ni}_{0.6}\text{O}$ from fresh catalyst in the form of MgO in used catalyst. Calcium remains as CaO, which, as in the catalyst before the reaction, is difficult to identify, due to the coincidence of the peaks that allow its identification with those of the support, much more abundant. However, it is possible to identify in this case the nickel carbide that appears, with the reduction in intensity of the Ni peaks, as a result of the disappearance of part of the Ni to appear as NiCx .

Compared to the previous ones, barium is transformed in the reaction stage into two different compounds: BaCO_3 and BaAl_2O_4 . These species exhibit certain peaks

represented in Fig. 5.10, with low intensity that implies a moderate formation of these elements.

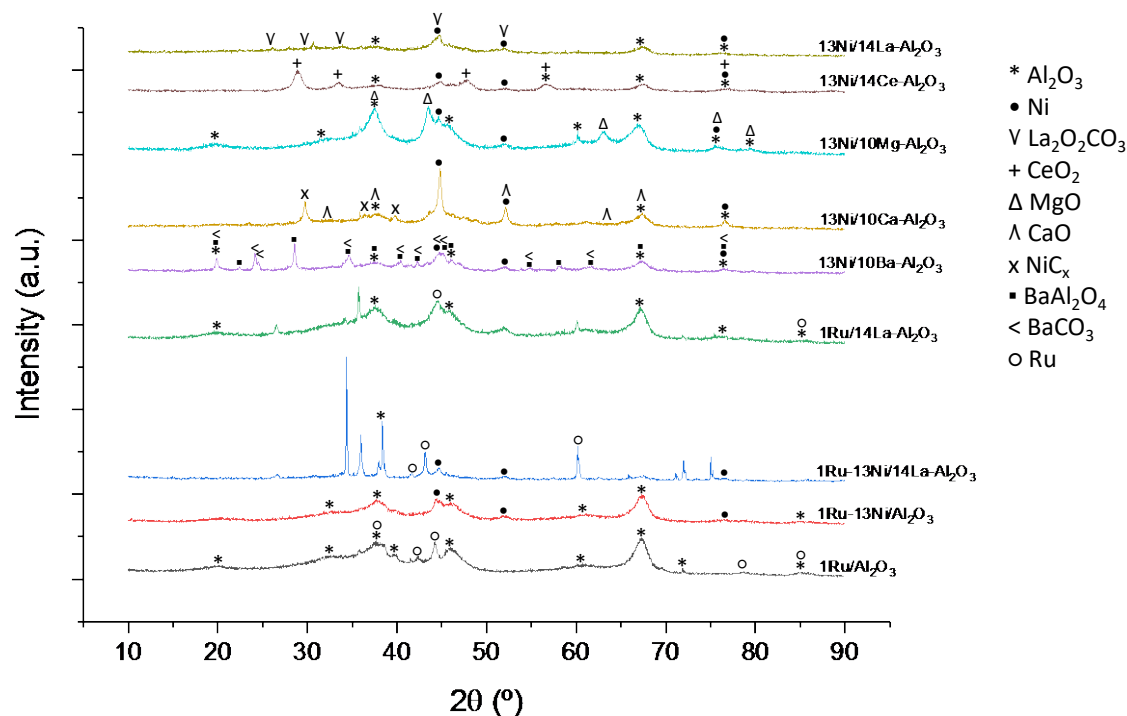


Fig. 5.10. XRD patterns of bi- and monometallic used-reduced catalysts supported over Al_2O_3 .

The 2θ position of the diffraction peaks of the XRD patterns determined by x-ray diffraction for the fresh and reduced catalysts (Fig. 5.9), and for the used catalysts (Fig. 5.10) are collected in the Table 5.5, contrasted with the bibliography.

Metallic species	JCPDS code	Value	Bibliography
Al_2O_3	077-0396	19.7, 34, 37.5, 44.5, 57, 61, 67.4, 85	[55,56]
Ni	087-0712	44.5, 51.6, 76.7	[16]
Ru	088-1734	38.5, 42.3, 44.2, 78.6, 84.9	[57,58]
Ba	006-0235	24.1, 34.5	[24,45]
CaO	086-0402	32.2, 37.3, 53.8, 64.1, 67.3	[27,60]
$\text{Mg}_{0.4}\text{Ni}_{0.6}\text{O}$	034-0410	37.4, 43.5, 63, 75.5, 79.4	[61,62]
MgO	087-0653	37.5, 43.5, 63, 75.7, 79.2	[61,62]
CeO_2	075-0076	28.9, 33.4, 47.7, 56.6, 76.8	[57,63]
$\text{Al}_{22}\text{La}_2\text{O}_{36}$	028-0502	25.8, 34.1, 37.5, 44.5, 45.9, 51.6	[25]
AlLa_3	025-1131	25.3, 30.8, 44.1, 51.3, 56.7	[25]
BaAl_2O_4	017-0306	19.7, 22.2, 28.4, 34.5, 37.5, 40.3, 42.2, 45.1, 45.9, 54.7, 58, 61.5, 67.2, 76.4	[27,45,64]
BaCO_3	005-0378	19.7, 24, 24.4, 34.5, 40.3, 42.2, 44.6, 45.1, 54.7, 61.5, 76.4	[27,64]
$\text{La}_2\text{O}_2\text{CO}_3$	025-0424	26, 30.5, 33.74, 44.6, 51.82	[65]

Table 5.5. XRD peaks for the metallic species of the catalysts analysed, determined graphically and contrasted with the bibliography.

The average particle crystal size of support and metals were estimated employing the Scherrer equation and a significant peak of the XRD patterns. The peaks used and the crystal size determined are collected in **Table 5.6**. After the reaction stage, an increase in crystal size is observed in all the species analysed, with the exception of Ru and alumina support. The increase in crystal size is a consequence of the sintering that takes place in the catalyst.

Species		Peak position (°)		Crystal size approximation of reduced catalyst (nm)	Crystal size approximation of used catalyst (nm)
Al ₂ O ₃		67.3		5	5
CeO ₂		28.8		7	10
MgO		62.9		7	10
BaO	BaAl ₂ O ₄	24.2	24.2	20	50
	BaCO ₃		28.6		50
Ru		44.2		20	5 and 20 (in 1Ru/Al ₂ O ₃)
Ni		51.9		< 5	15
CaO		67.3		10	25
Al ₂₂ La ₂ O ₃₆ /AlLa ₃	La ₂ O ₂ CO ₃	25.4	30.6	10	60

Table 5.6. Crystal size determined by Scherrer equation and a diffraction peak of XRD pattern for the species present in the reduced and used in reaction catalysts.

5.3.2. Activity tests

The catalytic activity was measured by the CH₄ yield obtained for each temperature analysed in the CO₂ methanation. The activity study is carried out primarily for Ni-based catalysts as a promoter and support of alumina, modified with lanthanides (La and Ce) in 14 wt.% And alkaline earth metals (Ba, Ca and Mg) in 10 wt.%. Its study was done for temperatures between 573 and 773 K, for a quantity of catalyst of 200 mg, corresponding to a weight hourly space velocity (WHSV) of 38.3 h⁻¹. The results obtained for the methane yield are reported in **Fig. 5.11**.

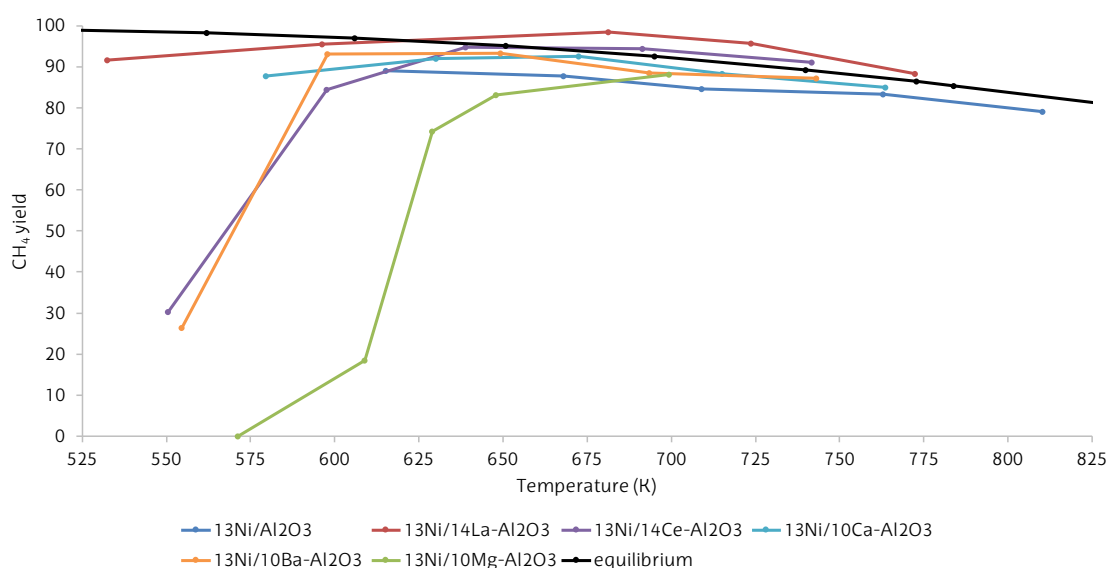


Fig. 5.11. Methane yield obtained for 200 mg for catalysts supported on alumina.

All the catalysts studied reach the maximum methane yield value established by the thermodynamic equilibrium in the temperature range, for a quantity of catalyst of 200 mg. In the case of the 13Ni/10Mg-Al₂O₃ catalyst, it needs a higher temperature to reach the equilibrium value, achieving at 700 K. This is followed by the 13Ni/14Ce-Al₂O₃ and 13Ni/10Ba-Al₂O₃ catalysts, which reach it at 639 K and 598 K, respectively. The rest of the catalysts start from the thermodynamic equilibrium value. To facilitate the comparison, the amount of catalyst is reduced to 125 mg to raise the WHSV value to 60.8 h⁻¹.

However, the resistance of the catalysts to H₂S poisoning is previously evaluated. For this, 50 ppm of H₂S are introduced with the reaction gases, determining the time necessary for the complete deactivation of the catalysts, representing them in Fig. 5.12.

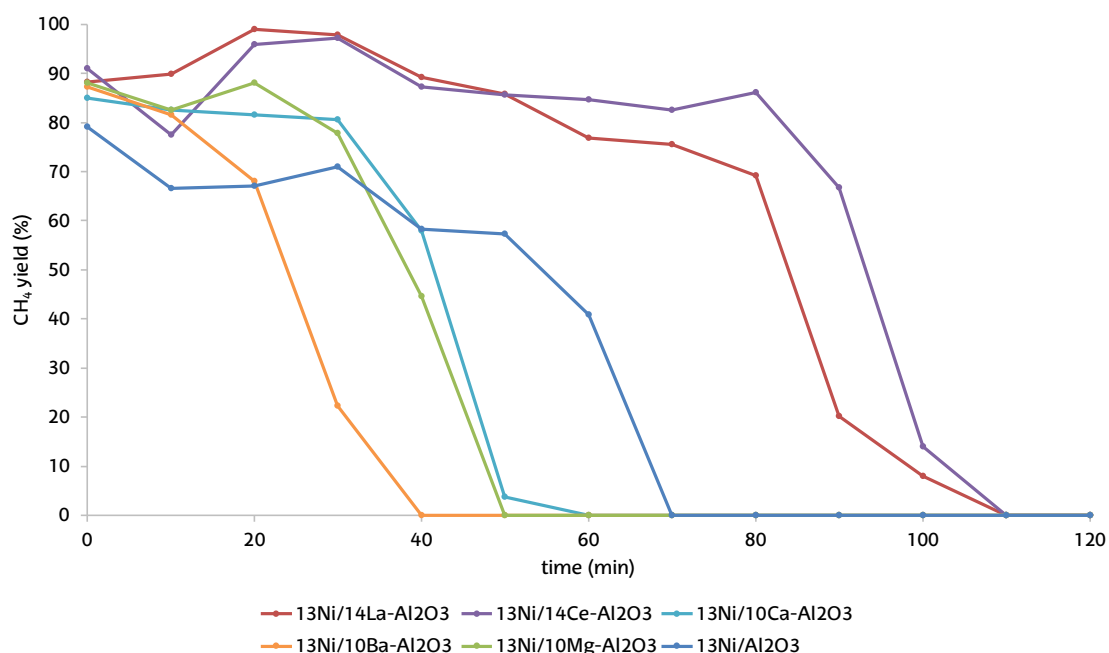


Fig. 5.12. Catalysts deactivation due to 50 ppm of H₂S at 773K.

The catalysts with the greatest resistance to deactivation are those modified with lanthanides (13Ni/14La-Al₂O₃ and 13Ni/14Ce-Al₂O₃), requiring up to 110 min for complete deactivation. On the contrary, those catalysts modified with alkaline earth are the first to deactivate, starting with 13Ni/10Ba-Al₂O₃ at 40 min, followed by 13Ni/10Mg-Al₂O₃ at 50 min and finally 13Ni/10Ca-Al₂O₃ at 60 min. In between is the 13Ni/Al₂O₃ catalyst, which improves the resistance to H₂S with respect to those modified with alkaline earth metals, but without reaching those modified with lanthanides, deactivating at 70 min.

The catalysts evaluated with a quantity of catalyst of 125 mg, were studied in a temperature range between 498 and 573 K, representing the results obtained in Fig. 5.13.

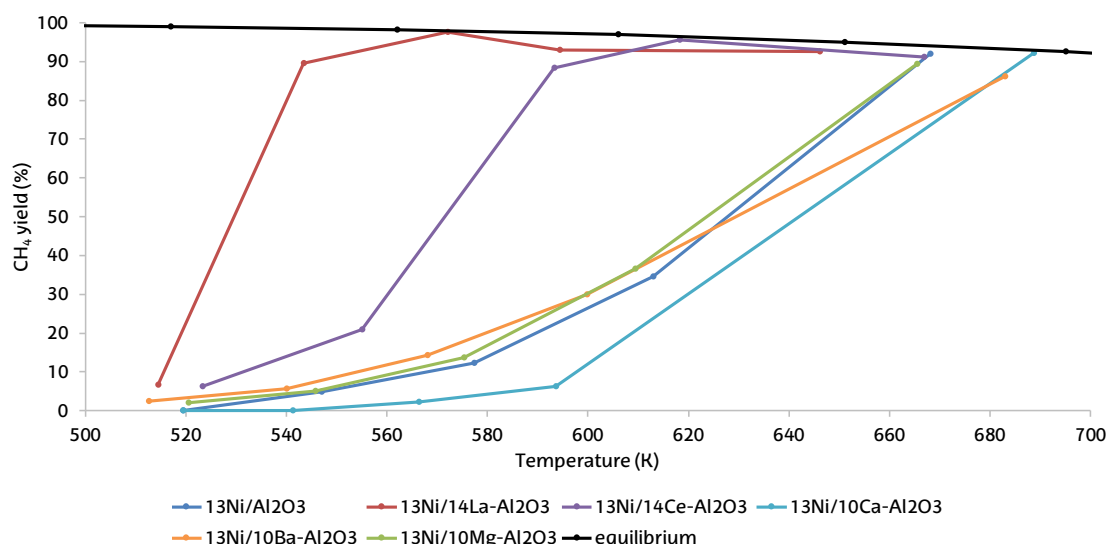


Fig. 5.13. Methane yield obtained for 125 mg of catalysts supported on alumina.

The reduction in the amount of catalyst (or increase in WHSV) increases the temperature necessary to achieve the maximum performance established by thermodynamic equilibrium. In the case of catalysts modified by alkaline earth metals (13Ni/10Ba-Al₂O₃, 13Ni/10Ca-Al₂O₃ and 13Ni/10Mg-Al₂O₃) and the monometallic catalyst (13Ni/Al₂O₃), the activity increases progressively until reaching the thermodynamic maximum at the highest temperature studied. 13Ni/Al₂O₃ and 13Ni/10Mg-Al₂O₃ catalysts reach a yield of 92 and 89% at 668 and 665 K respectively and 13Ni/10Ba-Al₂O₃ and 13Ni/10Ca-Al₂O₃ catalysts reach 86 and 90% at 683 and 688 K respectively. The catalysts modified with lanthanide metals reach the equilibrium temperature at lower temperatures. 13Ni/14Ce-Al₂O₃ reaches a methane yield of 96% at the temperature of 618 K. However, catalyst 13Ni/14La-Al₂O₃ at 543 K reaches a yield of 90%, reaching up to 98% at 572 K. Thus, it is shown that cerium but specially lanthanum addition enhances the activity to methane with respect to Ce or La-free and alkaline earth modified catalysts.

The high yields of catalyst 13Ni/14La-Al₂O₃ at low temperatures, would allow the methanation of a greater flow of reaction gases or, the use of a smaller amount of catalyst. Therefore, the feasibility of this hypothesis is compared in the case of catalyst 13Ni/Al₂O₃, for different amounts of catalyst. Fig. 5.14 compares the methane yield of catalyst 13Ni/Al₂O₃ for 200 mg of catalyst and 38.3 h⁻¹ of WHSV; 125 mg and 60.8 h⁻¹; and 60 mg and 128.75 h⁻¹.

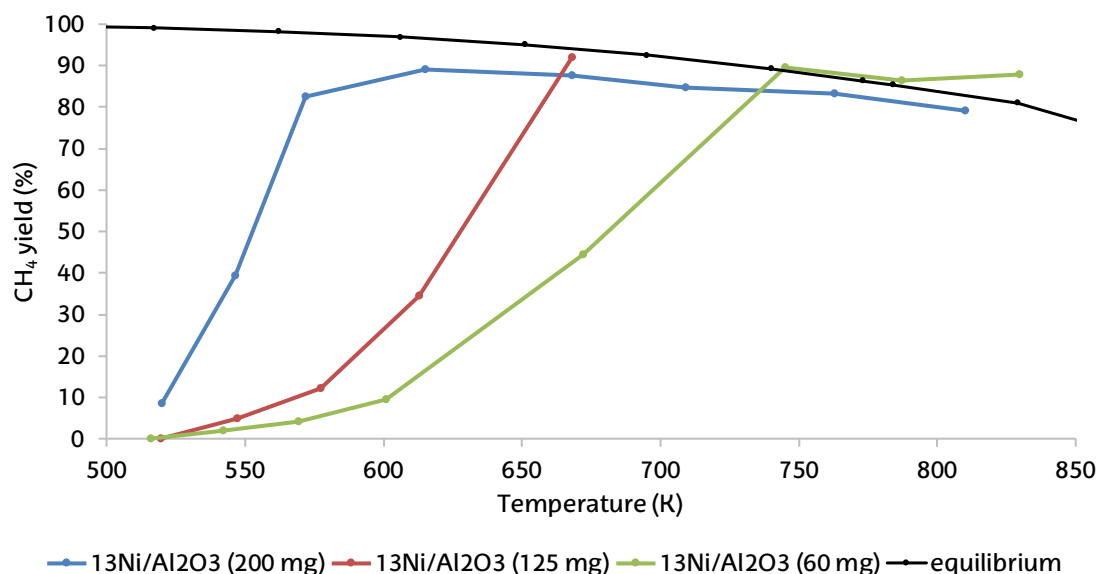


Fig. 5.14. Comparison of methane yield for different quantity of 13Ni/Alumina catalyst.

