Unveiling the deactivation by coke of NiAl$_2$O$_4$ spinel derived catalysts in the bio-oil steam reforming: Role of individual oxygenates

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**A R T I C L E   I N F O**

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Coke deposition
Catalyst deactivation

**A B S T R A C T**

The catalyst stability, mainly affected by coke deposition, remains a challenge for the development of a sustainable process for hydrogen production by steam reforming (SR) of bio-oil. In this work, the influence of oxygenates composition in bio-oil on the deactivation by coke of a NiAl$_2$O$_4$ spinel derived catalyst has been approached by studying the SR of a wide range of model oxygenates with different functionalities, including acetic acid, acetone, ethanol, acetaldehyde, acetyl, catechol, guaiacol and levoglucosan. A fluidized bed reactor was used in the following conditions: 600 and 700 °C; steam/carbon ratio, 3 (6 for levoglucosan); space–time, 0.034 g$_{\text{catalyst}}$/h/g$_{\text{Bio-oil}}$ (low enough to favor the rapid catalyst deactivation); and, time on stream, 5 h. The spent catalysts were analyzed with several techniques, including Temperature Programed Oxidation (TPO), X-ray Diffraction (XRD), N$_2$ adsorption–desorption, Scanning and Transmission Electron Microscopy (SEM, TEM) and Raman Spectroscopy. The main factors affecting the catalyst stability are the morphology, structure and location of coke, rather than its content, that depend on the nature of the oxygenate feed. The deposition of pyrolytic and amorphous coke that blocks the Ni sites inhibiting the formation of filamentous carbon causes a rapid deactivation in the guaiacol SR. Conversely, the large amount of carbon nanotubes (CNTs) giving rise to a filamentous coke deposited in the SR of aliphatic oxygenates only causes a slight deactivation. The increase in the temperature significantly reduces coke deposition, but has low impact on deactivation.

1. **Introduction**

Hydrogen is called to play a key role in future energy demand as a substitute for fossil fuels [1]. In fact, in the post-pandemic crisis scenario, the alternatives for the production and use of renewable H$_2$ are taking on great relevance, as for example in the economic recovery package of EU (NextGenerationEU) with €750 billion focused around the European Green Deal, where renewable energy projects highlight, especially wind, solar and kick-starting a clean hydrogen economy, with centralized bio-oil SR in a bio-refinery with units designed ad hoc for selective H$_2$ production. The liquid state and higher volumetric energy density of bio-oil facilitates its transportation, storage and treatment compared to biomass [7]. In addition, the SR of bio-oil avoids the costly dehydration steps required for the use of bio-oil as fuel or for its valorization in other catalytic processes [8].

Bio-oil is composed of an oxygenate mixture with the presence of different functional groups (carboxyl, ester, carbonyl, ether, phenolic and hydroxyl groups) and variable water content (depending on the origin of the biomass). The SR reaction of oxygenated hydrocarbons (C$_m$H$_n$O$_k$) to produce syngas (H$_2$ + CO) can be described by the following equation:

$$\text{C}_m\text{H}_n\text{O}_k + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$$

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C\textsubscript{2}H\textsubscript{4}O\textsubscript{2} + (n – k)\textsubscript{}H\textsubscript{2}O \rightarrow n\textsubscript{}CO + (n + \frac{m}{2} – k)\textsubscript{}H\textsubscript{2} \tag{1}

In addition to the main reaction (Eq. (1)), the water gas shift (WGS) reaction (Eq. (2)) takes place, and thus the overall SR equation for the oxygensates is defined by Eq. (3).

\begin{align*}
\text{CO} + \text{H}_2\text{O} &\leftrightarrow \text{CO}_2 + \text{H}_2 \tag{2} \\
\text{C}_n\text{H}_m\text{O}_k + (2n – k)\text{H}_2\text{O} &\rightarrow n\text{CO}_2 + (2n + \frac{m}{2} – k)\text{H}_2 \tag{3}
\end{align*}

H\textsubscript{2} yield is also affected by reactions occurring in parallel to oxygensates SR and WGS reactions, such as decomposition/cracking (Eq. (4)), which affects the catalyst stability due to coke deposition, SR of decomposition products (CH\textsubscript{4} and hydrocarbons, Eqs. (5) and (6)), and interconversion of oxygensates (Eq. (7)).

\begin{align*}
\text{C}_n\text{H}_m\text{O}_k &\rightarrow \text{C}_n\text{H}_m\text{O}_k + \text{gas} (\text{CO, CH}_4, \text{CO}_2, \text{C}_x\text{H}_y, \text{H}_2, \ldots) + \text{coke} \tag{4} \\
\text{CH}_4 + \text{H}_2\text{O} &\leftrightarrow \text{CO} + 3\text{H}_2 \tag{5} \\
\text{C}_n\text{H}_m\text{O}_k + a\text{H}_2\text{O} &\rightarrow a\text{CO} + (a + b/2)\text{H}_2 \tag{6} \\
\text{C}_n\text{H}_m\text{O}_k &\rightarrow \text{C}_r\text{H}_r\text{O}_r \tag{7}
\end{align*}

Moreover, the reactions for coke formation from gaseous products (Eqs. (8) and (9)) and its gasification reaction (Eq. (10)) should be considered, as they may affect catalyst stability and also the products yields when they are highly promoted.

**Hydrocarbon decomposition**: C\textsubscript{n}H\textsubscript{m} \rightarrow (b/2)H\textsubscript{2} + a\text{C} \tag{8}

**Boudouard reaction**: 2\text{CO} \leftrightarrow C + \text{CO}_2 \tag{9}

**Coke gasification**: Coke + H\textsubscript{2}O \rightarrow CO + H\textsubscript{2} \tag{10}

One of the main problems or bottlenecks of bio-oil SR is the rapid deactivation of the catalyst, which justifies that it receives a great attention, in order to prepare stable catalysts. Deactivation studies have generally been carried out with model oxygensates [9–20], with mixtures of oxygensates [21–23], and studies with raw bio-oil are limited. [24–29]. The results show the importance of the nature and location of the coke in the deactivation of the catalyst. Thus, the formation of carbon filaments has a reduced incidence in the deactivation, whose responsibility falls mainly on the formation of amorphous coke encapsulating the Ni sites. There is also a general tendency to relate the formation of deactivating amorphous coke to the SR of some families of oxygensates (phenols, carboxylic acids, furfural and saccharides, mainly).

