Functionalization of Cu₃BTC₂@IL composites with Pd(II) for catalytic applications

Edurne S. Larrea
Marta Iglesias
M. Isabel Arriortua
Dept. Mineralogy and Petrology, University of the Basque Country (UPV/EHU), Sarriena s/n, Leioa, Spain
edurne.serrano@ehu.eus
marta.iglesias@icmm.csic.es
maribel.arriortua@ehu.eus

Introduction

Metal-organic frameworks could be excellent supports for active catalytic species in order to obtain heterogeneous and reusable catalysts, easily removable from the reaction media.[1,2] Additionally, the presence of unsaturated metal centres in their pores provides a superb opportunity to tackle with reactions that requires more than one type of metal centre.[3] In order to obtain heterogeneous catalysts, we have immobilized Pd(II) into the pores of the well studied Cu₃BTC₂ MOF (BTC = benzene-1,3,5-tricarboxylate) with the help of imidazolium derivated ionic liquids (IL).

Preparation method

1st step: MOF@IL composite formation

Cu₃BTC₂ activation at 140ºC

IL molecules are located into Cu₃BTC₂ channels.

2nd step: MOF@IL composite functionalization

Cu₃BTC₂@0.4[BMIM][Cat] activation at 140ºC

The basic treatment assisted the protonation of the imidazolium cations present in the Cu₃BTC₂ channels. Pd(II) can establish a bond with the carbene containing the bimetallic catalyst.

Catalytic activity tests

Suzuki-Miyaura cross-coupling

R Solvent Base Cu₃BTC₂@0.4[BMIM][Cat] (t) C₁ C₂ C₃ S₁
Me MeOH K₂CO₃ 91% (1.5h) 61% 9% 21% 67%
MeO MeOH K₂CO₃ 67% (4h) 67% 0 0 100%

The catalyst seem to be active for the Suzuki-Miyaura cross-coupling. However, after during the reaction the catalysts suffers a structural transformation. For this reason, we concluded that the catalyst is not heterogeneous.

Sonogashira cross-coupling

Catalyst Solvent Base Cu₃BTC₂@0.4[BMIM][BF₄] 0.1Pd Toluene Et₃N 70% (22h) 0 70% 0%
Cu₃BTC₂@0.4[BMIM][BF₄] Toluene Et₃N 0% (20h)

The reaction with the Pd(II) functionalized MOF@IL composite does not yield the cross-coupling product, but the ethynylbenzene homocoupling reaction one. The not functionalized composite is not active for this reaction. Hence, the active species is the Pd(II)

Amine alkylation

For the alkylation of aniline the catalyst seem to be active but the yield of the reaction is quite low. The recovered catalyst maintained the catalytic structure. More work should be done to improve the conversion and to confirm the heterogeneous nature of the catalyst for this reaction.

Acknowledgements: This work has been financially supported by the “Ministerio de Economía, Industria y Competitividad” (MAT2016-76739-R (AEI/FEDER, UE)), the “ Gobierno Vasco” (Basque University Research System Group, IT630-13 and Dept. of Economic Development and Competitiveness, ELKARTEK program, LISOL (KK-2016/00095) project), which we gratefully acknowledge. The authors thank the technicians of SGIker (UPV/EHU).