The decrease in the amount of catalyst used, produces an increase in the temperature at which the thermodynamic equilibrium is reached, as previously observed. With a load of 200 mg of catalyst in the reactor the equilibrium temperature is reached at a temperature of 572 K, while for 125 mg the temperature needs to be raised to 668 K. Finally, for an amount of 60 mg the equilibrium temperature is not reached until it reaches 745 K.

For an amount of 60 mg of catalyst (128.75 h⁻¹) and a temperature range between 598 and 773 K, the improvement in the activity in the methane reaction of catalysts based on Ru, Ni and La on alumina in the Fig. 5.15 is evaluated.

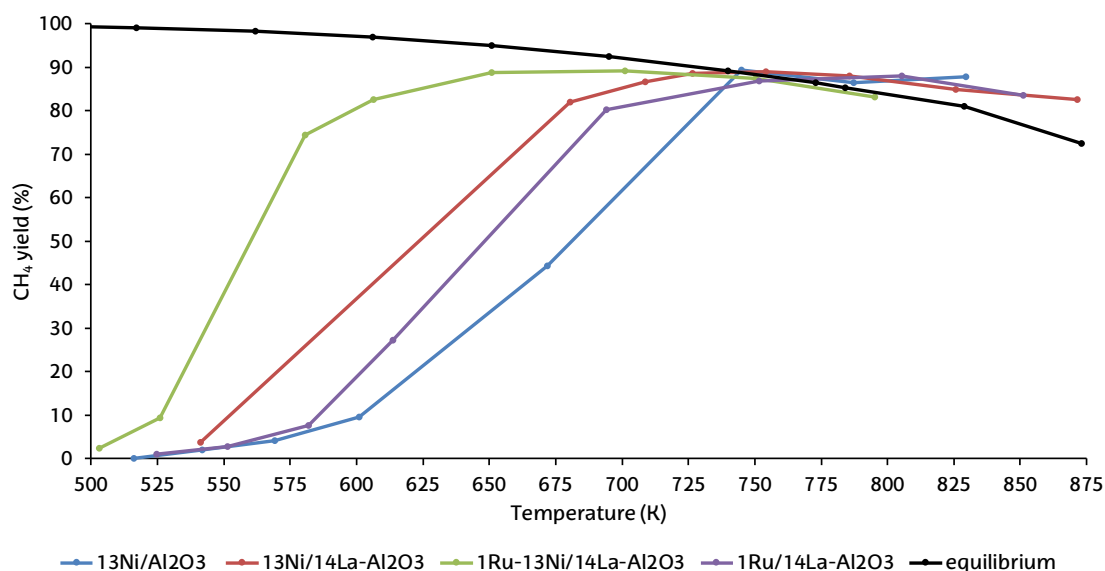


Fig. 5.15. Methane yield obtained for 60 mg of catalysts supported on alumina.

Catalyst 13Ni/Al₂O₃, as already seen in Fig. 5.14, achieves a maximum methane yield of 90% at 745 K. The addition of La reduces the value of the temperature necessary to reach a yield of 82% to 680 K (and 89% at 727 K). Substituting nickel for a noble metal, such as Ru, at a rate of 1 wt.% with La, it reaches 80% yield at 694 K. The difference between

the 1Ru/14La-Al₂O₃ and 13Ni/14La-Al₂O₃ catalysts is quite small, being the Ni-containing catalyst slightly better for the applied conditions. The incorporation of Ru into the 13Ni/14La-Al₂O₃ catalyst produces a strongly improvement in the methanation rate with respect to the other catalysts. At 581 K the methane yield reached by this catalyst is 74%, reaching a maximum value of 89% at 651 K.

Once the activity of the catalysts in the methanation reaction has been studied, as for catalysts modified with alkaline earth metals, the resistance of the catalysts to poisoning in the presence of 50 ppm of H₂S is determined. The results obtained for the deactivation of the catalysts are presented in Fig. 5.16.

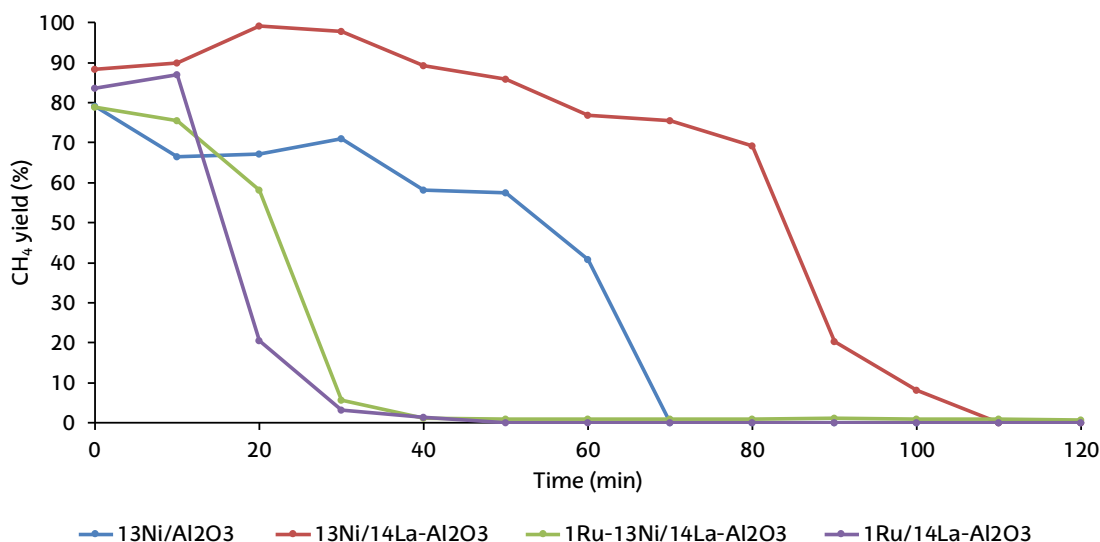


Fig. 5.16. Catalysts deactivation due to 50 ppm of H₂S at 773K.

The addition of 50 ppm of H₂S to the reaction gases more rapidly reduced the activity of catalysts with Ru as a promoter metal than those containing Ni as a promoter. Thus, 1Ru/14La-Al₂O₃ and 1Ru-13Ni/14La-Al₂O₃ are deactivated at 40 min. The addition of La to Ni, in addition to improving the methane activity of the catalysts, improves its resistance to H₂S poisoning, lengthening the deactivation from 70 min of catalyst 13Ni/Al₂O₃ to 110 min of catalyst 13Ni/14La-Al₂O₃.

After deactivation of the catalysts in the presence of H₂S, the methane yield of the catalysts was studied by eliminating H₂S from the feed at 773 K. In all the cases analysed, the catalysts did not recover the activity.

Finally, the catalysts were regenerated, employing a mixture of 3% O₂ and N₂, in order to eliminate the coke that blocks the catalytic action of the catalysts. Removed the coke of the catalyst surface, the catalysts were reactivated reducing with H₂. The recovered catalyst was used in a reaction stage, at 773 K. It was observed that the catalysts activity as methane yield was not recovered. During the reaction or deactivation stage, CO could have appeared as a by-product of the reverse water gas shift reaction. But it could also appear by the partial oxidation of the coke in the regeneration. In spite of everything, the presence of this gas has not been detected.

5.3.3. Discussion

The use of noble metals as a catalyst in the methanation reaction has been extensively studied in the literature, demonstrating high efficiency with greater thermal

stability, as observed in Garbarino's work [12]. Despite showing that the performance achieved for nickel-based catalysts is not as high as that obtained for ruthenium, the performance is high and with easier activation [9,12,42]. In order to complement the advantages of nickel and ruthenium as active metals in the methanation reaction, it was co-impregnated on the support. Thus, it was verified that the addition of ruthenium and nickel improved the performance of the catalyst, improving thermal stability and facilitating its activation, as determined in Liu's work [66].

The incorporation of alkaline earth metals and lanthanides that modified the support has been shown to reach higher activity, improving the interaction between support and metal [24,25]. The incorporation of alkaline earth metals has been experimentally found to improve the activity of the nickel catalyst, but less significantly than adding lanthanide metals. The alkaline earth metals due to their properties could increase the alkalinity of the catalyst, observing a reduction in the acid centres with low and medium strength and an increase in the basic centres with medium and high strength. This results in less interaction of nickel with alumina than observed for lanthanide-modified catalysts, which favours catalyst activity, due to the presence of more nickel on catalytic surface. Taking into account the results obtained for the catalysts incorporating alkaline earth metals, the general properties (particle size, dispersion or textural properties) analysed are similar to those of the monometallic catalyst, concluding with a similar activity. However, it is necessary to specify that according to what was observed in the reducibility study, the addition of barium facilitated the activation of the catalyst, contrary to what is observed for calcium and magnesium. These results agree with those obtained in Liang's work [24], in which little improvement was observed in the catalytic activity of the nickel catalyst in the presence of Ca or Mg. The methane yield determined for catalysts of Ni and Ni with 5% of Ca or Mg were around 50% in these cases at 623 K. However, the addition of Ba (from 1 to 7.5%) showed a reduction in the temperatures at which the catalyst is active for the methanation reaction, reaching a yield of 80% at 623 K, incorporating in that case 7.5% of Ba. The differences in performance obtained in our catalysts using 125 mg of catalyst instead of 500 mg are less significant, yielding methane being close to 50% in all of them.

A significant improvement in the activity of the nickel catalyst was produced by the addition of lanthanide metals, especially with La. Ce was incorporated as non-stoichiometric CeO₂, surface reducible metal centres of CeO₂ and bulk reducible metal centres of CeO₂ [44]. Ce⁴⁺ from CeO₂ interacted with Ni, as observed in the H₂-TPR analysis, improving its reducibility that facilitated its activation. There is a strong interaction with Ni, determined by XRD, which contributes to the strengthening of the interaction with the support and improved the dispersion of the metal on its surface, increasing the catalytic activity of the catalyst. Previous studies from our laboratory [18] have shown that the addition of cerium promotes the formation of active species, of nickel-aluminate spinel-like structure, which improves the yield of methane up to 75% at 647 K for the 13Ni/6Ce-Al₂O₃ catalyst, being necessary a temperature for the Ni catalyst of 723 K, to achieve the same performance.

The addition of lanthanum, like cerium, produced an improvement in the reducibility of the catalyst that facilitated nickel activation, increasing the amount of free NiO dispersed on the surface of the alumina [25,37,43]. This was caused due to a weakening of the interaction between NiO and the support by destroying partially metastable Ni-Al mixed oxide phase, caused by La incorporation [37,43]. On the other

hand, La interacted with the strongest acid and basic centres of alumina, taking place between $\text{La}^{3+}\text{-O}^{2-}$ pairs, as was observed by NH_3 -TPD, increasing the density of acid centres of higher strength [33]. La contribution was especially important in Ru and Ni catalysts, in which the number of acid centres increased more significantly. It implied a higher dispersion of the active metals on the surface of the support, as verified in the XRD results. In this analysis, La was dispersed, interacting with the support, forming species such as $\text{Al}_{22}\text{La}_2\text{O}_{36}$ and La_3Al , as was observed by XRD analysis. The Ni and/or Ru centres, facilitated by the structures made up of La and alumina, were dispersed over the surface. It helped to increase the activity of the catalyst in the methanation reaction, as it was deduced from the previous analyses and it was verified in the activity results. The increase in the yield to methane was observed from 34% for 13Ni/ Al_2O_3 to 65% for 13Ni/14La- Al_2O_3 at 650 K, just like in Garbarino's work [25], in which this important increase in activity is observed by the addition of lanthanum to the nickel catalyst, raising the yield from 72 to 90% to 625 K.

The most outstanding observation deduced from our work was the importance of the incorporation of Ru as a promoter, together with Ni, for the improvement of the activity of the catalyst in the reaction. An increase of 65% was observed for 13Ni/14La- Al_2O_3 up to 90% for 1Ru-13Ni/14La- Al_2O_3 at 650 K. The increase was due to the synergistic effect that occurs between Ru and Ni, due to the interaction that takes place between said metals as observed in H_2 -TPR and verified with the Liu's work [66]. Ru dispersed as RuO_2 and RuO_x across the surface of the support in contact with the NiO present, giving rise to Ru-Ni bimetallic particles. Ru decrease the reduction temperature of Ni, favouring its activation and facilitating its dispersion, which leads to increased activity as has been shown, contributing to this effect La.

Regarding the resistance of the catalyst to poisoning with H_2S , it was observed that the incorporation of alkaline earth metals exposes to a greater extent the active centres of the metal to the H_2S , facilitating its deactivation. The incorporation of lanthanide metals improved resistance to H_2S poisoning, due to the strong interaction between nickel and Ce or Ni and La, which makes it difficult to approach and block these centres, by reducing their affinity. Ni is more resistant to poisoning than Ru, which, in the presence of H_2S , was rapidly deactivated due to its greater affinity for this element (more electronegative) than for H_2 .

Once the catalyst was deactivated, the activity was not recovered, due to the morphological change that follows in the catalyst, in view of the analysed XPS and XRD results. An increase in the amount of oxygen and nickel at the catalyst surface was observed, along with a reduction for aluminium. This could involve the formation of an aluminate structure that covers the nickel, blocking the access of the reagents and their interaction, as the presence of sulphur in their content was not determined. Under these conditions, the catalyst could completely lose its activity, preventing its recovery.

5.4. Conclusions

The conclusions summarized below have been deduced from the development of this work.

- The addition of Ba, Ca or Mg in a proportion of 10% does not improve the activity of the nickel catalyst in a significant way, not appreciating important differences in the characterization.

- The addition of 14% of Ce improves the reducibility and dispersion of nickel, as suggested the characterization, by facilitating new anchor centres on the surface of the support, which improve its activity at lower temperatures.
- La (incorporated in a proportion of 14%) shows a strong interaction with alumina, which facilitates the incorporation of Ni. It was with greater dispersion and higher density of active centres, composed of easily reducible NiO species, which supposes an improvement in activity at lower temperatures.
- La-doped Ni/Al₂O₃ catalyst is competitive with Ru/Al₂O₃ catalyst. The incorporation of ruthenium as a promoter produces a strong interaction with nickel, increasing its catalytic activity reinforced by lanthanum, which increases dispersion and reducibility reaching a 90% methane yield at 650 K for a WHSV of 128.75h⁻¹.
- The strong interaction between La or Ce with Ni hinder the exposure and access of the H₂S to the active centres of the metal.
- The high temperatures (773 K) and the action of the H₂S produce the complete deactivation of the catalysts studied. A possible change in the morphology of the catalyst is determined, whereby the oxygenated structures of the support and the metals they incorporate, block access to the metal centres of the reagents.

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CAPÍTULO 6



Comparativa entre derivados de óxido de grafeno y alumina como soporte de catalizadores de Ni y modificados por lantano.

"Ninguna cantidad de experimentación puede probar definitivamente que tengo razón; pero un solo experimento puede probar que estoy equivocado."

ALBERT EINSTEIN

Extraído del artículo: *Graphene-based versus alumina supports on the CO₂ methanation using lanthanum promoted nickel catalysts.*

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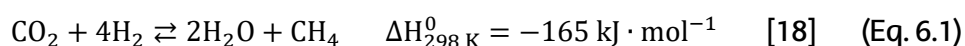
Abstract

The valorisation of CO₂ as a biofuel, transforming it through the methanation as part of the Power-to-gas (PtG) process, will allow the reduction of the net emissions of this gas to the atmosphere. Catalysts with 13 wt.% of nickel (Ni) loading incorporated into alumina and graphene derivatives were used and the effect of the support on the activity was examined at temperatures between 498 and 773 K and 10 bar of pressure. Among the graphene-based catalysts (13Ni/AGO, 13Ni/BGO, 13Ni/rGO, 13Ni-OI/GO, 13Ni/OI-GO and 13Ni/OI-GO Met), the highest methane yield was found for 13Ni/rGO (78% at 810K), being the only system comparable with the catalyst supported on alumina 13Ni/Al₂O₃ (89.5% at 745 K).

The incorporation of 14 wt.% of lanthanum (La) into the most promising supports, rGO and alumina, led to nickel-support interactions that enhanced the catalytic activity of 13Ni/Al₂O₃ (89.5% at lower temperature, 727 K) but was not effective for 13Ni/rGO. The resistance against deactivation by H₂S poisoning was also studied for these catalysts, and a fast deactivation was observed (in the presence of this compound). In addition, activity recovery was impossible despite the regeneration treatment carried out over catalysts.

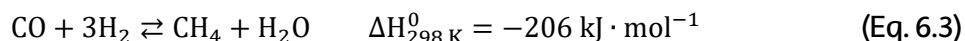
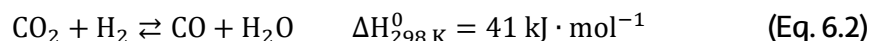
6.1. Introduction

The amount of carbon dioxide in the atmosphere is increasing due to anthropogenic causes, reaching values of 407.4 ppm in 2018 [1] and consequently, increasing the average global temperature. One of the main causes of these high values is the combustion of fossil fuels, being responsible for three quarters of the total CO₂ emissions [2]. Therefore, nowadays the main objective is focused on reducing the amount of CO₂ present in the atmosphere. Some of the strategies that are currently proposed are based on carbon capture to obtain bio energy (BECCS) [3], or through the capture by adsorption of CO₂ in microporous systems and its transformation for the utilization (CCU) [4], [5]. Among the applications of captured CO₂, the obtention of fuel stands out, in order to meet the energy demand without producing more CO₂ as in the case of methanol (MeOH) [6], [7], dimethyl carbonate (DMC) [8], [9], dimethyl ether (DME) [10]–[12], solid carbonate [13] and methane [14], [15]. In this sense, the catalytic hydrogenation of CO₂ constitutes an interesting way to produce methane from CO₂. This path requires hydrogen, which is already an efficient fuel, but with more disadvantages in terms of storage and transport than methane, due to its lower energy density [16]. Hydrogen production is one of the challenges in the recovery of CO₂ from the atmosphere, and the most sustainable method to get it is the electrolysis of water using electricity from wind or solar energy. Power-to-gas (PtG) is a technology that transforms surplus electrical power from renewable energy sources into methane as a gas fuel that can be stored or distributed through the natural gas network [17]. PtG process encompasses two principal stages: the electrolysis of water to obtain H₂ and the use of this H₂ in methanation of CO₂ captured from the atmosphere or industrial gaseous effluents to obtain CH₄. The hydrogenation of CO₂, which was studied by Sabatier is an exothermic reaction, as shown equation 1 (Eq 6.1).



This reaction is the combination of the Reverse Water Gas Shift (RWGS) (Eq. 6.2) and the CO methanation (Eq. 6.3). Due to the exothermicity of the reaction and according to the thermodynamic laws, as the temperature and pressure increase, the yield of the

reaction decreases [17]. That is exactly why the choice of a suitable catalyst and support has gained great importance, to achieve a proper dispersion of active centres and avoid hot spots.