This paper delves into the clarification of deactivation by coke of a catalyst derived from NiAl\textsubscript{2}O\textsubscript{4} spinel, which has been previously proven to have high activity and selectivity to H\text subscript{2} in the reforming of raw bio-oil and, more interestingly, it can be fully regenerated by coke combustion at 850 °C (with spinel reconstruction) [30]. For that purpose, we have studied the influence on the deactivation behavior and coke deposition of individual oxygenate compounds with varied functional groups present in bio-oil (acetic acid, acetaldehyde, acetol, ethanol, acetone, catechol, guaiacol and levoglucosan). The evolution along time on stream of the conversion and products yields in the SR of each individual compound have been analysed, as well as the amount, nature, morphology and location of the coke deposited on the catalyst used by means of several techniques: temperature programed oxidation (TPO), X-ray diffraction (XRD), N\textsubscript{2} adsorption–desorption, scanning and transmission electron microscopy (SEM, TEM) and Raman spectroscopy. The experimental conditions used are similar to those previously used in the SR of raw bio-oil with the same catalyst [31], which has allowed a direct comparison of the catalyst performance in the SR of each individual oxygenate with that obtained in the SR of raw bio-oil. The results have allowed establishing the main responsible of catalyst deactivation during SR of bio-oil, as well as the coke characteristics that mainly affect the deactivation of the catalyst. Consequently, interesting information is obtained to adjust the composition of the raw bio-oil in order to attenuate catalyst deactivation by coke. In addition, the oxygensates of greatest interest as model compounds for the comparison tests of catalyst deactivation for the SR of raw bio-oil are identified.

2. Experimental

2.1. Pure oxygenate compounds

The pure oxygenate compounds selected as representative of the major families of oxygensates in bio-oil are the following: acetic acid (AA) (Romil LTD, purity > 99.9 %), acetaldehyde (AD) (Merck KGaA, purity > 99 %), acetone (A) (ApplChem GmbH, purity ≥ 99.9 %), acetal (AT) (hydroxyacetone, Alfa Aesar GmbH, purity = 95 %), ethanol (E) (Merck KGaA, purity ≥ 99.9 %), 1,2-benzenediol or catechol (C) (Sigma-Aldrich, purity ≥ 99 %), levoglucosan (L) (1,1-Anhydro-β-D-glucopyranose, Acros Organics, purity > 99%), and 2-methoxyphenol or guaiacol (Alfa Aesar GmbH & Co, purity > 98 %) dissolved in 50 wt% of ethanol (G + E) due to its low solubility in water. Acetone, acetaldehyde, 1,2-benzenediol (catechol) and 2-methoxyphenol (guaiacol) are representative of relevant families of compounds in bio-oils such as ketones, aldehydes and phenols (among these, mainly guaiacols and catechols) [32,33]. Acetic acid, levoglucosan and acetic are present in remarkable concentrations in the bio-oil obtained from pyrolysis of pine sawdust [26,34]. The study of the catalyst behavior in the SR of ethanol is interesting because it may be coated with bio-oil for its stabilization and because the SR of bio-oil/bio-ethanol mixture (BO + E) is an interesting route for sustainable H\textsubscript{2} production from two biomass derived feeds [35].

2.2. Catalyst

The catalyst precursor (Ni-Al spinel, NiAl\textsubscript{2}O\textsubscript{4}) was prepared by coprecipitation method with a nominal Ni content of 33 wt% from Ni(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O and Al(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O with a NH\textsubscript{4}OH 0.6 M solution as a precipitating agent. The precipitation was carried out at 25 °C until the pH was fixed at 8. After aging for 30 min, the precipitate was filtered, washed with distilled water to remove the ammonium ions and dried at 110 °C for 24 h. Lastly, the catalyst was calcined at 850 °C for 4 h [30].

The physical properties of the fresh catalyst and deactivated samples (BET surface area, pore volume and mean pore diameter), were characterized by adsorption–desorption of N\textsubscript{2} in a Micromeritics ASAP 2920 for determining the reducibility of the metal species. The amount and nature of coke deposited on spent catalyst samples has been determined by Temperature Programmed Oxidation (TPO) in a TA-Instruments TGA-Q5000IR thermobalance, coupled in line with a mass spectrometer (Thermofar Balzers instrument) for monitoring the signal of CO\textsubscript{2}. The coke content has been quantified from the CO\textsubscript{2} spectroscopic signal, due to Ni oxidation during combustion process masks the thermogravimetric signal in samples with low coke content [30]. The X-Ray Diffraction (XRD) analysis of the reduced fresh and spent catalysts was carried out in a Bruker D8 Advance diffractometer with a CuK\textsubscript{α} radiation, from 10° to 80° with step of 0.04° in 20 and measurement time of 103 min. The scanning electron microscopy images of the fresh or spent catalysts were taken with a Hitachi S-4800 N field emission gun scanning electron microscope (FESEM), with an accelerating voltage of 5 kV and secondary electron detector (SE-SEM) and a Hitachi S-3400 N microscope with an accelerating voltage of 15 kV, using a backscatter electron detector (BSD-SEM). The transmission electron microscopy (TEM) images were obtained in a Philips CM-200 microscope using an accelerating voltage of 200 kV. The Raman spectra were carried out in a Renishaw InVia confocal microscope using an excitation wavelength of 514 nm, taking a spectrum in several areas of the sample for assuring reproducibility.
The N\textsubscript{2} adsorption–desorption isotherm and the BJH pore distribution of the fresh-reduced catalyst are shown in Figs. S1a and S1b, respectively, in the Supporting Information. An isotherm of type IV according to the IUPAC classification is observed in Fig S1a, which is associated with capillary condensation taking place in mesopores, with a hysteresis of the type H2, attributed to a difference in mechanism between condensation and evaporation processes occurring in pores with narrow necks and wide bodies (often referred to as ‘ink bottle’ pores). The BET surface area, pore volume and mean pore diameter for the fresh-reduced catalyst (Table 1) are 65.1 m\textsuperscript{2}/g, 0.24 cm\textsuperscript{3}/g and 13.1 nm, respectively. The TPR profile of the fresh catalyst (Figure S1c) has a maximum H\textsubscript{2} uptake at 760 °C, corresponding to the reduction of Ni species incorporated in the NiAl\textsubscript{2}O\textsubscript{4} spinel structure [30,36]. The XRD pattern of the fresh catalyst prior reduction (black curve in Figure S1d) shows intense peaks at 2θ = 37.2, 45.2 and 65.7° corresponding to the cubic structure of NiAl\textsubscript{2}O\textsubscript{4} spinel, whereas the XRD of the fresh-reduced catalyst (blue curve in Figure S1d) shows peaks corresponding to Ni\textsuperscript{0} (diffraction angle at 44.5° in (1 1 1) plane, 51.8° in (2 0 0) plane and 75.5° in (1 1 0) plane, JCPDS n° 00-004-0850) and Al\textsubscript{2}O\textsubscript{3} (37.3°, 45.6° and 66.8°, JCPDS n° 01-077-0396). This result indicates that the reduction treatment (at 850 °C for 4 h) completely converted NiAl\textsubscript{2}O\textsubscript{4} spinel into reduced Ni crystals supported on Al\textsubscript{2}O\textsubscript{3} (Ni/Al\textsubscript{2}O\textsubscript{3}), as previously reported [36]. The mean Ni crystal size in the reduced catalyst (calculated with the Debye-Scherrer equation using the diffraction peak at 2θ = 52°) is 9 nm (Table 2).