According to the literature, not only noble metals as ruthenium (Ru), rhodium (Rh) and palladium (Pd) have been found effective in CO₂ methanation, but also transition metals, as nickel (Ni), were also successfully employed [14], [15], [19]–[21]. Nickel-based catalysts are commonly reported due to their low price, availability and competitive activity, proposing them as an attractive alternative to noble metals [14], [15], [19]–[23]. Transition and noble metals are mainly supported over metal oxides such as Al₂O₃, SiO₂, TiO₂, CeO₂, Y₂O₃ and zeolites and even, in recent works, reduced graphene oxide (rGO) [14], [15], [19]–[30]. Among the cited supports, γ -alumina is the most typical support because of its high surface area leads to a better dispersion of the active metal on the surface [20]–[23], [25], [26], [28], [29]. Recent research has shown that modification of the γ -alumina support in nickel based catalysts for the methane reaction enhances the activity, especially at low temperatures [20], [31], [32]. In the case of modifying alumina support with different amounts of lanthanum (0, 4, 14 and 37 wt.%), it was concluded that the methane yield increases at low temperatures, up to a lanthanum loading of 14 wt.% [32].

Graphene has proven to be an interesting material for medical applications [33], [34], sensors (chemical, biological, gas or electrochemical among others) [35]–[42], electrocatalytic applications [43], [44], photovoltaic applications [45]–[47], energy storage applications [48], [49], or reinforcement of materials [50], [51], derived from its physicochemical characteristics. Recently, these promising properties of graphene have been applied to support catalysis of different reactions. [52]– [56]. Hybridization of the orbitals of the carbon atom for the formation of sp² bonds, results in the formation of 3 σ bonds and one delocalized π bond, drawing a double bond. In this way, the angle obtained between the bonds is 120° that gives the graphene structure the shape of honeycomb or hexagonal (shape). Caused by this peculiar two-dimensional structure, with delocalized π bonds, a conduction band and a valence band are generated which are in turn responsible for most of the conduction properties of the graphene. [57]. The ability to dissipate the heat originated from the exothermic methane reaction, added to the large surface area and mechanical strength of graphene, makes it a support of great interest for this application. Furthermore, graphene oxide (GO), obtained by exfoliation and oxidation of carbon. Although it involves a reduction in surface area and the thermal, electrical and mechanical properties of graphene, the production cost is significantly lower. Because it contains less hydroxyl, epoxy and carboxyl side groups, its centres are able to act as anchoring or nucleation centres, which could improve the dispersion of the metallic nanoparticles. In addition, the cost effectiveness and easy scale-up potential of GO, make it a promising support [57]. Reduced graphene oxide (rGO) is another product derived from graphene oxide, obtained by thermal, chemical or electrochemical reduction of graphene oxide. Like GO, rGO can be scale-up and manufactured on kilogram scale [58]. In the reduction phase to obtain rGO, despite the fact that a large part of the oxygen contained in its structure is eliminated, some functional groups of oxygen are maintained, so the interaction between the nanoparticles and the structure of the support is still favoured, which could increase its dispersion and stability [14]. Another graphene

derivative that can improve GO characteristics was obtained by the incorporation of an aminated group into the structure of graphene oxide. Aminated group reacts with oxygen atoms present in the graphene base layer, causing its replacement. The effect of this addition depends on the characteristics of the chain and the linked amino group. In the case of long chain compounds, such as oleylamine, it could give hydrophobic character to the resulting aminated graphene oxide [59]. Metals have been also incorporated into rGO supports in other works, with improved yields in different reactions, as described in several works [14], [60]–[64].

In the present work, the effect of graphene-based materials (provided by Graphenea), with 13wt.% of nickel, on CO₂ methanation was studied and compared with catalysts based on alumina. Among graphene materials: on one hand, commercial reduced graphene oxide (13Ni/rGO) and graphene oxide reduced with methylamine borane (MeAB) (13Ni/BGO) were analysed. On the other hand, commercial aminated graphene oxide (13Ni/AGO) and oleylamine aminated graphene oxide by three different procedures (13Ni-OI/GO, 13Ni/OI-GO and 13Ni/OI.GO (Met)) were the other graphene derivatives analysed. Finally, the best of these catalysts, which turned out to be 13Ni/rGO, was modified with 14 wt.% of lanthanum (13Ni/14La-rGO). Then, it was compared with catalysts supported on alumina (13Ni/Al₂O₃ and 13Ni/14La-Al₂O₃), to determine the most efficient system for the hydrogenation of CO₂.

6.2. Experimental details

6.2.1. Catalyst preparation

The catalyst 13Ni/AGO was prepared by wet impregnation method, mixing 2 g of aminated graphene oxide (AGO) (provided by Graphenea) with 1.48 g of nickel (II) nitrate hexahydrate (99.999%; Sigma-Aldrich) and 500 ml of ethanol (100%; Sigma-Aldrich). In order to incorporate the nickel into the AGO pore structure, the solution was sonicated for 2 h. Then, the solvent was removed on a rotary evaporator (Heidolph Laborota 4000) at 323 K under vacuum. The catalyst was dried in an oven for 2 h at 393 K. Finally, in a thermogravimetric analyzer (TGA/SDTA851 Mettler Toledo) under N₂-atmosphere and employing the temperature program of the *Table 6.1*, obtaining the calcined catalyst 13Ni/AGO.

Steps	T ^a range	T ^a ramp	Hold time
Humidity	273 – 378 K	1 K/min	1 h
Heating 1	378 – 453 K	1 K/min	1 h
Heating 2	453 – 493 K	1 K/min	
Heating 3	493 – 673 K	1 K/min	1h

Table 6.1. TGA program RGO.

The reduction of graphene oxide with methylamine borane (MeAB) to obtain 13Ni/BGO was carried out in two stages [65]. The first step consisted in the preparation of methylamine borane. To obtain it, 11.35 g of sodium borohydride (>98.0%; Sigma-Aldrich) and 20.26 g of methylamine hydrochloride (>98.0%; Aldrich) were dissolved with 600 ml of tetrahydrofuran (THF) (>99.9%; Honeywell) in a round bottom flask connected to a condenser and vigorously stirred. The reaction was carried out under N₂ atmosphere at room temperature for 12 h. The solution was then filtered in a Büchner funnel by vacuum filtration and the filtrate was concentrated under vacuum at room temperature in a rotary evaporator. The product was purified with methanol (>99.9%; Sigma-Aldrich). The second stage comprised the synthesis of 13Ni/BGO. 3 g of GO (100%; Graphenea) were dissolved

in 580 ml of MilliQ-water in a round bottom flask. After 2.22 g of nickel (II) nitrate hexahydrate (99.999%; Sigma-Aldrich) were added, the solution was sonicated for 2 h. Subsequently, 400 ml of water containing 27 g of MeAB were added to the solution under vigorous stirring. The obtained mixture was stirred overnight in a rotary evaporator before being concentrated at 313 K under vacuum. The collected concentrate was dried in an oven at 393 K for 2 h and was calcined in the TGA under N₂ atmosphere, following the program given in *Table 6.1*, obtaining the catalyst 13Ni/BGO.

Oleylamine aminated-catalysts were prepared by three different procedures to obtain three different catalysts, depending on when the nickel salt is added and if a purification step is included to remove the oleylamine excess [59]. The first one consisted of the mixture of GO (Graphenea) and oleylamine (70%;Sigma-Aldrich) in the same proportion (3 g), dissolved in 500 ml of ethanol with stirring for 30 minutes. The solution was sonicated for 2 h and the solvent was evaporated in a rotary evaporator at 323 K and vacuum. Once the sample was dried in an oven at 393 K for 2 h, the cooled solid was mixed with the appropriate amount of nickel salt and was dissolved in 500 ml of ethanol, repeating the previous procedure to obtain the 13Ni/OI-GO. The second oleylamine aminated-catalyst was prepared following the same procedure but introducing a methanol purification step of the sample once it was dried and cooled, before introducing nickel, and this catalyst was named 13Ni/OI-GO(Met). For the synthesis of the third type of these catalysts, 13Ni-OI/GO, the nickel salt was initially mixed with the oleylamine and ethanol, before proceeding as in the previous cases.

The catalysts supported on rGO, were also prepared also by wet impregnation method in two successive steps, mixing 2 g of rGO with 0.90 g of lanthanum salt (lanthanum (III) nitrate hydrate, 99.9%; Sigma-Aldrich), and 500 ml of ethanol. With the aim of incorporating lanthanum into the rGO pore structure, the solution was sonicated for 2 h. Then, the solvent was removed in a rotary evaporator at 323 K under vacuum. The modified support was dried in an oven for 2 hours at 393 K and finally calcined in a thermal gravimetric analysis (TGA) employing the temperature program of the *Table 6.1*. To incorporate the nickel on the rGO and La-rGO support, the procedure was similar to that followed for lanthanum. 1.76 g of nickel salt was added to the prepared support and was mixed with 500 ml of ethanol and sonicated. After evaporation of the solvent in the rotary evaporator (under vacuum at 323 K), it was dried in the oven for 2 h at 393 K, and was calcined with the temperature program of *Table 6.1* in TGA, obtaining the final catalysts 13Ni/14La-rGO and 13Ni/rGO.

The catalysts supported on alumina, were prepared by wet impregnation in two successive steps. 5 g of γ -Al₂O₃ (Merck) and 2.25 g of lanthanum salt (lanthanum (III) nitrate hydrate, 99.9%; Sigma-Aldrich) were mixed to obtain the 14 wt.% of La. After that, 20 ml of distilled water were added to the previous mixture and the pH value of the solution was adjusted to 8.5 [66], [67]. The solution was stirred overnight in a rotary evaporator and the solvent was eliminated, heating at 338 K under vacuum. The support obtained was dried in an oven at 373 K during 2 h and calcined at 673 K in air atmosphere for 2 h with a ramp of 1 K/min. Finally, nickel was incorporated into the bare alumina and lanthanum-modified support by wetness impregnation, thus obtaining 13Ni/Al₂O₃ and 13Ni/14La-Al₂O₃ catalysts.

Eventually, the calcined catalysts were pressed and sieved to the desired particle size range (0.42 mm < d_p < 0.50 mm). This particle size (d_p) was chosen in order to avoid

reagents bypassing near the wall, according to keep an internal pipe diameter-to-particle size ratio higher than 10 [68].

As it has been mentioned, and as a summary, the catalysts prepared were named, according to their nominal composition, as follows: 13Ni/AGO, 13Ni/BGO, 13Ni/OI-GO, 13Ni/OI-GO(Met), 13Ni-OI/GO, 13Ni/rGO and 13Ni/14La-rGO, 13Ni/Al₂O₃ and 13Ni/14La-Al₂O₃.

6.2.2. Catalyst characterisation

The N₂ adsorption method was employed to evaluate textural properties of the catalysts in the Autosorb 1C-TCD, after degassing the samples at 573 K for 3 h. The specific surface area was calculated using Brunauer-Emmett-Teller (BET) equation and pore volume and pore sizes were calculated by Barrett-Joyner-Halenda (BJH) method.

The Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyser in a Perkin-Elmer Optima 3300DV was employed to determine the composition of the catalysts. Prior to the analysis, the catalyst was disaggregated in an acid solution (75% HCl and 25% HNO₃, in volume). After that, disaggregating the catalyst in acid solution (mixture of HCl 3:1 and HNO₃ respectively), the composition and chemical elements were identified by their characteristic wavelength emission bands.

The elemental concentrations of carbon, hydrogen and nitrogen present in the catalysts were determined in a LECO Truspec CHN by heating up 30 to 100 mg of the catalysts up to 1223 K for 300 s under O₂ flow.

The structural properties of the catalysts were investigated by X-Ray Diffraction (XRD) and measurements were performed using a PANalytical X'Pert Pro diffractometer with a CuK α radiation ($\lambda=0.15418$ nm) operating at 40 kV and 30 mA. The collected XRD patterns were matched using the JCPDS database and crystalline phases were identified. Moreover, the average crystallite size was estimated by Scherrer equation [69]).

The reducibility of the catalysts was examined by Temperature Programmed Reduction with hydrogen (H₂-TPR) in a Micromeritics AutoChem II Instrument equipped with a thermal conductivity/TCD detector. The TPR profiles were recorded heating 10 mg of the sample from 323 K to 773 K for rGO supported catalysts and 50 mg from 323 to 973 K for alumina supported catalysts, at a ramp rate of 10 K/min. Prior to the analysis, the sample was pretreated in Ar stream (30 Nml/min) from room temperature to 473 K for 1 h. Later, the sample was cooled down to 323 K and the Ar was replaced by 5 vol%, H₂/Ar (45 Nml/min) stream to start the reduction.

X-ray Photoelectron Spectroscopy (XPS) was performed on a SPECS (Berlin, Germany) system equipped with a Phoibos 150 1D-DLD analyser and an Al K α (1486.6 eV) monochromatic radiation source with electrons output angle of 90°. XPS measurements allowed the study of the species present on the surface of the catalyst.

High resolution Scanning and Transmission Electron Microscopy (HR-STEM or only STEM) was employed to analyse the morphology of the catalysts. The measurements were carried out in a Schottky X-FEG (FEI Titan Cubed G2 60-300) transmission and scanning-transmission electron microscopy with resolution ≤ 0.136 nm at 300 kV and resolution in energy ≤ 0.3 eV. Additionally, the instrument was equipped with EDX Super-X for chemical analysis.

6.2.3. Activity test

The CO₂ hydrogenation activity was tested by measuring methane yield in a stainless steel fixed-bed reactor of 32 cm of length, with an outside diameter of 1/4" within a bench-scale plant (PID Eng&Tech) at 10 bar and a temperature range of 498-773 K.

Typically, the reactor was loaded with 200 to 60 mg of catalyst diluted with inert SiC in order to minimize possible thermal gradients in the catalytic bed (weight_{catalyst}/weight_{SiC}=1:4.5). Furnace temperature was adjusted to maintain the catalytic bed under isothermal condition using four thermocouples as showed in Fig. 6.1. The reactor was heated with a rate of 10 K/min under N₂ flow until the reaction temperature. The catalytic activity was studied with a temperature interval of 25 K from 498 K to 573K and with an interval of 50K from 573K to 773K. The first step was the catalyst activation, reducing the catalyst with a ratio of N₂ (99.999%, Air Liquide) to H₂ (99.999%, Air Liquide) equal to 3:1 (65 Nml/min of H₂) at 673 K during 4 h. Once the catalyst was activated, H₂ and CO₂ (99.98%, Air Liquide), the methanation reaction gasses, were fed in a volume ratio H₂/CO₂ of 4:1. In such way the reaction (eq. 1) was performed at a Weight Hourly Space Velocity (WHSV) of 128.75 g_{feed}/(g_{cat}·h)

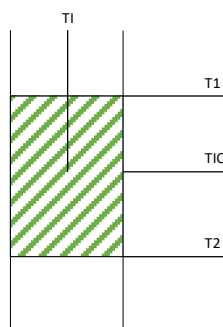


Fig. 6.1. Position diagram of thermocouples in the system. Control thermocouple (TIC), bed thermocouple (TI) and test thermocouples (T1 and T2).

The reaction was stabilized at each temperature for 120 min, analysing the products separated in a Peltier condenser. On one hand, after each reaction temperature, condensed water was collected and weighted. On the other hand, the gas stream was analysed in an on-line MicroGC Varian CP-4900 equipped with a high sensitivity TCD and two columns (10 m Molecular Sieve 5, 10 m Poraplot Q) and, in a complementary way, the flow was also measured in a mass flowmeter. The parameter used to evaluate the catalytic activity was the yield of methane, using the following equation:

$$\text{CH}_4 \text{ yield: } \eta_{\text{CH}_4} = \text{mol CH}_4^{\text{out}} / \text{mol CH}_4^{\text{out stoichiometric}} \cdot 100 \quad (\text{Eq. 6.4})$$

In the Eq. 6.4, η_{CH_4} symbolise the methane yield; $\text{mol CH}_4^{\text{out}}$ symbolise the flow rate of the methane out of the reactor; $\text{mol CH}_4^{\text{out stoichiometric}}$ symbolise the theoretical flow rate of the methane out of the reactor, based on the stoichiometry of reaction. Thus, if all CO₂ fed were converted to CH₄, the value of η_{CH_4} would be 100%.

6.3. Results and discussion

6.3.1. Catalyst characterisation

6.3.1.1. Chemical composition

The metallic content (nickel and lanthanum) of the catalysts was determined by ICP-OES and the corresponding data, with the nominal values, are collected in *Table 6.2*.

Catalyst	Content by ICP		$S_{\text{BET}}^{\text{a}}$ (m^2/g)	V_{p}^{b} (cm^3/g)	d_{p}^{c} (nm)	$d_{\text{XRD}}^{\text{d1}}$ (nm)	$d_{\text{XRD}}^{\text{d2}}$ (nm)
	Ni	La					
13Ni/AGO	18.5	0					
13Ni/BGO	1.3	0					
13Ni-OI/GO	27.4	0					
13Ni/OI-GO	52.9	0					
13Ni/OI-GO (Met)	38.8	0					
rGO	0	0	619	1.96	3.8	-	-
13Ni/rGO	12.93	0	452	1.30	3.8	8	6
13Ni/14La-rGO	15.59	11.41	258	0.70	3.8	80*	7
$\gamma\text{Al}_2\text{O}_3$	0	0	202	0.81	7.7	-	-
13Ni/ Al_2O_3	13.9	0	180	0.55	7.2	5	10
13Ni/14La- Al_2O_3	15.41	11.59	92	0.14	3.6	5	15

Table 6.2. Summary of the contents of Ni and La, specific area, particle size of Ni and turnover frequency.

^aThe surface area was calculated by the BET equation;

^bBJH desorption pore volume;

^cBJH desorption average pore diameter;

^d $D_{\text{XRD}}^{\text{d1}}$ (after reduction) and $D_{\text{XRD}}^{\text{d2}}$ (after reaction) are an approximation calculated from Ni (111) plane using Scherrer equation.

Catalysts containing amine groups shown higher content of nickel, because the decomposition of amine group, lead to a reduction of the support mass and consequently, the contribution of the nickel loading increased. It should be noted that, in the 13Ni/BGO catalyst, the reducing agent was incorporated into the catalyst instead of being removed in the cleaning stages, and this contribution was not considered for the composition calculations. That's why in this case the amount of incorporated nickel/metal was so low, 1.5wt.% instead of 13wt.%. This fact implies that it will be necessary to use a larger amount of catalyst to keep comparable operation conditions, namely, active metal loading and WHSV.