### 2.3. Reaction equipment, operating conditions and reaction indices

Runs have been carried out in an automated reaction system (MicroActivity-Reference, PID Eng & Tech.) that has been described in detail elsewhere [37], with a fluidized bed reactor. The catalyst (with particle size of 150–250 μm to avoid internal diffusional limitations) is mixed with inert solid (SiC, 37 μm particle size) in order to ensure good fluid dynamic behaviour of the catalytic bed (inert/catalyst mass ratio > 8/1). Prior to each steam reforming reaction, the catalytic bed is reduced in-situ by using H\textsubscript{2}-N\textsubscript{2} flow (10 vol% of H\textsubscript{2}) at 850 °C for 4 h, thus forming the active Ni\textsuperscript{0}/Al\textsubscript{2}O\textsubscript{3} catalytic system. The operating condition for the kinetic runs have been: atmospheric pressure; 600 and 700 °C, that are suitable for attaining high conversion in the SR of bio-oil; space time of 0.034 g\textsubscript{catalyst}/h/g\textsubscript{oxygenate} in order to favor catalyst deactivation by coke formation during not excessively long runs (of 5 h duration); steam-to-carbon (S/C) molar ratio of 3 (except for levoglucosan, with S/C = 6 due to its low water solubility), which is suitable for promoting WGS reaction (necessary to enhance H\textsubscript{2} yield) but without excessive penalty of energy requirements. This S/C ratio has been set by co-feeding water (307 Gilson pump) with the feed (injection pump Harvard Apparatus 22). The reaction products were analysed in a Micro GC Varian CP-490 connected in-line to the reactor through an insulated line (130 °C) to avoid condensation of the products. The gas chromatograph is equipped with three analytic channels: molecular sieve MSS for quantifying H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and CO; PPQ column for light hydrocarbons (C\textsubscript{1}-C\textsubscript{4}) to avoid condensation of the products, the gas chromatograph is equipped with three analytic channels: molecular sieve MSS for quantifying H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4} and CO; PPQ column for light hydrocarbons (C\textsubscript{1}-C\textsubscript{4}) to avoid condensation of the products, and Stabilwax for oxygenated compounds (C\textsubscript{6}-C\textsubscript{8}) and water. and Stabilwax for oxygenated compounds (C\textsubscript{6}-C\textsubscript{8}) and water.

In order to quantify the results, the following reaction indices were used:

\[ \text{Carbon conversion to gases: } X = \frac{F_{\text{out, gas}}}{F_{\text{in}}} \]  

(11)

where \( F_{\text{out, gas}} \) is the molar flow rate of the total carbon in gaseous product (CO\textsubscript{2}, CO, CH\textsubscript{4} and light hydrocarbons, in C units contained) at the reactor outlet, and \( F_{\text{in}} \) is the molar flow rate of the oxygenate at the reactor inlet C units contained.

\[ \text{H}_2 \text{ yield: } Y_{\text{H}_2} = \frac{F_{\text{H}_2}}{F_{\text{in}}} \]  

(12)

where \( F_{\text{H}_2} \) is the H\textsubscript{2} molar flow rate in the product stream and \( F_{\text{in}} \), is the stoichiometric molar flow rate, which is calculated as \( (2n + m/2 - k)/n \) \( F_{\text{in}} \) according to the global stoichiometry for the SR of each oxygenate (C\textsubscript{6}H\textsubscript{10}O\textsubscript{5}) (including the WGS reaction) (Eq. (3)).

### 3. Results

#### 3.1. Effect of feed composition on catalyst performance

In order to assess the catalyst activity, selectivity and stability for the different feeds studied, the evolution with time on stream (TOS) of carbon conversion to gas and yield of H\textsubscript{2} at 600 and 700 °C is shown in Fig. 1 (acetic acid (a), acetaldehyde (b), ethanol (c), acetal (d) and acetone (e)) and Fig. 2 (catechol (a), mixture guaiacol + ethanol (b) and levoglucosan (c)).

At 600 °C, the initial H\textsubscript{2} yield (fresh catalyst) varies between 42 % (for aceton, Fig. 1c) and 61 % (for acetaldehyde, Fig. 1b), with similar values (near 50 %) for the rest of oxygenates, thus evidencing similar reactivity at this temperature. The increase in temperature up to 700 °C enhances the carbon conversion to gas and H\textsubscript{2} yield at zero time on

### Table 1

<table>
<thead>
<tr>
<th>Sample*</th>
<th>( S_{BET}, \text{ m}^2/g )</th>
<th>( V_{pore}, \text{ cm}^3/g )</th>
<th>( d_{BJH}, \text{ nm} )</th>
<th>( C_{\text{oxygenate}}, \text{ wt}% )</th>
<th>( r_c \text{ g/(g h)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh-reduced</td>
<td>65.1 (±0.63)</td>
<td>0.24 (±0.01)</td>
<td>13.1 (±0.59)</td>
<td>505</td>
<td>0.843</td>
</tr>
<tr>
<td>AA-700</td>
<td>224</td>
<td>0.24</td>
<td>6.8</td>
<td>104</td>
<td>0.207</td>
</tr>
<tr>
<td>AA-700</td>
<td>125</td>
<td>0.34</td>
<td>13.4</td>
<td>22.1</td>
<td>0.034</td>
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<tr>
<td>AD-600</td>
<td>215</td>
<td>0.27</td>
<td>7.8</td>
<td>222</td>
<td>0.443</td>
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<tr>
<td>AD-700</td>
<td>70</td>
<td>0.25</td>
<td>13.9</td>
<td>2.40</td>
<td>0.005</td>
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<tr>
<td>E-600</td>
<td>266</td>
<td>0.44</td>
<td>11.1</td>
<td>1500</td>
<td>2.001</td>
</tr>
<tr>
<td>E-700</td>
<td>152</td>
<td>0.24</td>
<td>10.9</td>
<td>25.9</td>
<td>0.075</td>
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<tr>
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<td>201</td>
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<td>8.5</td>
<td>207</td>
<td>0.414</td>
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<tr>
<td>AT-700</td>
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<td>0.23</td>
<td>15.7</td>
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<td>0.27</td>
<td>8.7</td>
<td>989</td>
<td>1.974</td>
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<tr>
<td>A-700</td>
<td>139</td>
<td>0.27</td>
<td>10.1</td>
<td>104</td>
<td>0.207</td>
</tr>
<tr>
<td>C-600</td>
<td>147</td>
<td>0.46</td>
<td>19</td>
<td>509</td>
<td>1.018</td>
</tr>
<tr>
<td>C-700</td>
<td>198</td>
<td>0.33</td>
<td>9.2</td>
<td>555</td>
<td>1.109</td>
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<tr>
<td>G + E-600</td>
<td>85</td>
<td>0.25</td>
<td>19.7</td>
<td>332</td>
<td>0.664</td>
</tr>
<tr>
<td>G + E-700</td>
<td>77</td>
<td>0.14</td>
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<td>1014</td>
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<tr>
<td>L-600</td>
<td>83</td>
<td>0.25</td>
<td>13.7</td>
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<tr>
<td>L-700</td>
<td>64</td>
<td>0.24</td>
<td>15.0</td>
<td>0.56</td>
<td>0.001</td>
</tr>
</tbody>
</table>

* The spent catalyst samples are denoted with the name of oxygenated feed (AA = acetic acid; AD = acetaldehyde; E = ethanol; AT = acetal; A = acetone; C = catechol; G + E = guaiacol + ethanol; L = levoglucosan) and the SR temperature (600 or 700 °C).