As regarding catalysts supported on alumina and rGO, the theoretical Ni content, as active metal, was set at 13 wt.%, and for lanthanum modified supported catalysts a content of 14 wt.% La was desired. The catalyst 13Ni/ Al_2O_3 showed an experimental nickel loading slightly higher compared to the nominal value, which is in agreement with García-García I. *et al* [20] results over Ni catalyst supported on $\gamma\text{-Al}_2\text{O}_3$. However, the experimental content of nickel was higher than the target composition in the presence of lanthanum, probably due to some losses in support weight, associated to the reduction of its oxygen content. The nickel content analysed in the catalyst supported in rGO shows a value close to the nominal value.

6.3.1.2. BET measurements

The physical properties of the supports and the nickel catalysts were examined by nitrogen adsorption-desorption isotherms. All the samples exhibited IV-type isotherms (not shown) with a remarkable H2-type hysteresis loop, thus displaying a typical curve associated with the presence of mesoporous structure due to the presence of “ink-bottle” or cylindrical channels [70]. *Table 6.2* summarizes the specific surface area (S_{BET}), pore volume (V_{P}) and average pore size (d_{P}) of the catalysts, as well as the information corresponding bare alumina and rGO support materials

As regarding bare supports, rGO had a markedly larger surface area ($619 \text{ m}^2/\text{g}$) than alumina ($202 \text{ m}^2/\text{g}$), which could later lead to a better Ni dispersion [14]. With the addition of nickel, both supports underwent a significant loss of surface area and pore volume (from 619 to $452 \text{ m}^2/\text{g}$ and 1.96 to $1.30 \text{ cm}^3/\text{g}$ for rGO and from 202 to $180 \text{ m}^2/\text{g}$ and 0.81 to $0.55 \text{ cm}^3/\text{g}$ for alumina respectively), owing to the partial blockage of their small pores [71]. The incorporation of a support modifier, namely lanthanum, contributed negatively to the blocking effect of the pores. As a consequences, La-modified catalysts ($13\text{Ni}/14\text{La-rGO}$ and $13\text{Ni}/14\text{La-Al}_2\text{O}_3$) suffered not only a considerable reduction of the total surface area and pore volume, but also a decrease in the pore size in the case of alumina supported catalyst [32]

6.3.1.3. X-ray diffraction

Fig. 6.2 and *Fig. 6.3* show the XRD patterns of the fresh and used rGO and alumina supported catalysts studied respectively, being possible the identification of the main crystalline species. *Fig. 6.2* shows the crystalline species in a reduced state, prior to the use of the catalysts in reaction. The $\gamma\text{-Al}_2\text{O}_3$ support exhibits diffraction peaks at 37.5° , 44.5° and 67.4° mainly, corresponding to the alumina crystal plane of (331), (400) and (440) respectively [72], [73]. Peaks at 19.7° (111), 34° (220), 57° (422), 61° (511) and 85° (444) can also be used for the identification of the alumina, although they were more difficult to detect specially in the presence of metals [72], [73]. The diffraction peaks of the support observed in the XRD pattern after using the catalysts in the methanation reaction, do not show significant variations (*Fig. 6.3*).

The active metal, nickel, was found in its metallic form in both the reduced fresh and used catalysts. Nickel oxide was not detected in the reduced catalysts, nor in the used ones. However, in the presence of lanthanum modifying the support of rGO, nickel was associated with sulphur present in the graphene composition, forming a complex identified as Heazlewoodite. Ni peaks were observed at 44.5° (111), 51.6° (200) and 76.7° (220) [14]. The coincidence of some of the peaks of the XRD pattern of the alumina and the nickel produces their overlapping as occurs in the $13\text{Ni}/\text{Alumina}$ catalyst. These peaks show a widening, which make difficult to identify the crystalline phases to which they correspond.

The lanthanum detected in the XRD pattern was associated with the support, in the form of $\text{La}_2(\text{CO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, LaCO_3OH in the rGO used catalysts; and $\text{La}_2\text{O}_2\text{CO}_3$ in the alumina support in used catalyst. No diffraction peaks of La_2O_3 were detected in their XRD pattern, thereby suggesting that either the structure was amorphous or La_2O_3 was highly dispersed on the support [74]. After the reaction step, the La_2O_3 dispersed into the $13\text{Ni}/14\text{La-Al}_2\text{O}_3$ catalyst was transformed into the $\text{La}_2\text{O}_2\text{CO}_3$ species. In the rest of the

catalysts no compound of La were identified, moreover than the lanthanum carbonates aforementioned. This was probably due to the breakdown of the binding link between La and support, while the rest of the metal as La_2O_3 form remains dispersed in the rGO support, in smaller amounts.

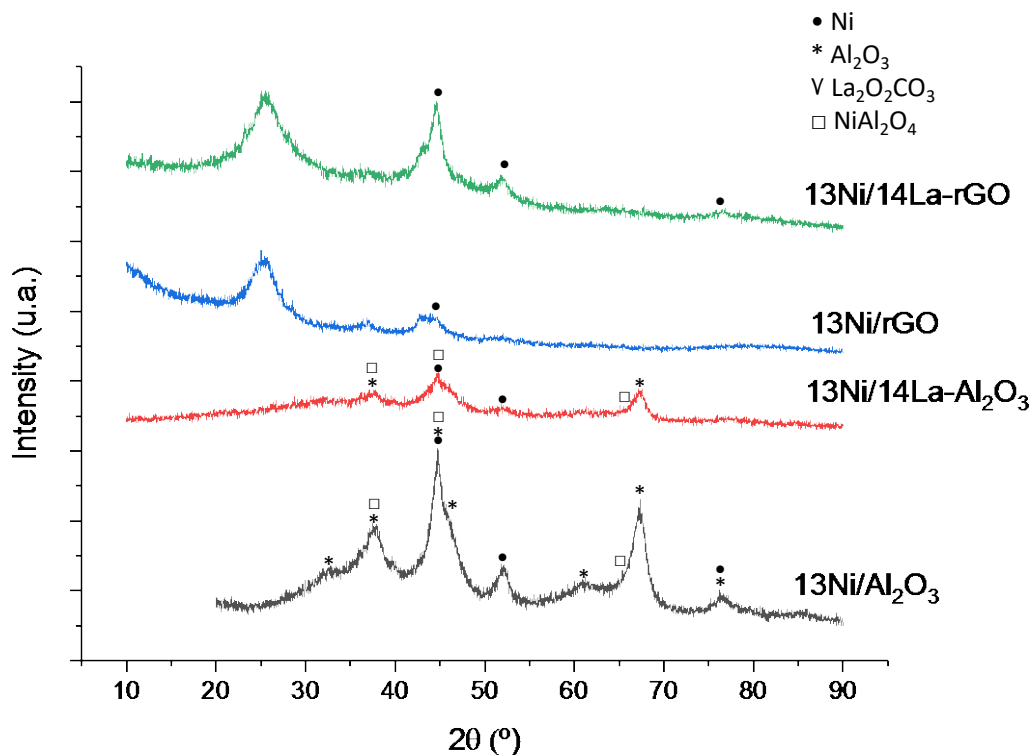


Fig. 6.2. XRD patterns of bi- and monometallic fresh-reduced catalysts supported over Al_2O_3 and rGO.

The addition of La to the $\text{Ni}/\text{Al}_2\text{O}_3$ fresh-reduced catalyst produced the attenuation of the Ni reflection peaks, because of the interaction between La-Ni-alumina that increased the dispersion of the metal in the support [14], [31], [32]. A similar effect was observed when comparing Ni_3S_2 and Ni, by adding La to the catalyst 13Ni/rGO, due to the strong interaction between Ni and La.

The XRD patterns of the catalysts supported in rGO showed several peaks that were not associated with the incorporated metals. These peaks represent the support, in the form of carbon (C) and a compound formed by carbon and silicon: silicon carbide or moissanite (SiC). The pattern observed after the reaction stage resembles that obtained for the rGO (Fig. 6.4) without the addition of metals to its composition. The peaks associated with CS_2 that were observed for used catalysts, like carbonated lanthanum compounds, were not identified in the fresh catalysts, due to their formation during the reaction step. These components appeared by the deposition of carbon and sulphur on the metal centres and the support, during the reaction stage. Its presence might be the

cause of the loss of activity of the catalyst and poisoning, which hinders the recovery of activity.

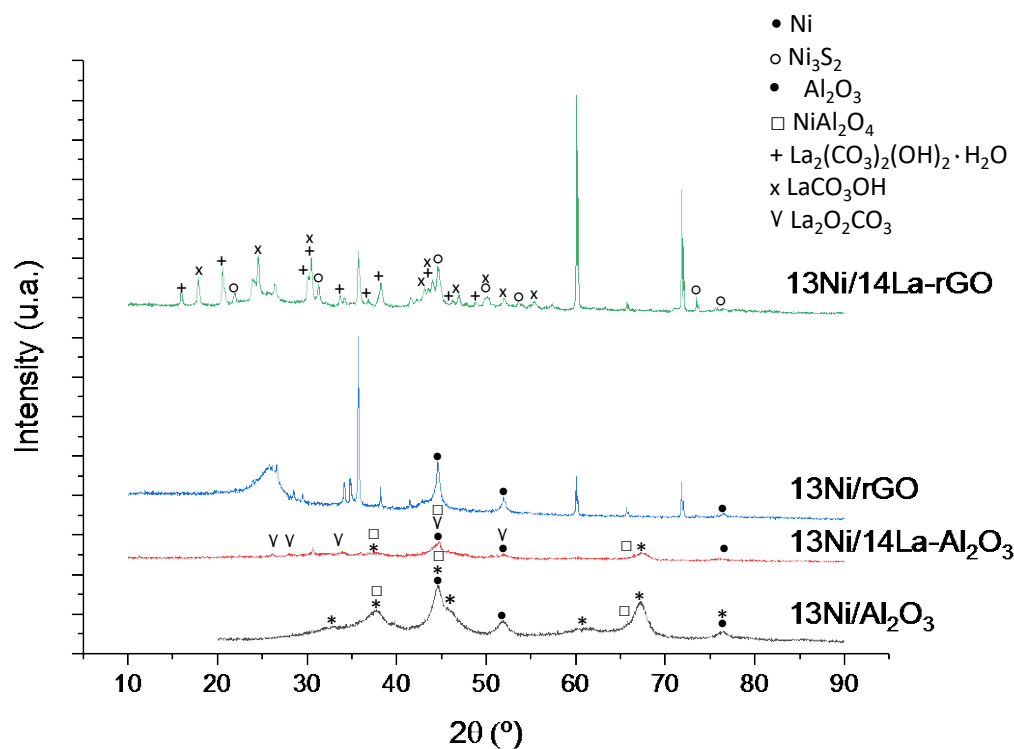


Fig. 6.3. XRD patterns of bi- and monometallic used catalysts supported over Al_2O_3 and rGO.

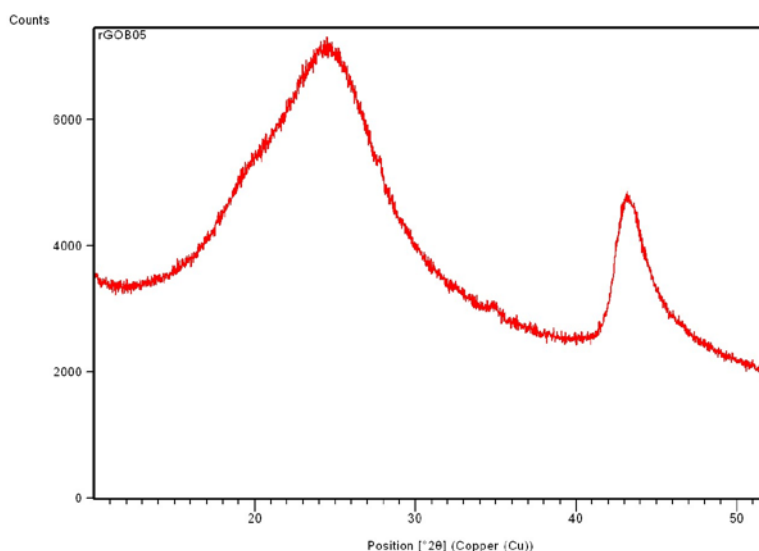


Fig. 6.4. XRD pattern of the reduced graphene oxide support.

The 2θ position of the diffraction peaks of the XRD patterns was determined by x-ray diffraction. The peaks were identified with the help of database: Joint Committee on Powder Diffraction Standards (JCPDS) for the fresh (Fig. 6.2) and used (Fig. 6.3) catalysts. The value and the species identified were contrasted with the bibliography and collected in Table 6.3. In the case of the XRD pattern of rGO (Fig. 6.4), two carbon species were

identified with the codes JCPDS 026-1076 at 43° and 44.6°; and 075-0444 at 25.9° and 44.6°.

Species	JCPDS code	Value	Bibliography
Al ₂ O ₃	077-0396	19.7, 34.0, 37.5, 44.5, 57.0, 61.0, 67.4, 85.0	[51], [52]
C	075-0444	25.9	[14]
Ni syn/Ni	004-0850/087-0712	44.5, 51.6, 76.7	[14]
NiAl ₂ O ₄	073-0239	37.2, 44.2, 64.3	
Ni ₃ S ₂	076-1870	21.8, 31.2, 44.5, 50.0, 55.3, 73.4, 78.0	[54]
La ₂ (CO ₃) ₂ (OH) ₂ · H ₂ O	046-0368	15.8, 20.5, 30.0, 30.3, 33.6, 36.7, 38.1, 43.9, 46.2, 48.8	[55]
LaCO ₃ OH	026-0815	17.8, 24.4, 30.3, 43.0, 43.9, 46.8, 50.0, 53.5, 57.2	[56]
La ₂ O ₂ CO ₃	025-0424	26.0, 30.5, 33.7, 44.6, 51.8	[57]

Table 6.3. XRD peaks for the metallic species of the catalysts analysed, determined graphically and contrasted with the bibliography.

The mean Ni crystallite size was estimated by XRD from the Ni (111) reflexion at $2\theta = 44.5^\circ$ (**Fig. 6.2** and **Fig. 6.3**) and results were listed in **Table 6.2**. Irrespective of the support and the presence of lanthanum, all catalysts were composed of small nickel crystallites with an average size of about 5-10 nm. After the reaction stage, an increase in crystal size was observed for the metal active centres in all the catalysts analysed. The increase in crystal size was a consequence of the sintering that takes place in the catalyst.

6.3.1.4. Temperature programmed reduction (H₂-TPR)

The H₂-TPR profiles obtained are collected in **Fig. 6.5** in order to determine the reducibility and the strength of metal-support interaction. Nickel showed four types of interaction with the support of alumina and three with the support of reduced graphene oxide, being more prominent those in which the peaks of the H₂-TPR spectrum were greater. Through the deconvolution of the H₂-TPR spectra in Gaussian peaks, it was possible to identify the reducible species present in the catalysts. In **Table 6.4** are included the peaks determined, corresponding to reducible NiO species divided into three types. α was fitted for amorphous NiO with weak interaction in the range of 373 to 523 K, β was suitable for NiO with weak-medium interaction between 523 and 773 K and γ was appropriate for NiO with medium interaction with the support. δ was related to Ni²⁺ with stronger interaction with the support (medium-strong) in the range of 773 to 1,023 K for the non-stoichiometric nickel aluminate (NiO-Al₂O₃). The stoichiometric nickel aluminate species (NiAl₂O₄) had a strong interaction with the support being harder to reduce needing a temperature higher than 1,073 K. This specie was not determined in the catalysts analysed, under the evaluated operating conditions [31], [79]–[82].

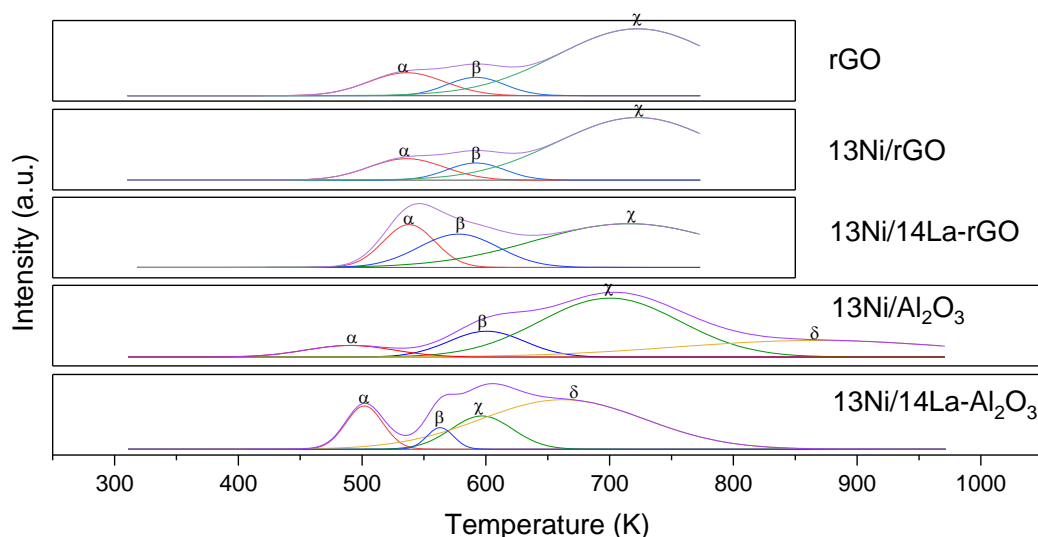


Fig. 6.5. H₂-TPR profiles of the investigated catalysts.

The reduced graphene oxide, as support, had a base reducibility in the absence of any metal, due to the presence of oxygen functional groups that allowed the easy union of metal nanoparticles to its structure and it acted as anchoring or nucleation centres. The nickel that was incorporated into the structure was attached to these anchoring centres, so that the peaks obtained in the H₂-TPR pattern appeared at the same temperature, but being quantitatively higher [14]. Specifically, the peak area determined in catalyst 13Ni/rGO was twice that obtained for rGO for peaks α , β and γ , due to the addition of the reducibility of metal, support and their interaction.

The identification of a peak δ next to γ in 13Ni/Al₂O₃ catalyst indicated a greater interaction between active metal and support (non-stoichiometric nickel aluminate formation). Despite the low amount of this species, its presence indicated a greater stability of the catalyst to deactivation by sintering, but also a lower reducibility. In the 13Ni/Al₂O₃ catalyst, peak α shifted to a lower temperature, than in 13Ni/rGO, which indicated that the interaction between amorphous NiO and support was lower. On the other hand, the decrease in the area of peak α was balanced out by an increase in peak β .

Catalyst	Peak area (a.u.)				Fraction of total area (%)			
	α	β	γ	δ	α	β	γ	δ
13Ni/Al ₂ O ₃	6.78	28.57	13.2	3.55	13.01	54.84	25.34	6.81
13Ni/14La-Al ₂ O ₃	7.53	9.61	38.25	2.67	12.97	16.55	65.88	4.60
rGO	15.25	9.27	74.14		15.46	9.40	75.15	
13Ni/rGO	32.66	19.84	158.78		15.46	9.39	75.15	
13Ni/14La-rGO	38.73	112.96	46.55		19.54	56.98	23.48	

Table 6.4. Gaussian fitting analysis of H₂-TPR profiles of the catalysts studied.