** The standard deviations evaluated from 3 repetitions.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>( d_{BJH}, \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh-reduced</td>
<td>9 (±1)*</td>
</tr>
<tr>
<td>AA-700</td>
<td>10</td>
</tr>
<tr>
<td>AD-700</td>
<td>9</td>
</tr>
<tr>
<td>E-700</td>
<td>12</td>
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<tr>
<td>AT-700</td>
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<td>A-700</td>
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<td>L-600</td>
<td>17</td>
</tr>
<tr>
<td>L-700</td>
<td>17</td>
</tr>
</tbody>
</table>

* The standard deviation evaluated from 3 repetitions.
stream in the SR of all oxygenates, with this increase being more significant for acetaldehyde, ethanol and acetol (almost 100% conversion), and also for acetic acid and catechol (around 93% conversion). However, it is less noticeable for the guaiacol + ethanol mixture, acetone and levoglucosan, thus evidencing the lower reactivity towards SR reactions at high temperature of the latter oxygenates. The low increase with temperature of the carbon conversion for the guaiacol + ethanol mixture (Fig. 2b), compared to that obtained with ethanol (Fig. 1c), gives evidence of a low effect of temperature for guaiacol, whose reactivity for SR reactions is noticeably lower than that of ethanol, acetic acid, acetaldehyde, acetol and catechol. Moreover, the initial H\textsubscript{2} yield in the SR of ethanol at 700 °C (70%) is lower than that obtained with the other oxygenates (around 80%), in spite of its high carbon conversion (100%). This result reveals the higher selectivity of the catalyst for H\textsubscript{2} forming reactions (steam reforming and WGS) in the SR of acetic acid, acetaldehyde compared to ethanol, whose reforming produces significant CH\textsubscript{4} formation (not shown). The high H\textsubscript{2} yield (80%) obtained in the SR of levoglucosan at 700 °C, in spite of its incomplete carbon conversion, should be attributed to the high S/C ratio used in the SR of this oxygenate (6), that significantly promotes WGS reaction.

Regarding the stability of the catalyst, overall, the conversion and H\textsubscript{2} yield remain constant or even increase (for acetic acid (Fig. 1a), acetol (Fig. 1d) and catechol (Fig. 2a)) at 600 °C and slightly decrease with TOS at 700 °C in the SR of all the studied oxygenates, except for guaiacol + ethanol mixture. The increase in conversion and H\textsubscript{2} yield with TOS can presumably be explained by the formation of a remarkable amount of filamentous coke (as shown later), which leads to an improved Ni dispersion and better accessibility of reactants due to the tip-growth

Fig. 1. Evolution with time on stream (TOS) of carbon conversion to gas (full markers) and H\textsubscript{2} yield (empty markers) in the SR of the light oxygenate compounds: acetic acid (a), acetaldehyde (b), ethanol (c), acetol (d) and acetone (e).
mechanism of carbon filaments [38]. Conversely, in the SR of the guaiacol + ethanol mixture (Fig. 2b) there is a fast decrease in conversion and H\textsubscript{2} yield at both 600 and 700 °C, until the values corresponding to the thermal reaction routes (in the absence of catalyst) are reached. Therefore, this result evidences a much faster deactivation rate of the catalyst in the SR of this mixture than for rest of the oxygenates studied.

3.2. Characterization of deactivated catalyst samples

In order to identify the causes responsible for the deactivation of NiAl\textsubscript{2}O\textsubscript{4} catalyst, and for a better understanding of its deactivation behavior in the SR of the different oxygenates, a thorough characterization of the spent catalyst samples has been performed, by using complementary techniques, that include TPO, SEM and TEM images, XRD, TPR, Raman spectroscopy and N\textsubscript{2} adsorption–desorption. These techniques have allowed determining the amount, nature, morphology and structure of the coke deposited in the catalyst, as well as the changes in the metal sites and porous structure of the catalyst. It should be noted that Ni oxidation was ruled out as deactivation cause, as no significant reduction peaks were observed in the H\textsubscript{2}-TPR profiles of selected deactivated catalyst samples (results not shown here), thus indicating the absence of oxidized species. This is an expected result, which was previously observed in the oxidative steam reforming (OSR) of raw bio-oil with this type of catalyst [39], and it is due to the highly reducing environment in the SR reaction, with a high H\textsubscript{2} content. The results of the rest of characterization techniques are presented in the following sections. The spent catalyst samples have been denoted as X-N, where X identifies the oxygenate feed (AA = acetic acid; AD = acetaldehyde; E = ethanol; AT = acetol; A = acetonitrile; C = catechol; (G + E) = guaiacol + ethanol; L = levoglucosan) and N is the SR temperature (600 or 700 °C).

3.2.1. TPO analysis

Figs. 3 and 4 show the TPO profiles of the deactivated catalysts used in the SR of the oxygenates at different temperatures, obtained from the spectroscopic signal of CO\textsubscript{2} released during coke combustion (as explained in section 2.3). These results provide qualitative information on the nature and/or location of the coke in the structure of the catalyst [40]. Several authors differentiate the amorphous and filamentous coke contents of coke deposited on Ni catalysts by deconvolution of the TPO profiles. Thus, Hu et al. [41], relate each type of coke to one of the two peaks of the TPO, so that the amorphous/paraffinic coke burns at lower temperature than the graphitic/filamentous coke. This identification of the two types of coke allowed verifying that with the addition of Fe there is a higher attenuation of the deposition of the graphitic/filamentous coke in the Fe-Ni/Al\textsubscript{2}O\textsubscript{4} catalysts used in the steam reforming of toluene. The same authors characterize the coke over a Ni/α-Al\textsubscript{2}O\textsubscript{3} catalyst in the steam reforming of two hydrocarbons (toluene and methyl-naphthalene) and two oxygenates (phenol and ethanol) distinguishing amorphous coke from carbon nanotubes (CNTs), whose combustion is identified with the peak at higher combustion temperature [42]. Subsequently, these authors have verified the relevant effect of the steam reforming temperature (in the 500–800 °C range) on the content of the two types of coke and on the quality of the CNTs, proving the existence of a maximum of both at 650 °C [43]. The identification of these two types of coke of different nature by deconvolution of coke combustion TPO profiles was also used to quantify the formation of CNTs on Ni catalysts from the volatiles from polyolefins pyrolysis [44].