TPR patterns of La-modified supports, showed a splitting of the peaks at temperatures between 500 and 700 K. The peak at 505 K was increased, corresponding with the rise of free NiO species in the alumina support, which was increased by adding La to the catalyst [32], [79], [83]. Based on the results and the literature observations, the incorporation of La weakened the interaction between NiO and Al₂O₃ support, by destroying partially metastable Ni-Al mixed oxide phase [79], [83]. In this way, there was an increase in medium-strong interactions and the decrease in the reduction

temperature of all the species present in the catalyst. The addition of lanthanum to the rGO support produced a similar effect to that observed for alumina, increasing the amount of medium-low interaction NiO (β -peak) with respect to that of medium-strong interaction NiO (γ -peak). In this sense, lanthanum caused the weakening of nickel interactions with the support for both alumina and rGO supports. A weaker interaction of the active metal with the support meant a greater reducibility of the catalyst, but it could increase the deactivation of the catalyst due to the breaking of the bonds of the active metal with the support, resulting in metal sintering.

Based on the results obtained and the literature, the catalysts activated by the reduction at 673 K must be almost completely reduced for the reaction conditions between 498 and 773 K for CO₂ methanation.

6.3.1.5. HR-STEM

STEM combined with EDX was employed to analyse the morphology of the catalysts, in addition to mapping its surface to locate and identify the content of C, O, N, S and Ni elements. *Fig. 6.6* showed the STEM-EDX images, mapping results were also depicted for the following catalysts: 13Ni/AGO, 13Ni/BGO, 13Ni-OI/GO, 13Ni/OI-GO, 13Ni/OI-GO Met, 13Ni/rGO and 13Ni/14La-rGO. GO-based catalysts (13Ni-OI/GO, 13Ni/OI-GO and 13Ni/OI-GO Met) showed the presence of sulphur dispersed on the catalyst surface, as part of the GO support composition due to its synthesis method. In the 13Ni-OI/GO catalyst, the amount of sulphur observed was considerably lower than for the other two catalysts, probably due to the elimination of the oleylamine impregnation step, which in turn allowed a stronger anchoring of sulphur species on the support. These undesirable species were partially removed when the metal was simultaneously impregnated with the oleylamine through a single stage. However, based on STEM images, in the absence of sulphur less nickel was fixed. This metal was well dispersed in all the catalysts, mainly due to the formation of Ni-C σ bonds that promoted the stacking of the layers [14]. Thus, the main difference observed among the graphene-based catalysts was the particle size that depends mainly on the support. The Ni particle sizes determined for the different catalysts are listed in *Table 6.5*, for both fresh-reduced and used catalysts. With the exception of the 13Ni/AGO catalyst, whose Ni particle size was 68.5 nm, the other catalysts showed small particle size values, distributed homogeneously throughout the surface of the support. As inferred from *Table 6.5*, the addition of lanthanum led to slightly bigger nickel particles (5-20 nm), maintaining an homogeneous dispersion [32]. It should be pointed out that particle sizes determined by HR-STEM analysis were comparable to crystallite sizes estimated by XRD, with the exception of 13Ni/14La-rGO used catalyst, which due to sintering caused by H₂S and temperature increases its size significantly, measuring the Ni₃S₂ crystallite size. When compared with XRD data, it was reasonable to assume that on average active nickel particles (around 5-25 nm) were composed of one or at most two-three crystallites (about 5-10 nm), thereby proving the mainly monocrystalline nature of the samples.

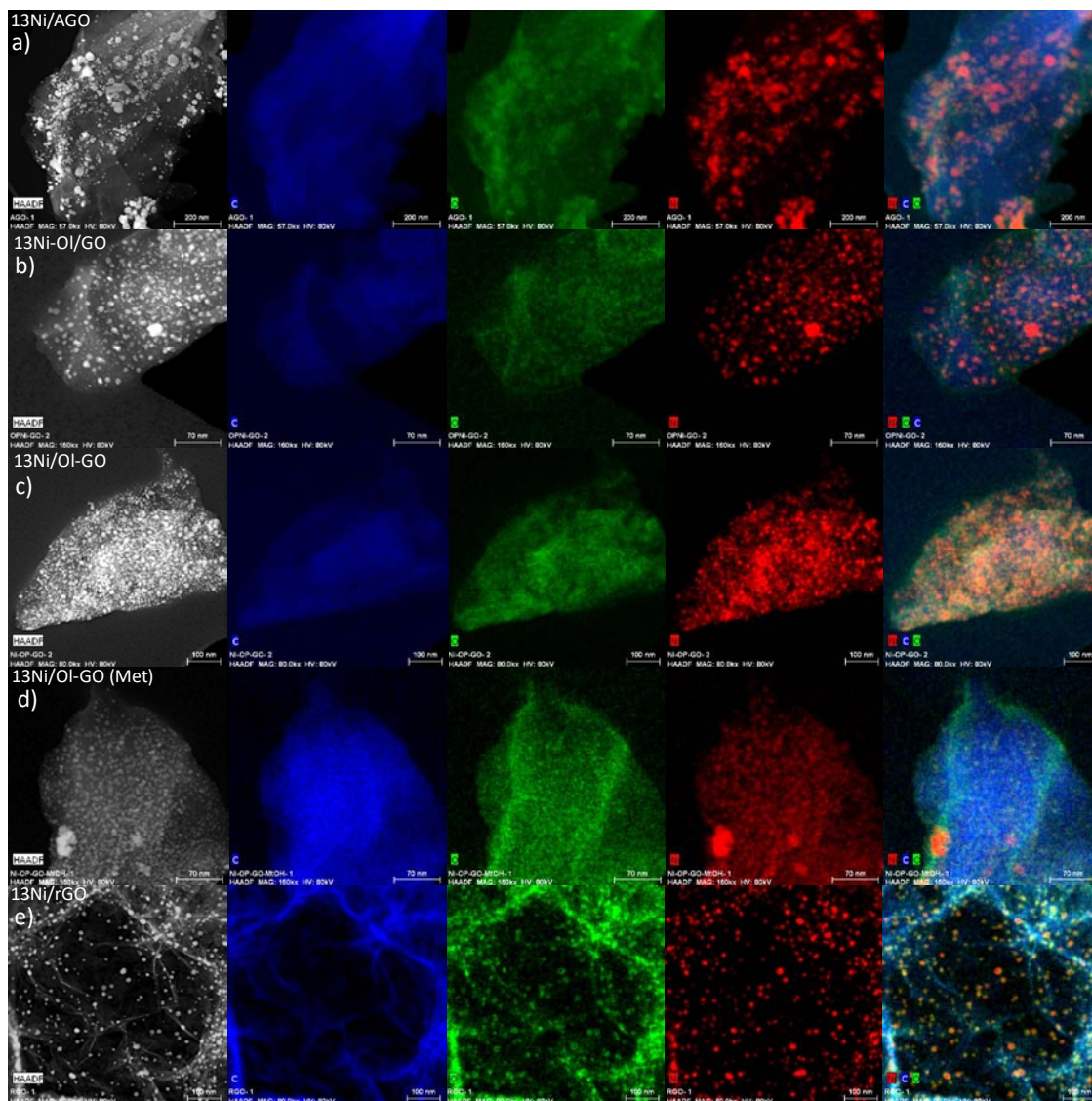


Fig. 6.6. STEM-EDX images and element mapping of a) 13Ni/AGO, b) 13Ni-OI/GO, c) 13Ni/OI-GO, d) 13Ni/OI-GO Met and e) 13Ni/rGO used catalyst.

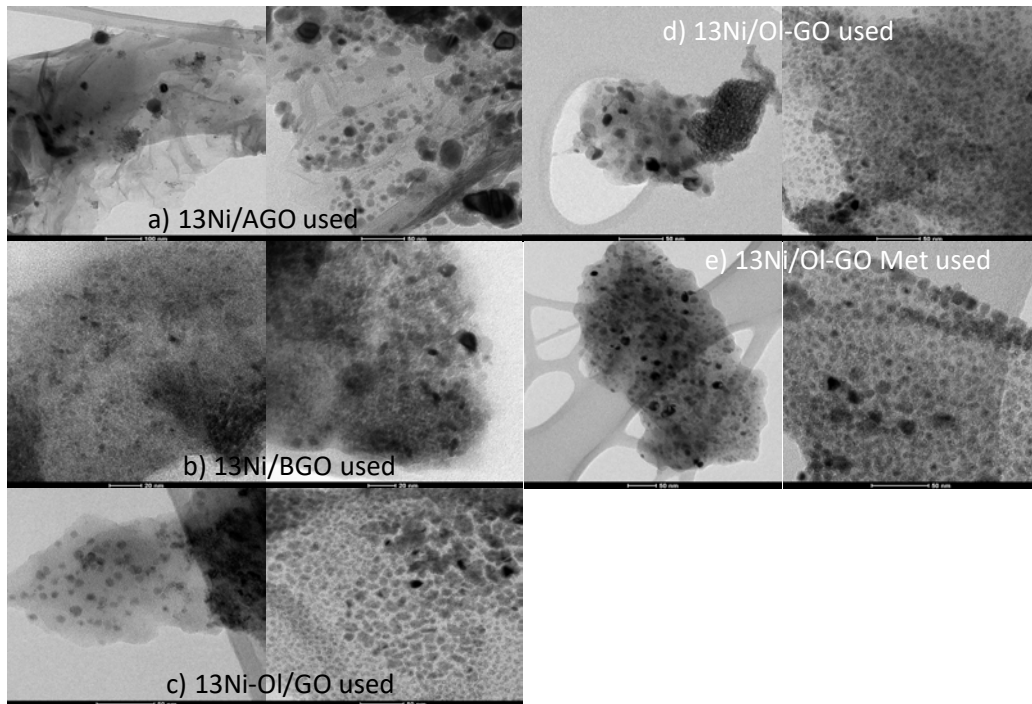


Fig. 6.7. TEM micrographs of a) 13Ni/AGO used, b)13Ni/BGO used, c) 13Ni-OI/GO used, d) 13Ni/OI-GO used and e)13Ni/OI-GO Met used.

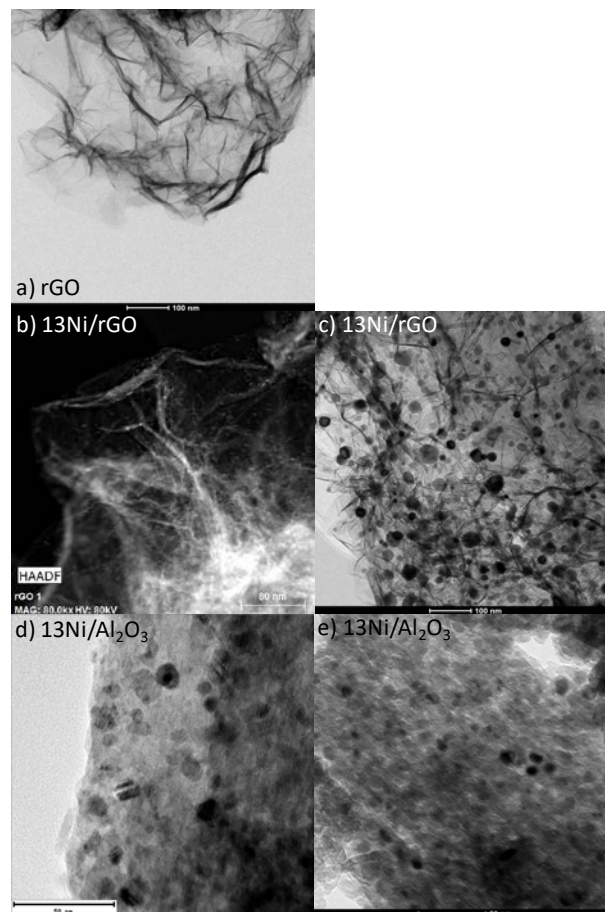


Fig. 6.8. STEM micrographs of a) rGO, b) 13Ni/rGO fresh, c) 13Ni/rGO used, d) 13Ni/Al₂O₃ fresh, e) 13Ni/Al₂O₃ used, f) 13Ni/14La-Al₂O₃ fresh, g) 13Ni/14La-Al₂O₃ used, h) 13Ni/14La-rGO fresh and i) 13Ni/14La-rGO catalyst.

After reaction, used catalysts were also studied by HR-STEM and TEM and the corresponding images are showed in *Fig. 6.7* and *Fig. 6.8*. This analysis revealed no significant morphological differences when compared to fresh-reduced catalysts. However in terms of particle size, some variations were detected. For catalysts 13Ni/Al₂O₃, 13Ni/14La-Al₂O₃, 13Ni/rGO and 13Ni/14La-rGO a growth of their size was identified (from 10.0 to 13 nm), which was mainly attributed to the sintering caused by high temperatures and the action of H₂S in the catalysts [84]. Conversely, the particle size of graphene oxide based catalysts 13Ni/AGO, 13Ni-OI/GO, 13Ni/OI-GO and 13Ni/OI-GO (Met), was reduced owing to the loss of the oxygen that made up the Ni complexes. Therefore, it could be stated that in the absence of this oxygen anchoring the metal to the support with strong interaction, metallic particles were divided into smaller aggregates [14].

	Particle size by STEM (nm)		Particle size by XRD (nm)	
	Fresh catalyst	Used catalyst	Fresh catalyst	Used catalyst
13Ni/AGO	69±18	23±7		
13Ni/BGO	12±5	-		
13Ni-OI/GO	23±6	7±2		
13Ni/OI-GO	26±6	14±3		
13Ni/OI-GO (Met)	8±2	6±2		
13Ni/rGO	11±4	13±4	~8	~6
13Ni/14La-rGO			~80*	~7
13Ni/Alumina	10±3	12±3	~5	~10
13Ni/14La-Alumina			~5	~15

Table 6.5. Metallic particle size of the different catalysts determined by STEM and XRD

*Average of Ni₃S₂ crystallite size (at 22°) instead of Ni (44.5°).

6.3.1.6. XPS

X-ray photoelectron spectroscopy was used to provide information about the oxidation state and the chemical environment of the nickel present on the surface of all the investigated catalysts. The Ni 2p_{3/2} region of each freshly-reduced sample was plotted in *Fig. 6.9* and *Fig. 6.11* while the spectra of the used catalysts were depicted in *Fig. 6.10* and *Fig. 6.12*. In both cases, and according to literature, Ni 2p_{3/2} spectra exhibited a doublet of two multiplet splits located in the range of 854-862.6 eV and 865-890 eV [85]. Focusing on the lower energy multiplet, three nickel contributions were detected at 854-854.5, 855.7-857.2 and 860.8-862.6 eV, which were attributed to Ni⁰, Ni²⁺, and Ni²⁺ satellite, respectively [86].

As for alumina supported catalysts, the contribution of metallic nickel was higher than the nickel oxide phase, thanks to the in-situ reduction stage carried out in the XPS Chamber. However, this reduction treatment was not applied to graphene supported catalysts and as a result, instead of metallic Ni, Ni²⁺ was the main oxidation state on the surface of these catalysts. At this point, it should be mentioned that is a very common issue the oxidation of metallic particles during the sample preparation and introduction into the XPS chamber. Nevertheless, when compared to the used counterparts, the intensity of superficial NiO was lower, suggesting that after reaction metallic nickel was partially oxidized [87]. This treatment was not applied in graphene supported catalysts,

with a greater intensity of nickel oxide peak, than of metallic nickel. However, despite observing a greater intensity in the nickel oxide peak, it was lower than that obtained in the case of the used samples, where the intensity of the oxide peak was much greater than that of the metal.

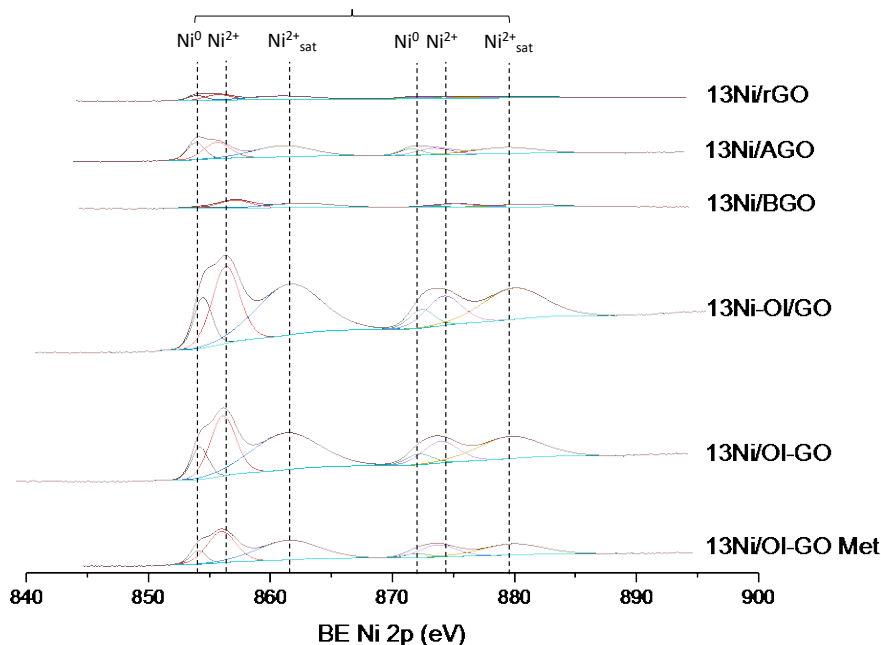


Fig. 6.9. XPS spectra of Ni $2p_{3/2}$ region of fresh Ni-catalysts based on graphene.

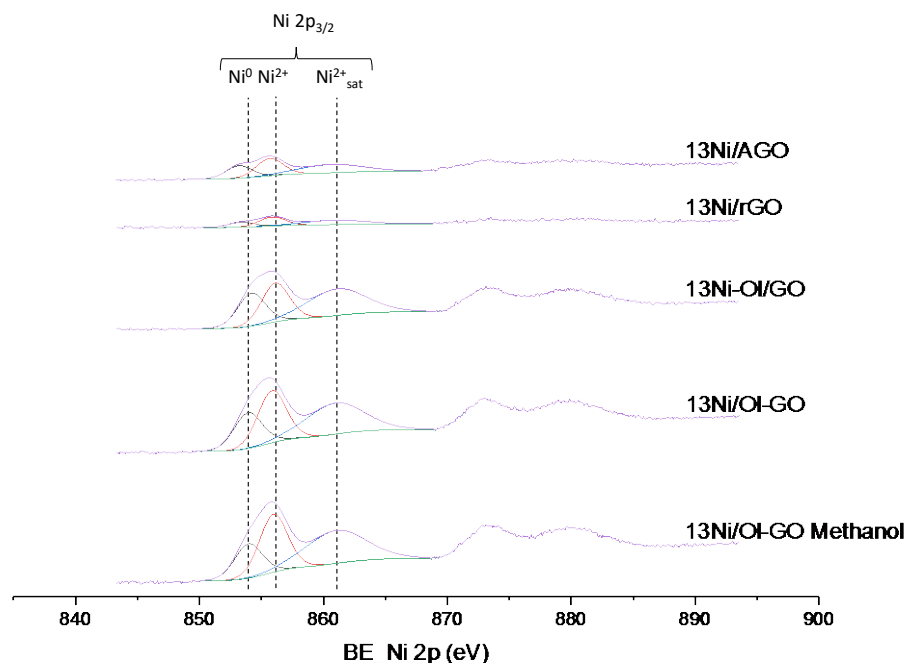


Fig. 6.10. XPS spectra of Ni $2p_{3/2}$ region of used Ni-catalysts based on graphene.