The size and location of combustion peaks in Figs. 3 and 4 evidence differences in the amount and nature of coke deposited with the different oxygenates and at different temperature. Noticeably, in the TPO profiles of Figs. 3 and 4 there is apparently a unique combustion
peak, with maximum in the 500–550 °C range for the SR at 600 °C. This maximum shifts towards higher combustion temperature for the catalyst used in the SR at 700 °C, which suggests that the coke evolves into a more condensed and graphitic-like structure, with lower H/C ratio, and therefore, a higher combustion temperature is required [40].

A shoulder burning at low temperature is also observed in the TPO profiles for the samples deactivated at 600 °C with catechol and guaiacol + ethanol (Fig. 4), which is more noticeable for the latter, but is not observed in the SR of the non-phenolic oxygenates (Fig. 3). This result confirms the previously reported relevant role of phenolic compounds as precursors of the coke burning at low temperature (deposited near metal sites, causing its partial or total encapsulation), deposited in the SR of bio-oil over this catalyst [8]. Taking into account the similar amount of this coke type deposited for catechol and for the mixture (guaiacol + ethanol), with only 50 wt% of guaiacol, it can be concluded that the latter is more prone to its formation.

The results of TPO profiles also provide information on the content of coke deposited, estimated from the total area under the TPO profiles, because the calculation of coke content from TGA results (Figure S2) is masked by the mass increase due to Ni oxidation. The results of coke deposition rate, calculated assuming linear coke deposition over the reaction, the coke content notably decreases with reforming temperature in the SR of non-phenolic compounds, but, conversely, it increases in the SR of phenolic compounds (catechol and guaiacol), which suggests a different mechanism of coke formation and evolution for the two groups of compounds. At 600 °C, the amount of coke follows the order: ethanol > acetone > acetic acid ≈ catechol > guaiacol + ethanol > acetaldehyde ≈ acetol > levoglucosan, whereas at 700 °C the order is guaiacol + ethanol > catechol ≫ acetone > ethanol > acetic acid > acetaldehyde > acetol > levoglucosan. It should be noted that S/C ratio used in the SR runs with levoglucosan (S/C = 6), is significantly higher than that used with the rest of oxygenates (S/C = 3), which contributes to the lower coke content obtained with levoglucosan at any temperature.

Comparing the results of Table 1 with the deactivation results (Figs. 1 and 2), it is noteworthy that there is no direct relationship between the amount of coke and the deactivation rate. This result has been also reported in previous works on oxygenates reforming [38,45–49], and is explained by the fact that other characteristics of the coke (morphology, structure and location) have a greater impact on deactivation than its content. In addition, it is observed that with similar TPO profiles in terms of peak position (as is the case of coke for the SR of guaiacol + ethanol and catechol at 600 °C) the deactivation rate is different (much faster in the SR of guaiacol + ethanol). Consequently, although the TPO profile of the coke provides valuable qualitative information on the level of condensation and heterogeneity of the coke, to understand the deactivation of the catalyst it is necessary to complete the information on the coke with other characterization techniques of the deactivated catalyst, which will be shown in subsequent sections.

3.2.2. Physical properties of deactivated catalysts

The textural properties of fresh and deactivated samples (BET surface area, average pore diameter and pore volume) have been determined by means of N₂ adsorption–desorption and are displayed in Table 1. The N₂ adsorption–desorption isotherms of spent catalyst samples are shown in Fig. 5 (ethanol and (guaiacol + ethanol) feeds) and Figure S3 of
Supplementary Information (rest of feeds).

All the samples have isotherm of type IV, but differently to the fresh-reduced catalyst, a H3-type hysteresis cycle is observed for most of the isotherms of catalyst samples used in SR of pure oxygenate compounds, which does not exhibit any limiting adsorption at high P/P₀, and is associated to aggregated of plate-like particles giving rise to slit-shape pores [50]. Overall, the shape of the isotherms in Figs. 5 and S3 for spent catalysts does not change with SR temperature, but there are significant differences in the values of textural properties (BET surface area, mean pore diameter and pore volume, gathered in Table 1). In the region of low partial pressures (P/P₀ ≈ 0), the volume adsorbed in samples of catalyst used in the SR of aliphatic oxygenates and catechol at 600 ºC increases noticeably due to the high BET surface area of these samples (which is more than double that of fresh catalyst). This result can be explained by the deposition of porous carbon structures, such as carbon filaments (in agreement with the SEM images shown later, in Figs. 9 and 10), and is consistent with the high stability observed in the SR at 600 ºC of these oxygenates. In the samples of catalyst used at 700 ºC and with the lowest values of coke deposition (SR of acetaldehyde, acetol and levoglucosan), the physical properties resemble those of the fresh catalyst. On the other hand, the significantly lower total volume adsorbed at high pressures (P/P₀ ≈ 1) in the sample of the catalyst used in the SR of (guaiacol + ethanol) mixture at 700 ºC (Fig. 5a) evidences the partial blockage of the mesopores, thus causing a decrease in BET surface area and mean pore volume (in spite of a high presence of carbon filaments). This partial blockage of the porous structure would contribute to a rapid deactivation, as observed in the SR at 700 ºC of this feed (Fig. 2b).

3.2.3. Metallic and structural properties of spent catalyst

The XRD was carried out to analyze the crystalline structure of the catalyst and of the coke, and also to determine the average size after reaction of Ni metal crystals, by means of Debye-Scherrer equation, at 2θ = 51.8º (Ni²⁺ (200) plane). Fig. 6 shows the XRD diffractograms of spent catalyst samples used in the SR of oxygenates at 600 ºC (graph a) and at 700 ºC (graph b). The XRD diffractogram of the fresh catalyst is also shown in Fig. 6 for comparison. The same diffraction peaks as in the fresh-reduced catalyst are observed in the spent catalyst samples. Therefore, the presence of NiO is not detected, in agreement with H₂-TPR results, which corroborates the high reducing capacity of the reaction medium to keep the active metal in a reduced state.

Moreover, the XRD pattern of most of the spent catalysts shows the presence of a broad peak at a diffraction angle 2θ = 26 º, which corresponds to high crystallinity cokes (graphite carbon), a characteristic peak usually identified in catalysts used in the steam reforming of pure
oxygenate compounds (or some mixtures), such as ethanol \([51]\), acetone \([52]\) or acetic acid \([53]\). The intensity of this peak is in a reasonable agreement with carbon amounts (Fig. 5). Thus, its intensity is high for all the samples deactivated at 600 °C, except for levoglucosan, and for the samples deactivated at 700 °C with phenolic compounds or acetone in the feed, but it is not observed for levoglucosan, acetaldehyde and acetol, due to their low coke content (<3%). Nevertheless, there is not a linear relationship between the intensity of this peak and the amount of coke, which is consequence of differences in the crystallinity level of the different coke deposits.