XPS of the La $3d_{5/2}$ and La $3d_{3/2}$ core level spectra of the 13Ni/14La- Al_2O_3 and 13Ni/14La-rGO samples (Fig. 6.11 and Fig. 6.12) clearly evidenced the presence of this promoter on their surface. Indeed, the position of the main peak at 835.0 eV and the characteristic distance between this main peak and its satellite of about 4 eV undoubtedly

confirmed the existence of La_2O_3 on the surface of the catalysts [32]. However it was not possible to quantify the Ni interacting with La due to the superposition with the Auger LMM line of Ni 2p 3/2 and La 3d 3/2 in the case of the catalyst 13Ni/14La- Al_2O_3 and 13Ni/14La-rGO. Nonetheless, the Ni 2p_{3/2} corresponding triplet moves toward lower binding energy, while the La 3d_{3/2} doublet increases its bond energy, producing the overlapping of the corresponding peaks, confirming the interaction that occurs between La^{3+} and Ni^{2+} [32].

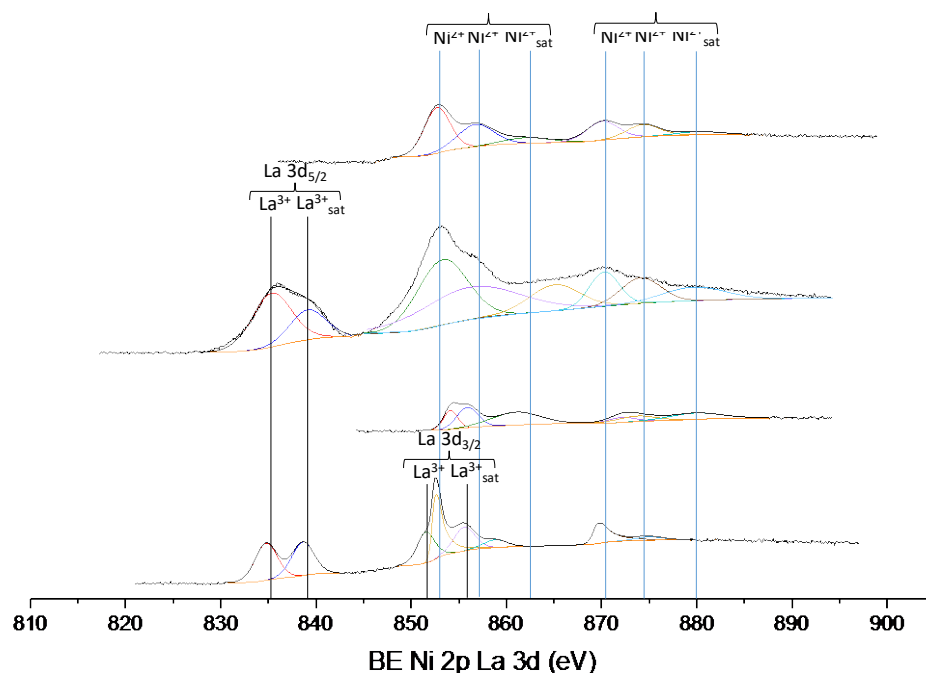


Fig. 6.11. XPS spectra of La 3d_{5/2}, La 3d_{3/2}, Ni 2p_{3/2}, Ni 2p_{1/2} regions of fresh catalysts.

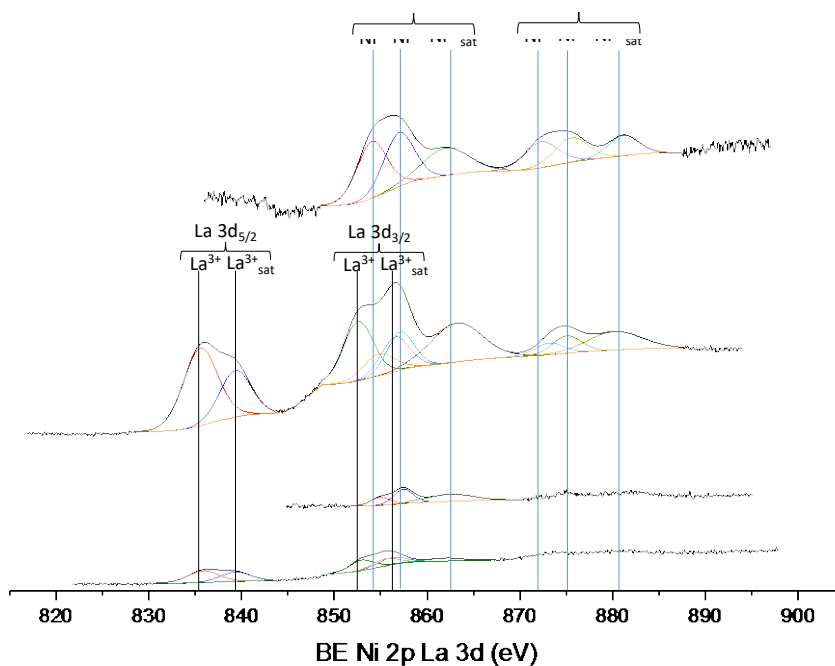


Fig. 6.12. XPS spectra of La 3d_{5/2}, La 3d_{3/2}, Ni 2p_{3/2}, Ni 2p_{1/2} regions of used catalysts.

In addition to the identification of all elements present at the surface level, this technique was also useful for the quantification of these species, namely, metallic nickel, carbon, oxygen, sulphur and lanthanum modifier, and for the determination of their interactions. In the case of catalysts supported on graphene, this technique allows to identify the amount of active metal (Ni), carbon and oxygen, and nitrogen, sulphur and support modifier (La) when present; and through the oxidation state, determine the bonds in which they were found. The results of this analysis for both freshly-reduced and spend catalysts were summarized in *Table 6.6*. As can be deduced, the proportion of Ni varies depending on the support used. In inorganic supported catalysts the nickel content of the surface was lower than for organic supported catalysts, based on graphene. Graphene was made up of extensive but shallow layers, so most of the metal content incorporated in these supports can be detected on the surface by XPS. When compared to ICP results the tendency of Ni content varied, thus suggesting that the composition of the bulk was different from the surface.

	Fresh catalyst						Used catalyst					
	C/Al (%)	O (%)	Ni (%)	N (%)	S (%)	La (%)	C/Al (%)	O (%)	Ni (%)	N (%)	S (%)	La (%)
13Ni/Al₂O₃	40.4	56.5	2.7	-	-	-	37.7	59.1	2.6	-	-	-
13Ni/14La-Al₂O₃	35.7	60.3	*	-	-	3.4	26.7	64.9	5.3	-	-	3.1
13Ni/rGO	88.3	9.8	1.1	0.8	-	-	91.6	6.0	0.5	-	-	-
13Ni/14La-rGO	86.9	9.4	2.0	-	-	1.7	83.4	14.7	0.9*	-	-	1.0
13Ni/AGO	73.8	15.4	6.9	3.9	-	-	85.4	9.8	2.3	2.4	-	-
13Ni/BGO	16.5	32.9	2.1	1.4	0.3	-	-	-	-	-	-	-
13Ni-OI/GO	44.3	34.3	13.2	5.0	3.3	-	52.2	29.4	6.4	2.9	-	-
13Ni/OI-GO	16.7	52.8	21.1	2.6	6.8	-	65.5	22.5	7.2	3.3	1.5	-
13Ni/OI-GO (Met)	22.1	50.4	16.5	3.7	7.3	-	57.9	28.8	8.1	3.5	1.7	-

Table 6.6. Surface atomic values obtained by XPS analysis of the different catalysts studied *presence of Ni, but cannot be quantified (2p line of Ni overlapped with 3d line of La).

According to the results obtained by ICP and HR-STEM-EDX, values of XPS also indicated that, excepts for 13Ni/BGO catalyst, nickel was mostly contained into the bulk of the catalysts, or linked to carbon atoms in deep layers of the catalysts. On the other hand, sulphur was only detected in the fresh-reduced catalyst supported on graphene oxide, denoting that it was not eliminated in the synthesis step. This content was higher for oleylamine incorporated catalysts, as verified by HR-STEM. As for used samples, the amount of this sulphur decreased, even disappearing despite feeding H₂S, due to subsequent reaction and regeneration steps. These steps may remove the sulphur content from the catalyst surface, not being detected with this technique. As general trend, the amount of carbon in graphene-based catalysts increased significantly with respect to fresh catalysts, which in turn caused a reduction of oxygen, nitrogen and nickel proportions. This fact may be due to the appearance of carbon deposits from the reaction, which covered the catalyst surface and reduced its catalytic activity. The amount of nitrogen detected by the XPS analysis depends on the catalyst preparation technique used and of the amine groups incorporated, so that the highest content was observed for the 13Ni-OI/GO catalyst when nitrogen was incorporated with oleylamine. In the other catalysts that incorporate oleylamine, the nitrogen content was lower, and probably lost after two stages of calcination, as shown in the CHN analyses in *Table 6.7*. In the 13Ni/AGO catalyst, the high nitrogen content was due to the group amino incorporated in its

preparation. The rest of the catalysts have a lower nitrogen content, corresponding to the amount originally present in GO or rGO originally.

	C (%)	H (%)	N (%)
13Ni/AGO	65.8	2.5	3.9
13Ni/BGO	4.9	0.4	0.4
13Ni-OI/GO	43.6	1.5	3.9
13Ni-OI-GO	6.2	1.2	0.8
13Ni-OI-GO (Met)	20.6	1.7	1.8
13Ni/rGO	68.2	-	1.25

Table 6.7. Percentages of carbon, hydrogen and nitrogen measured through CHN analysis of the catalysts prepared.

Finally, the higher oxygen content than carbon detected in XPS for catalysts incorporating oleylamine can be explained by the greater presence of oxygenated hydrocarbons, such as the hydrocarbon chain that make up oleylamine. Therefore, as the amount of oleylamine increases, so does oxygen (as verified in elementary CHN analyses). In turn, the higher content of functional oxygen groups, the anchoring of nickel is facilitated.

6.3.2. Activity tests

The catalytic behaviour of synthesized catalysts, based on 13wt.% Ni supported on graphene-based oxides or alumina and modified with 14wt.% lanthanum, was investigated for CO₂ methanation. Runs were carried out with 200 mg of catalyst, at temperatures between 573 and 773 K and a weight hourly space velocity of 38.3 h⁻¹. For the evaluation of the catalytic performance methane yield parameter was selected (Eq. 4), and the obtained results are reported in Fig. 6.13.

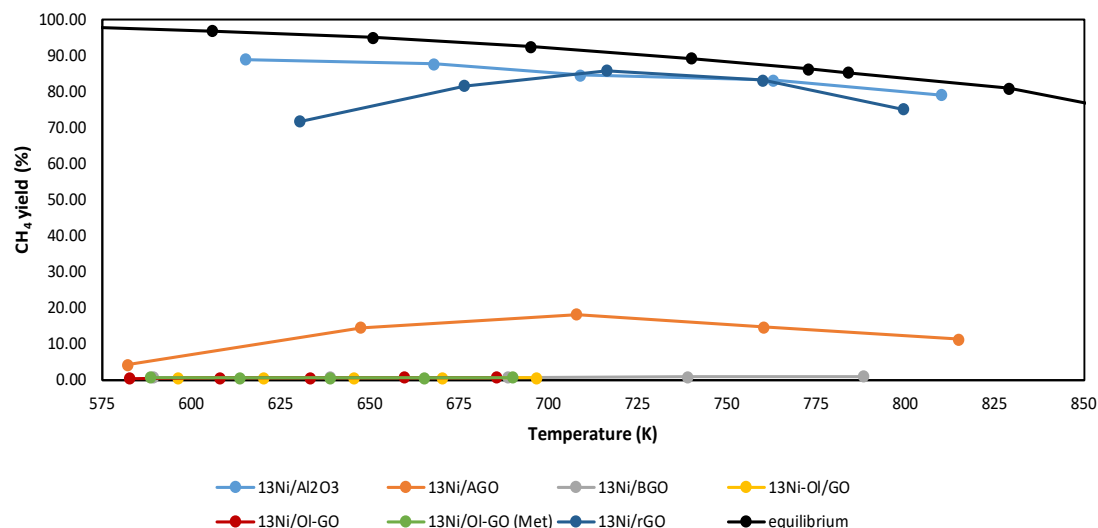


Fig. 6.13. Methane yield obtained for investigated supported nickel catalysts.

Firstly, the very low catalytic performance of oleylamine-containing aminated catalysts (13Ni-OI/GO, 13Ni-OI-GO and 13Ni-OI-GO (Met)) should be highlighted, since these samples showed methane yields close or equal to 0.

In the case of 13Ni/BGO catalyst, the observed activity was also negligible. Indeed, owing to its synthesis method the metal content of this catalyst in the bulk (1.3 wt.%) as well as on the surface (2.1%) was very low, and as a result, despite its good dispersion (as observed by STEM), it was not enough to increase the methane yield above 3%. On the other hand, the catalytic activity of the 13Ni/AGO catalyst was significantly better than its counterpart 13Ni/BGO, reaching a maximum methane yield of 18.3% at 708 K. This improved activity, when compared to oleylamine containing catalysts, was mainly attributed to the fact that having 12 carbon atoms instead of 18 of the oleylamine facilitated the access of the reagents to the catalyst. Even so, this catalyst was less active than catalysts supported on rGO and alumina, which achieved the highest methane yield (around 90% at 710 K). Specifically, both 13Ni/Al₂O₃ and 13Ni/rGO samples exhibited a great catalytic performance, being practically equivalent at intermediate temperatures (from 700 K to 760 K) although both at lower temperatures (600-700 K) as well as at high-thermal levels (>760 K) the 13Ni/Al₂O₃ catalyst was superior to 13Ni/rGO.

Based on these results, the promising 13Ni/Al₂O₃ and 13Ni/rGO catalysts were the samples selected to be optimized by modifying their supports with lanthanum. Nevertheless, prior to this study, a complementary analysis was carried out over 13Ni/Al₂O₃ sample in order to determine the optimum catalyst amount. Thus, the catalytic activity of CO₂ methanation reaction was evaluated from 525 to 850 K using three different amounts of 13Ni/Al₂O₃, namely, 200 mg (38.3 h⁻¹), 125 mg (60.8 h⁻¹) and 60 mg (128.75 h⁻¹) and the obtained results are shown in Fig. 6.14.

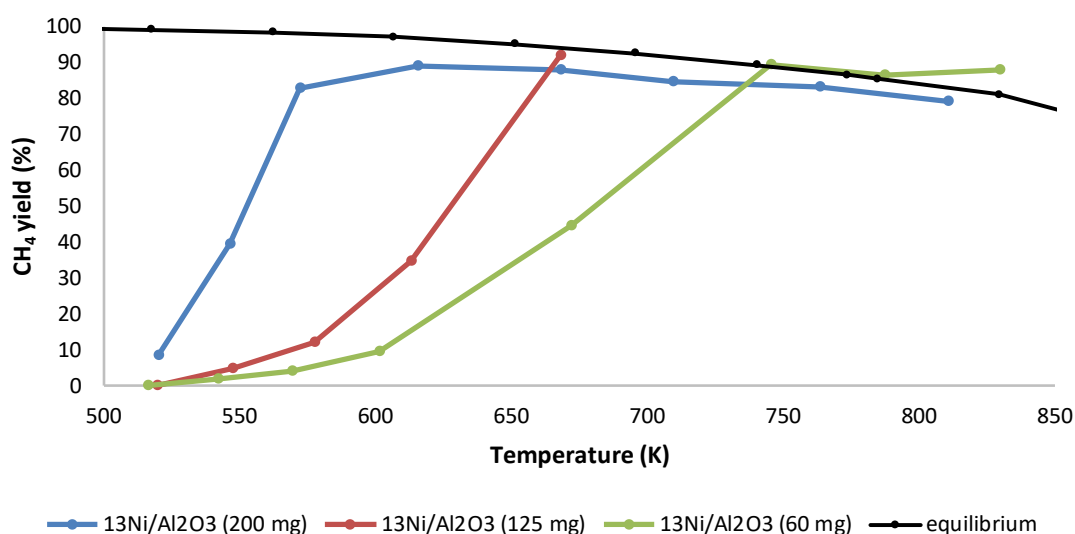


Fig. 6.14. Comparison of methane yield for different quantity of 13Ni/Alumina catalyst.

As expected, as the amount of catalyst was reduced or the WHSV was increased, the temperature needed to reach the maximum yield set by the thermodynamic equilibrium increased. With a load of 200 mg of catalyst in the reactor, the equilibrium conversion was reached at 572 K, while for 125 mg the temperature needed to be raised to 668 K and for an amount of 60 mg the equilibrium temperature was not reached until 745 K. For a catalyst quantity of 60 mg, equilibrium was reached in the study temperature range, with a little more difficulty to increase performance.

Once the quantity of 60 mg of catalyst was chosen, the effect of lanthanum (14 wt.%) on the activity of both alumina and rGO-supported catalysts was examined. For that purpose, runs were performed operating with a WHSV of 128.75 h⁻¹ and in the

temperature range of 598–773 K. The corresponding activity results are depicted in Fig. 6.15.

The $13\text{Ni}/\text{Al}_2\text{O}_3$ catalyst achieved a maximum methane yield of 90% at 745 K, as already seen at Fig. 6.15, while its analogous La-modified sample ($13\text{Ni}/\text{La}-\text{Al}_2\text{O}_3$), reached the same value at lower temperatures (and 89% at 727 K). That means that the incorporation of La into alumina support considerably reduced the temperature necessary to reach equilibrium. However, for rGO supported catalysts, no significant improvement was observed when La was incorporated, being the light-off curve of both catalysts (as-synthesized and modified) practically identical up to 725 K and only slightly higher for La-modified catalyst ($13\text{Ni}/\text{La}-\text{rGO}$) from 725 K to 798 K. Furthermore, and despite the modification with La, the alumina supported catalyst was still more active than the analogous rGO-supported catalyst. This fact denoted that the method of incorporating Ni on a support with larger surface area, such as the rGO, and its subsequent modification with lanthanum (La-rGO) was not successful for achieving greater dispersion of the active centres on the surface of the support and therefore, neither for improving the activity of rGO-supported catalysts with respect to alumina-supported samples.

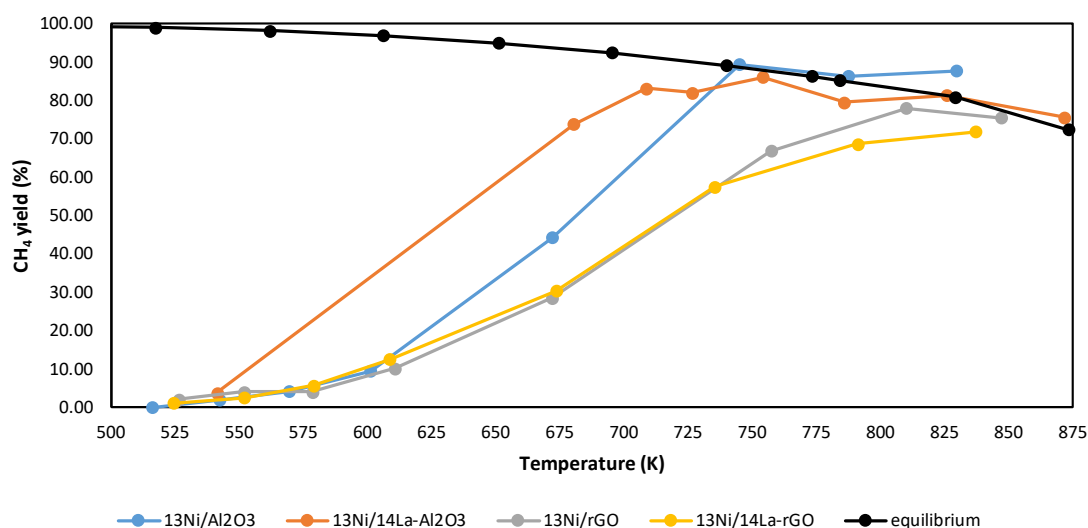


Fig. 6.15. Methane yield obtained for 60 mg of catalysts supported on alumina and rGO.

As a final research point, the resistance of these for catalysts, against H_2S was examined, since this compound constitutes one of the most common poisoning factor in CO_2 methanation. For this purpose, (the last four, $13\text{Ni}/\text{Al}_2\text{O}_3$, $13\text{Ni}/\text{La}-\text{Al}_2\text{O}_3$, $13\text{Ni}/\text{rGO}$ and $13\text{Ni}/\text{La}-\text{rGO}$) catalysts were tested at 773K, the highest performance temperature, in presence of 50 ppm of H_2S , which was co-fed with the other reaction gases, and the time necessary for the complete deactivation of the catalysts was determined. The methane yield evolution with time on stream for each catalyst was plotted in Fig. 6.16. The presence of H_2S in the reaction stream rapidly reduced the activity of rGO-supported catalysts, deactivating them completely in only 20 min in the case of the $13\text{Ni}/14\text{La}-\text{rGO}$ and in 50 min in the case of the $13\text{Ni}/\text{rGO}$, although the latter suffered a vertiginous decrease to 10% yield in just 15 minutes. This rapid deactivation, was expected considering the high operation temperature, which reduced the catalytic performance with time on stream by thermal deactivation. Regarding alumina supported catalyst, the addition of 14wt.% of La to $13\text{Ni}/\text{Al}_2\text{O}_3$, apart from improving the obtained methane yield, enhanced markedly its

resistance to H₂S poisoning, lengthening the deactivation time from 70 min for the 13Ni/Al₂O₃ to 110 min for the catalyst 13Ni/14La-Al₂O₃.

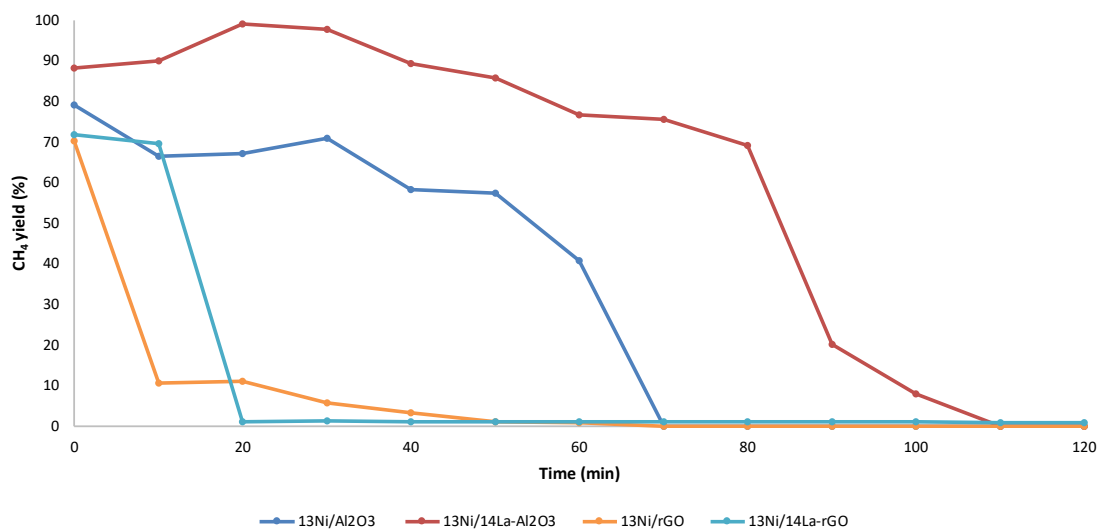


Fig. 6.16. Catalysts deactivation due to 50 ppm of H₂S at 773K

Immediately after the complete deactivation of the catalysts, H₂S was eliminated from the feed and again, the methane yield of the catalysts was analysed. However, in all cases, catalysts did not recover the activity.

Finally, in order to complete the research done in this work, the possibility of catalyst regeneration was examined. To this end, deactivated samples were treated with a mixture of 3% O₂ and N₂ at 773 K, in order to eliminate either the sulphur or coke deposits, that is, the main responsible for the decline in activity. After calcination, the catalysts were reactivated by reduction with H₂ (following the conditions aforementioned in the experimental section) and their activity was again evaluated by means of methane yield at 773 K. From the obtained results (not shown) it was clearly inferred that after regeneration treatment catalysts were not able to recover their previous methane yield, showing values of 0%. This finding was probably be connected to the fact that during the reaction and/or deactivation stage CO could have appeared as a by-product of the reverse water gas shift reaction or from the partial oxidation of the coke in the regeneration step. Nonetheless, the presence of this gas has not been detected.

6.3.3. Discussion

In this work, graphene in the form of aminated graphene oxide (AGO) and reduced graphene oxide (rGO) have been used as support. In addition, other graphene derivatives have been compared in the methanation reaction to avoid the hot spots that may be produced by the exothermicity of the reaction, employing the heat conductive capacity showed by graphene and its derivatives [53]–[56]. Among the catalysts prepared, the best support for nickel as an active metal was rGO. This catalyst was in turn doped with lanthanum, showing very small differences in its activity, and in both cases being lower than catalysts with the same active metal supported in alumina, with which it was compared.

The use of nickel-based catalysts as active metal present in different activity values depending on the type of support used. The metal-support interaction was a factor of great influence on the activity of a catalyst. That is why, catalysts based on GO modified

with oleylamine (13Ni-OI/GO, 13Ni/OI-GO and 13Ni/OI-GO (Met)) presented such low activity values. The addition of this aminated group was proposed to offer a hydrophobic environment that facilitated the exit of water as a byproduct, facilitating the methane formation reaction. The union of the oleylamine and the active nickel centres was produced homogeneously by the surface of the GO and there was interaction between them, as determined by STEM characterisation. However, probably this interaction hindered the adsorption of reactants on the metal sites.

Something similar occurred in catalyst supported on GO, reduced with MeAB (13 Ni/BGO). In this case, MeAB was incorporated into the catalyst, reducing the proportion of metal centres present. It was observed that the proportion of nickel with respect to the total decreased considerably from 13% to 1.5%. Despite having a lower nickel content than 13Ni/OI-GO, 13Ni/OI-GO (Met) and 13Ni/OI/GO, the performance is higher (3%). Considering the moles of CH₄ per minute and mole of nickel, it is observed that the efficiency of 13Ni/BGO (1.63) catalyst is greater than 13Ni/OI-GO (0.01), 13Ni/OI-GO (Met) (0.02), 13Ni/OI/GO (0.03) and 13Ni/AGO (0.70) catalysts. However, it does not reach the value of the 13Ni/Al₂O₃ (4.55), 13Ni/14La-Al₂O₃ (3.93), 13Ni/rGO (4.03) and 13Ni/14La-rGO (3.61) catalysts.

On the other hand, the catalyst based on graphene oxide aminated with dodecylamine (13Ni/AGO) showed an agglomeration of nickel cores, distributed evenly across the surface of the support. These centres agglomerated together with functional nitrogen and oxygenated groups that served as nucleation or anchoring centres for the active metal, thus facilitating and strengthening the metal-support interaction, as observed by HR-STEM. However, due to a lower dispersion of active centres, the catalytic activity achieved was lower than expected for the amount of nickel present in this catalyst.

In the 13Ni/rGO the support was partially reduced, but unlike the 13Ni/BGO catalyst, it retains oxygen atoms tightly bound to the GO structure by forming functional groups of oxygen and eliminating the most weakly bound oxygen atoms. These oxygen functional groups facilitated the deposition, anchoring and dispersion of the Ni metal particles on the rGO structure homogeneously, as observed in STEM. The bond that occurs between metal and support was a strong bond, as confirmed by TPR analysis, resulted in high stability of the catalyst at temperature and therefore high activity of the catalyst in the reaction. The ability to conduct heat quickly through its surface reduced of hot spots formation usually present in the exothermic methanation reaction, resulted in better temperature control that reduces catalyst deactivation. However, the bonds between the oxygen functional groups and the organic structure of the support have greater sensitivity to temperature, which causes a progressive deactivation of the catalyst as the temperature increases. This was further confirmed with a TGA analysis (*Fig. 6.17*), where the progressive loss of support mass can be observed as the temperature increases in an inert atmosphere. It was significant that the loss of mass occurs despite the increase in temperature with a small ramp and that it continues to decrease by keeping the temperature constant at a value of 673 K.

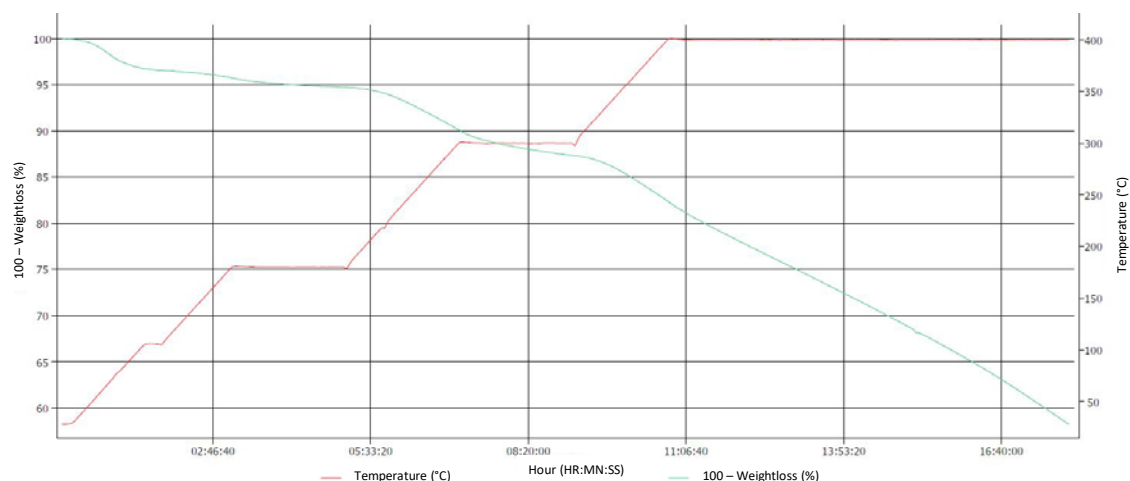


Fig. 6.17. Loss of mass of the support rGO with the temperature, with increase of 1K/min up to 673K, keeping at constant temperature until the total loss of mass.

The rGO catalyst exhibits greater activity than the rest of graphene-based catalysts, but due to its temperature sensitivity, it is necessary to improve the activity in the methanation reaction, as it could only be used at moderate temperatures to increase the life of the catalyst and, thus, with a lower value of WHSV to improve performance at these conditions.

An inorganic support, such as that of the alumina, guarantees greater thermal stability against deactivation of the catalyst at studied temperatures (498-773 K), compared to graphene oxide derived catalysts. In fact, the 13Ni/Al₂O₃ catalyst achieves higher methane yield (89.5%) at a lower temperature (745 K) than the 13Ni/rGO catalyst (78% at 810 K), making it a more active catalyst, with a greater number of metal centres and more accessible. This contrasts with the results obtained in the work of Hu et al. [14], in which they incorporate 20 wt.% nickel by wet impregnation on rGO, having reduced graphene via hydrazine hydrate. The authors determined that nickel-supported catalysts in rGO achieved higher methane yield (80%) at a lower temperature (623 K) than alumina-supported catalysts (65%). In addition, they demonstrated that their 20Ni/rGO catalyst maintained its activity over time at a temperature of 723 K, which justifies its stability against thermal deactivation. The difference in the results with catalyst 13Ni/Al₂O₃ was mainly due to the operating pressure, being the atmospheric in the work of Hu et al. The 13Ni/rGO catalyst, despite the differences in operating pressure, maintains a similar methane yield value, at temperature of 810 K. The thermal stability of the rGO, like that achieved in the work of Hu et al, was achieved with an increase in the ramp to raise the temperature of the system, from 1 K/min to 10 K/min. With these new conditions, 1,273 K were reached, without losing more than 20% of mass, as shown in Fig. 6.18 in the TGA analysis.

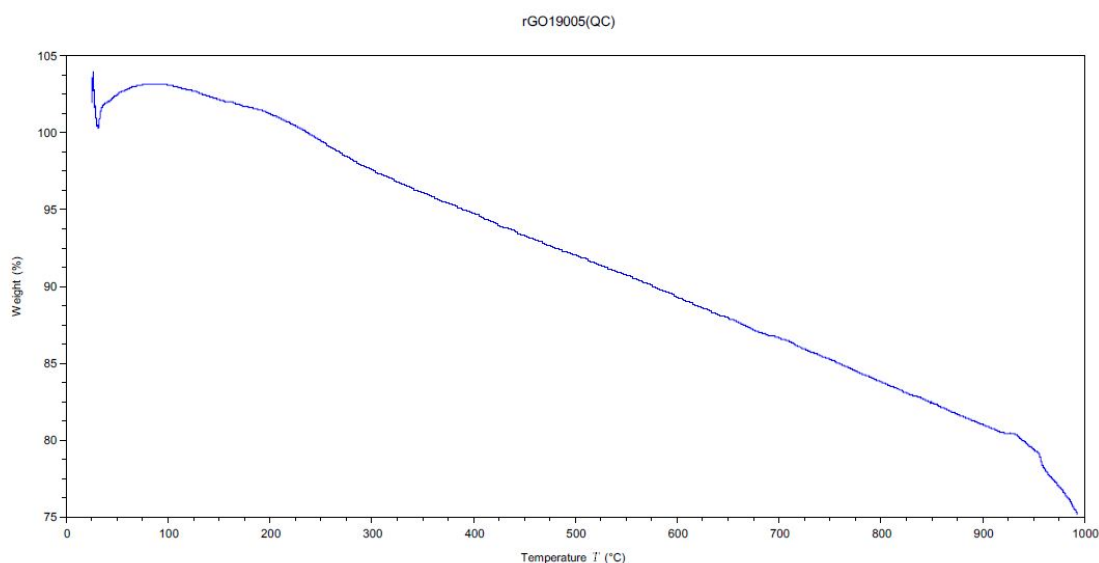


Fig. 6.18. Loss of mass of the support rGO with the temperature, with increase of 10K/min up to 1,273K (Graphenea).

Methanation has been studied extensively using nickel catalysts supported on alumina. However, the vast majority of these works were carried out under atmospheric pressure conditions. In Italiano et al. [88] work a methane yield of 75% was reached at 673K with 15Ni/Al₂O₃. In Quindimil et al. [89] 80% was reached at 673K with 12Ni/ Al₂O₃. In Garbarino et al. [32] they reached up to 85% at 673K with 16.7Ni/Al₂O₃. In Ahmad et al. [52] 87% was obtained at 573 K with 12 Ni/Al₂O₃, which was close to 89.5% at 672 K that was obtained for 13Ni/Al₂O₃, when working with 10 bar of pressure and 128.75 h⁻¹ of WHSV.

The addition of lanthanum, as support modifier, improves the catalytic activity of nickel in the temperature range between 523 and 750 K. The work of Garbarino et al. [32] shows a result very similar to that observed in this work by adding lanthanum as a promoter, improving the yield to methane from 82% to 623 K for 16.7Ni/Al₂O₃, up to 92% at 623 K for 16.7Ni-14La/Al₂O₃ under atmospheric pressure. The addition of lanthanum to the nickel catalyst improves the catalytic activity, as an effect of a greater interaction between nickel-lanthanum-alumina. This was justified by the interaction observed in XRD and H₂-TPR, whereby there was a weakening of the signal corresponding to the nickel peaks, especially that corresponding to the nickel centres more strongly attached to the support. However, there was also a slight decrease of the peaks corresponding to the alumina, which indicates that there was also an interaction of the lanthanum with the support. XPS analysis confirms the existence of an interaction between La and Ni, determined by the superposition of its spectra. This interaction results in the reduction of the nickel particle size and an improvement in the dispersion of the metal through the surface of the support. This effect was more significant in the catalyst supported on alumina than in the one supported on rGO, due to the above mentioned interaction between lanthanum and alumina. Due to the interaction between La, Ni and alumina, the resistance of the catalyst against H₂S poisoning was increased, making more difficult to block the active centres of the metal. This effect was mainly the cause of the contribution of alumina, since as observed in Fig. 6.16, the presence of lanthanum in the 13Ni/14La-rGO catalyst did not mean an improvement in the resistance to H₂S poisoning.

6.4. Conclusions

The CO₂ methanation was studied over catalysts composed of 13 wt% of nickel and different supports based on graphene and alumina. Among graphene-based supports, the best option is the 13Ni/rGO catalyst because unlike 13Ni/AGO, 13Ni/BGO, 13Ni-OI/GO, 13Ni/OI-GO or 13Ni/OI-GO Met retains functional oxygen groups in an accessible way. These allow the anchoring of the active metal to its surface, reaching 78% methane yield values at 810 K and 10 bar.

The ability of graphene oxide derived supports to conduct and dissipate the heat produced in the exothermic methanation reaction probably results in a slight decrease of the hot spot formation and a better uniformity in the temperature thorough the catalyst particle. However, in spite of avoiding hot spots in the catalyst, the progressive increase in temperature causes the rupture of oxygen bonds in the catalyst structure, causing the loss of active centres and loss of catalytic activity.

The use of a graphene oxide derived supports in methanation is not suitable, based on what has been observed in terms of activity or resistance to poisoning, since it did not improve the results obtained for the alumina supported catalysts. A deep study of methods to stabilize this supports when temperature is increased should be performed

Lanthanum interacts with nickel and alumina support, producing a reduction in nickel particle size (from 10 to 5 nm), which improves its dispersion. This, in turn, produces an increase in catalytic activity at lower temperatures (from 44% to 82% at 673K) due to synergetic effect on the catalytic activity of these metals. Finally, the incorporation of lanthanum results in the improvement of the resistance of the catalyst to H₂S poisoning (from 70 to 110 min), making it difficult to block the active centres of the metal and by inhibiting the formation of the S²⁻ bond on the metal surface.