The calculated average values of Ni\(^0\) particles for fresh-reduced and spent catalysts are gathered in Table 2. It should be noted that the calculation is possible only with low-moderate coke content (below 120 wt%), because a high coke content hinders the measurement of metal crystal size from XRD diffractograms (as it masks the Ni\(^0\) diffraction peaks). The values of average size of Ni\(^0\) crystallites of all used catalysts in Table 2 are around that of fresh catalyst (9 nm), except for SR of levoglucosan, that slightly increases. This moderate sintering of Ni\(^0\) crystals could be the responsible of the moderate deactivation rate observed in the SR of levoglucosan (Fig. 2c), in spite of the low coke content deposited in these experiments (Fig. 5).

3.2.4. Morphology and location of coke

Figs. 7 and 8 show the BSD-SEM images for the catalyst used in the SR of oxygenates at 600 and 700 °C, respectively. The BSD-SEM images allow determining the presence of some type of elements on the external

Fig. 7. BSD-SEM images of the catalysts used in the SR of acetic acid (a), acetaldehyde (b), ethanol (c), acetol (d), acetone (e), catechol (f), guaiacol + ethanol (g) and levoglucosan (h) at 600 °C.
surface of the particles based on the brightness intensity [47]. Thus, the high brightness intensity of the fresh catalyst (Figure S4) indicates the presence of heavy elements (Ni and Al) constituting the catalyst phases (Ni crystals and Al₂O₃). In contrast, the particles of the spent catalysts are generally homogeneous and exhibit a low brightness intensity (dark appearance), which indicates the majority presence of coke on the particle external surface. However, the catalyst used in the SR of levoglucosan at 700 °C (Fig. 8h) shows an homogeneous high brightness intensity, similar to that of the fresh catalyst, which confirms the very low coke deposition observed in the TPO results. On the other hand, the catalyst used in the SR of acetaldehyde at 700 °C (Fig. 8b) shows heterogeneous particles, some with high brightness intensity and others with a dark appearance, which is indicative of the heterogeneous coke deposition.

Additionally, these images also show differences in the particle shapes and textures that can be correlated with the coke content (Table 1). When the coke content is low (below 20 wt%), the particle shape of the spent catalysts (SR of levoglucosan at 600 °C (Fig. 7h) and acetaldehyde, acetol and levoglucosan at 700 °C (Fig. 8b, 8d and 8h, respectively)) is similar to that of the fresh catalyst, being irregular with a smooth surface and sizes in between 150 and 250 μm (original catalyst particle size). When the coke content is moderately high (between 20 and 120 wt%), the particle texture of the spent catalysts (SR of acetic acid, ethanol and acetone at 700 °C (Fig. 8a, 8c and 8e, respectively)) changes to a rough surface keeping the original catalyst particle size. In particular, the catalyst used in the SR of acetic acid at 700 °C (Fig. 8a)
shows bare catalyst particles with fragments of coke shells, evidencing the low mechanical strength of the superficial coke shells. When the coke content is high (above 200 wt%), the particles of the spent catalysts (rest of the experiments) have a rough surface and are remarkably smaller than the original catalyst particle size, which may indicate a collapse of the catalyst particles due to the excessive coke growth.

Figs. 9 and 10 show the SE-SEM images of the spent catalyst surfaces. In general, at 600 °C (Fig. 9), the images show the formation of carbon filaments from all the model compounds with different characteristics (heterogeneous in size and texture). In particular, the carbon filaments from SR of ethanol (Fig. 9c) show a rough surface, indicating the growth/deposition of carbon along the filaments. Additionally, the formation of an amorphous carbon phase is observed in the catalyst used in the SR of guaiacol + ethanol (Fig. 9g), and in comparison with the catalyst used in the SR of ethanol (Fig. 9c), this carbon phase is inferred to be formed from guaiacol. At 700 °C (Fig. 10), the SE-SEM images clearly show the predominant formation of carbon filaments from acetic acid, acetaldehyde, ethanol, acetone and catechol. The aforementioned peculiar feature of the carbon filaments from ethanol is highly noticeable at this temperature (Fig. 10c), indicating the growth/deposition of carbon along the filaments is favored. A second carbon phase in between the filaments is observed in the SR of guaiacol + ethanol (Fig. 10g), probably due to the formation of pyrolytic carbon from guaiacol (as explained in discussion section) which is more predominant on some regions of the catalyst surface (Figure S5). On the other hand, the surface of the spent catalysts with low coke content (SR of acetol and levoglucosan (h) at 600 °C.

**Fig. 9.** SE-SEM images of the catalysts used in the SR of acetic acid (a), acetaldehyde (b), ethanol (c), acetol (d), acetone (e), catechol (f), guaiacol + ethanol (g) and levoglucosan (h) at 600 °C.
levoglucosan, Fig. 10d and 10 h, respectively) resembles that of the fresh catalyst, which confirms no significant coke deposition.

To study the location of coke on the catalyst surface, Figure S6 shows contrasts of BSD-SEM and SE-SEM images for selected spent catalyst samples. In the spent catalyst with carbon filaments, Ni crystals are often visualized on the tip of the filaments, but not for all the cases. Interestingly, for the catalyst used in the SR of acetic acid at 600 °C (Figure S6c), a large filament was captured showing various Ni crystals along it, which indicates that various Ni crystals may be involved in the growth of large filaments. To complement these observations, selected spent catalyst samples were also analyzed using TEM, and the images (Figures S7 and S8) evidence the formation of hollow carbon filaments (carbon nanotubes) with thick walls (probably multiwall carbon nanotubes, MWCNT) and the presence of Ni crystals on the tip of or along the filaments with no evidence of sintering. Particularly, the catalysts used in the SR of guaiacol + ethanol at 600 and 700 °C (Figure S7) showed two carbon phases (amorphous and filaments). The presence of Ni crystals on the tip of the filaments is an expected observation based on the tip growth mechanism commonly described for the formation of carbon filaments on different Ni catalysts used in the SR of oxygenates [38,42,54,55]. It also explains the catalyst stability observed in the experiments for the SR of acetic acid, acetaldehyde, ethanol, acetol, acetone, catechol and levoglucosan (Figs. 1 and 2) in spite of the high content of filaments, because Ni crystals are exposed and accessible for the reactants. However, the rapid catalyst deactivation observed for the SR of guaiacol + ethanol in Fig. 2b is associated to the formation of a

![Fig. 10. SE-SEM images of the catalysts used in the SR of acetic acid (a), acetaldehyde (b), ethanol (c), acetol (d), acetone (e), catechol (f), guaiacol + ethanol (g) and levoglucosan (h) at 700 °C.](image-url)
second carbon phase at 600 and 700 °C, which is also observed in the SR of raw bio-oil [31,34]. This carbon phase is formed from guaiacol and has an amorphous nature at 600 °C and a pyrolytic nature at 700 °C based on the coke combustion characteristics (Fig. 4a and 4b, respectively).

3.2.5. Structural properties of coke

Fig. 11 shows the Raman spectra of selected spent catalyst samples to further study the structural properties of coke. All the samples show the typical D (corresponding to disordered aromatic structures, at ~1343 cm⁻¹) and G (corresponding to condensed, ordered or graphitic aromatic structures, ~1589 cm⁻¹) bands as commonly found for various carbon structures, and the corresponding second-order bands in the 2500–3500 cm⁻¹ region (Figure S9) [31,56,57]. At 600 °C, the G and D bands have similar features for all the spent catalyst samples (SR of ethanol, acetol, guaiacol + ethanol and levoglucosan) with noticeable different intensities for the D band. The intensity ratio between the D and G band (I_D/I_G) determined from deconvolution (procedure described in the SI document and results summarized in Table 3) is notably higher for the coke formed from the SR of ethanol, and consecutively decreases for the coke corresponding to acetol, levoglucosan and guaiacol + ethanol. At 700 °C, the D and G band features are significantly different. Thus, the coke formed from ethanol has narrow D and G bands, the G band has a shoulder at 1605 cm⁻¹ and noticeable higher I_D/I_G ratio. The spectra of the coke formed from levoglucosan present a high noise level, which is coherent with the low coke content determined from the TPO analysis.

Moreover, the Raman spectra mostly correspond to carbon nanotubes (CNT) with different structural qualities, in coherence with the results of SEM and TEM analyses, which revealed the presence of CNT in the catalysts used in the SR of ethanol, acetol, guaiacol + ethanol and levoglucosan at 600 °C and ethanol and guaiacol + ethanol at 700 °C. The spectrum for ethanol at 700 °C is very close to that of MWCNT, exhibiting dominant narrow D and G bands [58–60]. The intensity ratio between the D3 (assigned to amorphous carbon) and G bands (I_D3/I_G) (listed in Table 3) provides an indicator for measuring the quality of carbon nanotubes [59], indicating that those formed from ethanol at 700 °C would have the highest purity having the lowest I_D3/I_G ratio (0.06).

It is also observed that the Raman spectra for the catalyst used in the SR of guaiacol + ethanol at 600 and 700 °C is typical of carbon structures with different degree of order [61], which is in agreement with the formation and deposition of a second carbon phase between the filaments. This result is in agreement with the BSD-SEM (Fig. 8g) and SE-SEM (Fig. 10g) images discussed above. Based on the I_D/I_G ratio, being higher at 700 °C than at 600 °C, the second carbon phase is predominantly amorphous with ordered domains below 2 nm, but it is more structured at 700 °C, which is consistent with the higher combustion temperature observed in the TPO analysis (Fig. 4b). This relationship between TPO and Raman spectroscopic analyses has been also observed for this catalyst used in the SR of raw bio-oil [31], evidencing the formation of carbon filaments and amorphous carbon with different degree of order, which indicates an analogy between coke deposition in the SR of guaiacol and raw bio-oil.

4. Discussion

The deactivation of the catalyst in the oxygenates SR can be explained by the steps in Fig. 12, where the nature of the coke is key.

4.1. Coke as the main cause of deactivation

The characterization of deactivated catalyst samples (amount and morphology of coke deposits, sections 3.2.1, 3.2.4 and 3.2.5, as well as physical, metallic and textural properties, section 3.2.2 and 3.2.3) has allowed establishing the deactivation causes of the NiAl₂O₄ spinel derived catalyst in the SR of the different oxygenates at 600 and 700 °C. Firstly, Ni oxidation has been ruled out as a deactivation cause, due to the absence of reduction peaks (TPR) or NiO XRD diffraction peaks in all the spent catalysts, which is coherent with the highly reducing atmosphere along the SR reactions, and is in agreement with the results reported for the SR of raw bio-oil [31]. Secondly, Ni sintering does not appear to be a relevant cause of deactivation of this catalyst, since it is not observed a significant increase in the average Ni⁰ crystal size, except for SR of levoglucosan, where a slight deactivation is

![Fig. 11. Raman spectra of the catalysts used in the SR of ethanol, acetol, guaiacol + ethanol and levoglucosan at 600 °C (a) and 700 °C (b).](image-url)
4.2. Relevance of coke nature in deactivation

By relating the results of TPO analysis and SEM images of the deactivated samples (sections 3.2.1 and 3.2.4) to the deactivation rate of the catalysts, it has become clear that deactivation is directly related to the nature of the coke, in agreement with previous results in literature for different catalysts [38,45-49]. Thus, a large amount of filamentous coke is deposited in the SR of most of the pure oxygenates studied (especially at 600 °C), but it does not cause a significant impact on the activity of the catalyst. The increase in S(BET) (Table 1) and the BSD-SEM images (Figs. 7 and 8) for the catalyst used in the SR of oxygenates (such as acetic acid, acetaldehyde, ethanol, acetal and acetone) evidences the deposition of a porous and filamentous coke with contents in the catalyst above 20 wt%, but that does not hinder the access of reactants to metal sites in the reaction time studied. However, for a high time on stream, it can create a slight plug on pores or it may grow as clumps of entangled filaments that encapsulate metal particles [47], which can originate a decrease in activity as that observed at high reaction time in the SR of ethanol (Fig. 1c).

The low values of S(BET) in the catalyst used in SR of guaiacol + ethanol (only slightly above that of fresh catalyst) is explained by the formation of both i) filamentous coke that is probably stacked on the surface of the catalyst and causes an increase in BET surface area (with high contribution of ethanol to the formation of this type of coke), and ii) an amorphous carbon phase in between the carbon filaments, probably due to the formation of pyrolytic carbon from guaiacol, which is promoted at high temperature, and that clogs the porous structure and contributes to the rapid deactivation observed for the mixture (guaiacol + ethanol) (Fig. 2b). This formation of pyrolytic coke by repolymerization of phenols in bio-oil is well established in the literature [62].

According to the literature, the importance of the catalyst in the nature of the coke should be pointed out. Thus, Zhang et al. [48], observed the prevalent formation of amorphous coke from guaiacol on Ni/Al2O3 catalyst, whereas carbon nanotubes are preferentially formed on Ni/SBA-15 catalyst.

4.3. Role of the different oxygenates in deactivation

Due to the filamentous nature of coke, the catalyst stability is high in the SR of non-phenolic oxygenates, (Fig. 1), as well as in the SR of catechol (Fig. 2a) and levoglucosan (Fig. 2c). Conversely, the catalyst undergoes complete deactivation after 300 min reaction in the SR of the guaiacol + ethanol mixture at both temperatures studied. Taking into account the high stability observed in the SR of ethanol (Fig. 1c), it can be concluded that guaiacol is the responsible of the rapid catalyst deactivation observed in Fig. 2b.