6.5. Acknowledgements

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6.6. References

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CAPÍTULO 7



Conclusiones y proyecciones futuras

"La ciencia siempre se equivoca. Nunca resuelve un problema sin crear otros diez."

GEORGE BERNARD SHAW

El presente trabajo de tesis, se ha centrado en el estudio exhaustivo de nuevos sistemas catalíticos para la reacción de metanación de CO_2 , principalmente basados en níquel como metal activo y alúmina como soporte. Estas formulaciones han sido comparadas con otras más innovadoras empleando soportes derivados del óxido de grafeno. El adecuado desarrollo de los planteamientos definidos en los **capítulos 4, 5 y 6**, ha permitido justificar el **objetivo principal** de esta tesis: se han conseguido desarrollar sistemas catalíticos más eficientes y otros más resistentes al envenenamiento por H_2S en la reacción de metanación de CO_2 . Sin embargo, y aunque no todos los sistemas planteados han logrado mejorar la actividad o la resistencia del catalizador al H_2S , el estudio de sus propiedades físico-químicas, ha permitido determinar aquellas características que aportan los metales o soportes sobre el catalizador y su relación con la actividad y resistencia al H_2S . Esto permitirá desarrollar sistemas catalíticos más eficientes en próximos estudios.

En este **capítulo 7** se recogen las **conclusiones** más relevantes determinadas para los diferentes planteamientos definidos en los capítulos anteriores, junto con algunas ideas sugeridas para plantear **próximos trabajos**, y finalmente unas **conclusiones generales** deducidas de un estudio más amplio de todo el trabajo desarrollado en esta tesis.

Efecto de la adición de Co, Cr, Fe y Mo al catalizador de $\text{Ni}/\text{Al}_2\text{O}_3$. Estudio sobre la actividad, resistencia al envenenamiento por H_2S y regeneración.

En este trabajo se demostró la alta eficiencia del catalizador monometálico $\text{Ni}/\text{Al}_2\text{O}_3$ y de los catalizadores bimetálicos con Co, Cr, Fe y Mo en la reacción de metanación de CO_2 . La comparativa de estos sistemas catalíticos permitió determinar las características aportadas por los promotores al catalizador monometálico, en relación a las propiedades texturales y fisicoquímicas, al efecto en la actividad catalítica y resistencia a la presencia de H_2S , y a la capacidad de regeneración de esos sistemas catalíticos. De este estudio se deducen las siguientes conclusiones:

1. La incorporación de Cr, Fe y Mo sobre el catalizador $\text{Ni}/\text{Al}_2\text{O}_3$ produce una reducción de la dispersión del metal activo, debido a la formación de aglomeraciones, que aumentan el tamaño de partícula del metal. Como consecuencia, el área superficial del catalizador se reduce significativamente, reduciendo la interacción con los reactivos que disminuye la actividad a temperaturas inferiores a 700 K.
2. La actividad del catalizador $\text{Ni}/\text{Al}_2\text{O}_3$ en la obtención de metano se reduce a medida que aumenta la concentración de Mo, debido al bloqueo por este metal de los centros activos de Ni. Sin embargo, cuanto mayor concentración de Mo, mayor es el tiempo de resistencia del catalizador al envenenamiento por H_2S .
3. La incorporación de Fe al catalizador monometálico reduce la dispersión del Ni, no obstante, a medida que aumenta la temperatura se incrementa la actividad de los centros activos, alcanzando un valor de rendimiento a metano del 87% a 742 K, superior al del catalizador $\text{Ni}/\text{Al}_2\text{O}_3$ a las mismas condiciones.
4. El Co inhibe la formación del enlace S^{2-} del H_2S en la superficie del metal, en aquellos centros en los que se observa una mayor interacción entre Co y Ni. Evitando este enlace se reduce la sulfuración del soporte y el sinterizado del metal como consecuencia de la temperatura y del azufre, que permite la recuperación de un 13% de la actividad tras una etapa de regeneración que elimine el H_2S que pueda seguir presente.

5. El estudio del TOF ha permitido relacionar la reducción de la actividad del catalizador a menores temperaturas con la mayor interacción entre los promotores del catalizador, debido a la reducción de la calidad de los centros activos libres disponibles.

Efecto de la adición de alcalinotérreos (Ba, Ca y Mg) y lantánidos (La y Ce) como modificadores del soporte de alúmina en catalizadores basados en Ni y/o Ru.

La modificación del soporte de alúmina con metales alcalinotérreos y lantánidos tuvo un efecto significativo en las propiedades del catalizador, facilitando la reacción que aumentó su rendimiento cuantitativamente. Su efecto es también notable en lo referido a la resistencia del catalizador al envenenamiento por H₂S. Las ideas más destacadas que se recogen de este estudio, se indican a continuación:

6. La incorporación de Ba, Ca y Mg muestran un efecto poco significativo en la actividad del catalizador Ni/Al₂O₃, debido a una escasa interacción con el soporte.
7. El Ce unido al soporte facilita el anclaje de nuevos centros metálicos de Ni, mejorando su dispersión y reducibilidad. Es por ello, que el catalizador Ni/Ce-Al₂O₃ alcanzó un mayor rendimiento, del 96%, a menores temperaturas (618 K) que el catalizador Ni/Al₂O₃ (92% a 668 K).
8. En el catalizador Ni/La-Al₂O₃, la fuerte interacción entre La y soporte facilita la incorporación del Ni en forma de especies NiO fácilmente reducibles, con mayor dispersión y mayor densidad de centros activos. Esto supone una destacada mejora en el rendimiento a metano de este catalizador (98%) a menor temperatura (572 K) que el catalizador Ni/Al₂O₃ (92% a 668 K), resultando por tanto el catalizador Ni/La-Al₂O₃ competitivo frente a catalizadores de metales nobles como el de Ru/Al₂O₃.
9. La adición de Ru como promotor, en combinación con el Ni produce un significativo aumento del rendimiento a metano, debido a una fuerte interacción entre ambos metales. La incorporación de La modificando el soporte en el catalizador Ru-Ni/La-Al₂O₃ mejora la dispersión y reducibilidad de ambos metales, permitiendo alcanzar un alto valor de rendimiento a metano (90%) a una temperatura menor (650 K), para un valor de velocidad espacial de 128,75 h⁻¹. Si se compara con el catalizador Ni/Al₂O₃, no se alcanza un rendimiento del 90% hasta alcanzar los 745 K a la misma velocidad espacial, siendo para el Ni/La-Al₂O₃ del 82% a 680 K.
10. La fuerte interacción entre La o Ce y Ni con el soporte reduce la exposición y dificulta el acceso de las moléculas de H₂S a los centros activos del metal, dificultando su envenenamiento. Sin embargo, la presencia de Ru, debido a su alta sensibilidad al H₂S facilita la desactivación del catalizador.
11. Las altas temperaturas (773 K) y la acción del H₂S producen la completa desactivación de los catalizadores estudiados, sin capacidad de recuperar su actividad tras una etapa de regeneración con O₂. Es posible que se deba a un cambio en la morfología del catalizador, por el cual las estructuras oxigenadas del soporte y los metales que conforman el catalizador bloqueen el acceso de los reactivos a los centros metálicos.

Efecto del empleo de soportes basados en derivados de óxido de grafeno para la metanación de CO₂ con Ni como metal activo y La como promotor.

El óxido de grafeno y sus derivados debido a sus propiedades conductoras del calor y la electricidad, facilitan el control de la temperatura, uniforme en todo el sistema catalítico que conforma como soporte. Con este objetivo se compara su eficiencia en la reacción de metanación de CO₂ con respecto a catalizadores soportados en alúmina, empleando como metal activo Ni y como modificador del soporte La. Se concluye de este estudio:

12. La capacidad de conducción del calor de los derivados del óxido de grafeno permiten disipar el calor de reacción, evitando la formación de puntos calientes que desactiven rápidamente el catalizador por sinterizado. Sin embargo, el aumento de la temperatura de reacción produce la ruptura de los enlaces de oxígeno de la estructura del catalizador, que permiten la fijación del metal, causando la progresiva pérdida de centros activos y de la actividad del catalizador. El sistema catalítico que presenta mayor estabilidad térmica, dificultando la pérdida de grupos funcionales de oxígeno que permitan el anclaje del metal activo a su superficie, es el catalizador Ni/rGO, alcanzando un rendimiento del 78% a 810 K.
13. La incorporación de La modificando el soporte de alúmina, por su interacción entre soporte y Ni produce una reducción de los centros del metal que mejoran su dispersión, aumentando la actividad catalítica a menores temperaturas. Su adición sobre el soporte de rGO no proporciona beneficios sobre la actividad, debido a que los centros funcionales de oxígeno del rGO a los que se une el Ni son los mismos a los que se une el La, no pudiendo proporcionar una mejora en la dispersión al no disponerse de más centros de anclaje.
14. A diferencia de lo ocurrido con el soporte basado en alúmina, en el soporte de rGO, la ausencia de la interacción con el La y el reducido número de centros metálicos que se incorporan, facilita la desactivación por efecto del H₂S.
15. Soportes basados en rGO mejoran la dispersión del calor de la reacción, pero debido a la fuerte disminución de los grupos funcionales de oxígeno en la reducción del GO, se limita el número de centros metálicos que pueden incorporar y por tanto su dispersión. Es por ello, que estos sistemas catalíticos son menos eficientes que los basados en alúmina como soporte.

De lo observado en los resultados obtenidos en las partes que conforman este trabajo de tesis, se pueden recoger tres conclusiones principales, que respondan a todo lo observado durante el desarrollo de este amplio proyecto. Las conclusiones generales son:

- La incorporación de metales como promotores, siempre que se haga en las proporciones adecuadas, y sean activos y selectivos en la reacción de metanación de CO₂, proporcionan beneficios en la actividad catalítica, resistencia al envenenamiento por H₂S, a la coquización o al sinterizado. Todo ello debido a los beneficios aportados respecto a la dispersión y reducibilidad del metal activo, siendo esto específicamente comprobado para el catalizador Ni/Al₂O₃.
- La adecuada elección del metal modificador del soporte puede mejorar significativamente la actividad catalítica y la resistencia a la desactivación del catalizador, debido a una fuerte interacción con el soporte, pero también con el metal. A causa de esta interacción, se reduce el tamaño de partícula del metal

activo, dispersándose con mayor facilidad por toda la superficie del soporte, incrementando la actividad catalítica y dificultando la formación de enlaces entre S^{2-} y el metal activo, en este caso el Ni.

- Los derivados del óxido de grafeno son estructuras de gran utilidad por sus propiedades conductoras y su alta área superficial que, aplicadas a la catálisis, pueden mejorar la dispersión de los metales y evitar la formación de puntos calientes, por la adecuada dispersión del calor. Sin embargo, para ello el número de grupos funcionales de oxígeno que permiten la incorporación del metal debe ser mayor. De lo contrario, la actividad catalítica sería muy baja, siendo menor a la que se puede conseguir con sistemas catalíticos soportados en alúmina, que no dispersan el calor de reacción.

A partir de este trabajo se plantean una serie de ideas para futuros trabajos que podrían ahondar en el conocimiento de los sistemas catalíticos aquí planteados, ofreciendo catalizadores viables para su aplicación a escala industrial con mayor eficiencia y capaces de resistir la presencia de H_2S en la corriente gaseosa de reactivos. En primer lugar, atendiendo a lo observado, un estudio de los sistemas catalíticos con Co, Cr, Fe y Mo como promotores empleando una velocidad espacial mayor permitiría una comparación más detallada del efecto del promotor en la actividad. De manera que, por la combinación de varios promotores, se pudiera obtener un catalizador más eficiente (como puede ser con la adición de Fe), más resistente al H_2S (como puede ser la adición de Mo) y con capacidad de recuperación de la actividad (como puede ser el caso del Co). Para ello sería necesario un estudio en mayor profundidad de las proporciones más adecuadas de estos promotores para su funcionamiento combinado.

El óxido de grafeno y sus derivados son sistemas prometedores en distintos campos dadas sus provechosas propiedades, y el campo de la catálisis no es una excepción. En este trabajo se ha determinado que el sistema más beneficioso para su empleo como soporte del catalizador en metanación de CO_2 es el rGO. Sin embargo, en la etapa de reducción del GO se pierde la gran mayoría de los grupos funcionales de oxígeno, que sirven de anclaje de los centros metálicos del catalizador. Por ello, para aumentar el número de centros metálicos, y por ende, la dispersión de los mismos por la amplia superficie del soporte rGO, es necesario un mayor control de la etapa de reducción para alcanzar un equilibrio entre cantidad de grupos funcionales de oxígeno y propiedades conductoras. Esto permitiría operar a menores temperaturas, evitando la desactivación debido a la descomposición de la estructura de carbono con la temperatura, y mejorando de este modo su actividad. Alcanzado este objetivo, la incorporación de promotores que mejoren la resistencia al envenenamiento por H_2S , como el Mo, o su capacidad de regeneración, como el Co, convertirían este sistema catalítico en un sistema competitivo en metanación de CO_2 .

Finalmente, basado en el problema de la dispersión del calor que eleva la temperatura del catalizador de forma heterogénea, pudiendo provocar la desactivación del mismo por el sinterizado, además del empleo de soportes de óxido de grafeno que dispersen el calor, se plantea el uso de catalizadores estructurados. Estos sistemas se han comenzado a analizar en el desarrollo de esta tesis, pero la desigual impregnación del catalizador a través de los canales de los monolitos desarrollados por impresión 3D o por plegamiento de láminas de aluminio, dificultan una actividad catalítica homogénea y reproducible. Por ello, se plantea un estudio más exhaustivo de este tipo de sistemas, por medio del adecuado control de la viscosidad de la disolución del catalizador, que permita

la homogénea impregnación de toda la superficie del soporte, evitando el bloqueo de los canales para que pueda circular el flujo a través de ellos, llegando los reactivos a todos los centros metálicos del catalizador.



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AUTOCAD ●●●●●●●●
ORIGIN ●●●●●●●●
CHEMDRAW ●●●●●●●●
ASPEN ●●●●●●●●

RESEARCH INTEREST

Heterogeneous catalysis
New energy sources
Valorization of CO₂
Obtaining biofuels



ABOUT ME

The path followed during the academic and professional training process has allowed me to develop my knowledge and skills, applied in the fields of biofuels and bioenergy. Volunteering, jobs and training have strengthened my skills working as a team, leading projects or fostering my creativity and empathy.



EDUCATION

► **University of the Basque Country** March 2017 – Present
PhD in **chemical engineering** developing new metal **catalysts**, supported on **alumina** and **graphene** derivatives, resistant to H₂S poisoning and more efficient in the reaction of CO₂ **methanation**.

► **University of Granada** Sept. 2015 – July 2016
Master in **biotechnology**, applying the knowledge acquired in the **biofuels** sector, developing the **work to conclude the master** focused on obtaining **biodiesel** by **enzymatic** processes from fish waste oils.

► **University of Salamanca** Sept. 2009 – June 2015
Chemical **engineering** with specialization in the field of **biofuels** for the development of the project for the production of **biokerosene** with refined oil from Camelina seeds.



PUBLICATIONS

► A study of deactivation by H₂S and regeneration of a Ni catalyst supported on Al₂O₃, during methanation of CO₂. Effect of the promoters Co, Cr, Fe and Mo. David Méndez-Mateos, V. Laura Barrio, Jesús M. Requies and José F. Cambra. *RSC Adv.*, 10 (2020), 16551-16564.

► Reuse of immobilized lipases in the transesterification of waste fish oil for the production of biodiesel. Marta Marín-Suárez, David Méndez-Mateos, Antonio Guadix and Emilia M. Guadix. *Renewable Energy*, 140 (2019), 1-8.

► Pon color a tu vida y los hongos se encargarán del resto. Mario A. Martínez, Yesica M. Melero, David Méndez-Mateos, Sergio Parejo, María Pinel, Cristina Rodríguez, Maribel N. Tenasaca, Jose Antonio-Gómez, Elisabet Aranda. *Boletín Drosophila*, 22 (2016), 19-22.



CONTRIBUTION TO CONFERENCES

► XXIII International Conference on Chemical Reactors: CHEMREACTOR-23 (Ghent, 2018).

UNIVERSITY TEACHING

Subject: Environmental Science and Technology (2018).

Degree: Industrial Engineer.

ECTS: 6.

OTHER ACTIVITIES

Tutor of student projects 2018. ELHUYAR foundation.

SKILLS

Persistence	●●●●●●
Empathy	●●●●●●
Teamwork	●●●●●●
Leadership	●●●●●●
Creativity	●●●●●●
Proactivity	●●●●●●

Oral and poster presentation, “Power-to-gas: bimetallic catalysts supported on Al₂O₃ and sulphur containing biogas” **David Méndez-Mateos**; Victoria Laura Barrio Cagigal; José Francisco Cambra Ibáñez.

▶ 4th International Symposium on the Catalysis for Clean Energy and Sustainable Chemistry (Bilbao, 2018).

Oral presentation, “Improvement of heat transfer in Katalco-coated metal monolith for methane production from biogas” **David Méndez-Mateos**, Victoria Laura Barrio Cagigal and José Francisco Cambra Ibáñez.

▶ III Workshop de Jóvenes Biotecnólogos (Granada, 2016).

Poster presentation, “Producción de biodiesel a partir de aceites de pescado mediante lipasas de Candida Antártica” **David Méndez-Mateos**, Marta Marín-Suárez, Pedro J. García-Moreno, Antonio Guadix, Emilia M. Guadix.



RESEARCH PROJECT PARTICIPATION

▶ Process for methane generation in remote areas from renewable electric energy. ENE2014-53566-P, 01/01/2015-31/12/2017. V. Laura Barrio Cagigal and José F. Cambra Ibáñez.

▶ Advanced catalytic and photocatalytic technologies for methane production from renewable energies. MINECO. 01/01/2018-31/12/2020. V. Laura Barrio Cagigal.



COURSES

▶ Swagelok fluids seminar (organised by Válvulas y Conexiones Ibérica in Bilbao, 2018, 3 h).

▶ Good Laboratory Practices (II): Waste Management (organised by University of Basque Country in Bilbao, 2018, 25 h).

▶ Improving English – Medium Instruction and Teaching Skills at Level B2+ (organised by University of the Basque Country in Leioa, 2018, 30 h).

▶ Fundamentals and Applications of X-ray Photoelectron Spectroscopy (organised by SGIKER in Leioa, 2017, 20 h).

▶ Introduction to Characterization of Adsorbents and Catalysts (organised by RSEF and RSEQ in Jarandilla, 2017, 22 h).

▶ Aspen Plus: Process Modeling (organised by AspenTech in Bilbao, 2017, 10 h).