The origin of long and heterogeneous carbon filaments in the SR of aliphatic oxygenates (Figs. 9 and 10) can be attributed to the reaction of CO (Boudouard reaction, Eq. 9) and CH4 decomposition (Eq. 8) [51,63,64]. As CH4 decomposition is favoured above 750 °C, in the conditions of this study the main origin of this coke is probably the exothermic Boudouard reaction, whose extent is favoured at lower temperature. Moreover, in the SR of ethanol at 600 °C with the same catalyst, the contribution to the formation of filamentous coke by the route of dehydration to ethylene over the acid sites of the Al2O3 support followed by the ethylene decomposition on the Ni-Al2O3 interface has been proved [36]. Also, acetone is an important precursor of filamentous coke [14,65], which can explain the higher amount of coke deposited in the SR of acetone than in the SR of acetic acid.

The formation of filamentous coke is also significant in the SR of the phenolic compounds, as revealed by SEM images (Fig. 9f, 9g, 10f and 10g), and the high combustion peak located at high temperature in the TPO profiles (Fig. 4). But differently to the SR of aliphatic oxygenates, the presence of a small coke fraction burning at low temperature (amorphous and encapsulating coke) is observed in the SR at 600 °C of catechol and more notoriously in the SR of the guaiacol + ethanol mixture (Fig. 4a). For this latter feed, the formation of this amorphous carbon phase could explain the lower amount of filamentous coke deposited at this temperature (Fig. 9g) compared to the SR of ethanol (Fig. 9c). Thus, the formation of encapsulating coke on metal sites hinders the mechanisms of filamentous coke formation, which requires diffusion of C species through Ni metal particles, their precipitation on the base of the Ni crystallite and the formation of a carbon filament growing in size [51,66]. This synergy in the mechanism of formation of each type of coke from each oxygenate makes it difficult to understand the mechanism of coke formation from a complex mixture such as raw bio-oil.
4.4. Effect of temperature

The difference in the results of coke amount at 600 and 700 °C can be explained by the effect of temperature on the reactions involved in their formation (mainly Boudouard reaction (Eq. 9) and polymerization reactions) and their elimination (gasification reaction, Eq. (10)). Thus, the polymerization and gasification reactions are favored with the increase in temperature, whereas the Boudouard reaction is disfavored. Consequently, the increase in the reaction rate of gasification and the lower extent of Boudouard reaction explain the sharp reduction of coke amount on the catalyst observed in the SR of aliphatic oxygenates at 700 °C [67]. Nevertheless, in the SR of phenolic oxygenates the coke amount is higher at 700 °C, especially for the guaiacol + ethanol mixture, because guaiacol polymerization (with pyrolytic carbon formation, Fig. 10g) is favored to a greater extent than gasification. A similar result was previously reported for other heavy oxygenates like glucose and m-xylene [14,20].

This effect of temperature on coke formation is very important in the reforming of levoglucosan, where the coke amount is 16.7 wt% at 600 °C and 0.5 wt% at 700 °C. Considering the ease of cracking of this oxygenate [68] it can be understood that the increase in the cracking rate favors the SR of the intermediates to a greater extent than their polymerization, which explains the low coke deposition. The extent of thermal cracking is different for each oxygenate in the bio-oil depending on its functionality, which affects the results of the raw bio-oil SR, and in particular deactivation. Moreover, increasing the temperature above 700 °C also favors the gasification of the coke retained in the catalyst, attenuating its development towards filamentous structures. However, as aforementioned, this strategy has the unfavorable effect of Ni sintering. It should be noted that this problem is minimized with the NiAl2O4 spinel derived catalyst, which recovers its spinel structure by controlled calcination, recovering the dispersion and size of the Ni0 crystals in successive reaction-reduction-regeneration cycles [30].

4.5. Comparison with deactivation in the SR of raw bio-oil

In a previous study of the deactivation of the same NiAl2O4 spinel derived catalyst in the SR of raw bio-oil [31] was found that the coke is mainly constituted of short and heterogeneous filaments, representing much lower amounts than those formed in this work from aliphatic oxygenates, being remarkable the presence of amorphous and encapsulating coke. Based on the results of the present work, the formation of this coke may be attributed to the high content of guaiacols and catechols, and heavier phenolic compounds in raw bio-oil, whose polymerization significantly inhibits the mechanisms of formation of abundant and long carbon filaments on the catalyst surface from aliphatic oxygenates present in bio-oil.

Consequently, the phenolic compounds have a relevant role in the deactivation of the NiAl2O4 derived catalyst during the SR of raw bio-oil. Nevertheless, the decrease in carbon conversion [31] is faster than that observed in the SR of the guaiacol + ethanol mixture (Fig. 2b), which evidences the significant contribution of other compounds in bio-oil, most probably heavier phenolic compounds, to the deactivation of the catalyst. Moreover, a synergistic effect of the presence of different compounds in bio-oil (with different functionalities) could also contribute to a more rapid deactivation in the SR of bio-oil than in the SR of each pure oxygenated compound. Consequently, in order to establish a mechanism that faithfully represents the reality of coke formation and catalyst deactivation in the SR of raw bio-oil, the study of pure oxygenated model compounds is not sufficient, but studies of co-feeding of binary mixtures and progressively more complex mixtures are required. However, based on the results of this work, it is advisable to separate the phenolic components from the raw-bio-oil to mitigate the deactivation by coke, although this implies a decrease in the H2 yield and the formation of a byproduct stream.

5. Conclusions

The deactivation of the NiAl2O4 spinel derived catalyst in the SR of oxygenates at 600–700 °C is a consequence of coke deposition, whose effect on the deactivation rate highly depends on the oxygenates nature, which determines the coke nature and its deactivation ability. Thus, the formation of filamentous coke from the aliphatic oxygenates by the Boudouard reaction has a reduced deactivation effect, because it does not block the porous structure of Al2O3. However, the formation of amorphous and Ni-encapsulating coke in the SR of guaiacol leads to a rapid deactivation of the catalyst. The increase in temperature from 600 to 700 °C has low impact on deactivation because it favors the extent of encapsulating coke formation reactions by polymerization but attenuates the formation of filamentous coke by promoting its gasification.

Presumably, in the SR of raw bio-oil a synergy between the mechanisms of coke formation from the different oxygenates present is to be expected. But according to the results of this work, the formation of encapsulating coke from phenolic oxygenates is preferential and inhibits the formation of filamentous coke from aliphatic oxygenates. Consequently, the results of this work can be applied to: i) use guaiacol as oxygenate model to test the stability of new catalysts and adapt the reaction conditions in order to minimizing deactivating coke, and ii) design of pretreatment methods of bio-oil in order to eliminate the guaiacol and phenolic components in order to minimizing the formation of this coke.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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