

Role of Mo in catalysts based on noble metals in hydrodeoxygenation reactions

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1. Introduction

The use of bio-energy as a renewable alternative to fossil fuels is nowadays attracting more and more attention. The bio-fuel from biomass seems to be a potential energy substitute for fossil fuels since it is a renewable resource that could contribute to sustainable development and global environmental preservation and it appears to have significant economic potential¹. The problem is its high oxygen content, which gives undesirable properties for combustion. To remove oxygen, catalytic hydrodeoxygenation (HDO) reactions are carried out. Monometallic Mo/Si, Pt/Si as well as bimetallic PtMo/Si catalysts were prepared and evaluated in the hydrodeoxygenation (HDO) reaction of dibenzofurane (DBF) as a model molecule in biomass derived bio-oil.

2. Experimental

In this study, a bimetallic PtMo catalyst supported on silica containing 2 wt% of metal and a Pt/Mo molar ratio equal to 1 was prepared by incipient wetness impregnation method. Moreover, Pt and Mo monometallic samples, with a total metallic loading of 1%wt, were also synthesized in order to evaluate the synergism between both phases. The prepared catalysts were characterized by different experimental techniques (XRD; H₂-TPR, N₂ physisorption, NH₃-TPD, TEM and XPS) in order to understand its structure, texture and acidic properties, as well as, to correlate catalyst structure-catalytic activity. For the activity tests, 0.25 g of fresh catalysts (particle size 0.85–1.00 mm) were used, diluted with SiC to 3 cm³. Catalytic activity was measured on DBF at 275 °C and 1.5 MPa of H₂; the H₂ flow rate was 30 mL·min⁻¹ and the organic feed flow 0.18 mL·min⁻¹.

3. Results and discussion

The BET surface area values of the monometallic samples do not differ considerably compared to the bimetallic one (Table 1). The bare support isotherm is of type II, characteristic of materials with meso and macroporosity. The supported catalysts underwent an increase of N₂ adsorbed at relative pressures higher than 0.8, indicating the presence of pores of larger diameter. The increase in volume is due to the fact that the active phase is mainly deposited in the interparticular voids of fume silica². XRD showed the presence of MoO₃ diffraction peaks in the case of monometallic Mo/Si sample while no peak was evidenced in the case of Pt/Si one. For PtMo/Si, the presence of tiny diffraction peaks due to the presence of Pt⁰ was only observed. These results show that in the bimetallic sample Mo is dispersed and instead Pt is more agglomerated if compared to monometallic sample. If TPR and TPD data are considered, the behavior of Mo noticeably changes under the presence of Pt. Thus, the TPR profile of Mo/Si sample shows a broad reduction profile with a hydrogen consumption H₂/Mo equal to 1.01, due to the reduction of Mo(VI) into

Mo(IV). Instead, in the bimetallic sample the hydrogen consumption is very low. In line with this, a similar behavior is observed from NH_3 -TPD data (Table 1). Mo/Si sample desorbs a large amount of ammonia mainly in the range of weak strength acidity. Nevertheless, the acidity is much more moderate in the case of monometallic Pt and bimetallic PtMo samples. These data point to a kind of interaction between Pt and Mo that modulates the reducibility and acidity of the bimetallic catalysts.

Monometallic catalysts were evaluated in the HDO reaction of dibenzofuran, at 275 °C and 15 bar of pressure (Figure 1). These catalysts fail to achieve the conversion values obtained with the bimetallic catalysts, the best conversion being that of the monometallic Pt catalyst, which showed a HDO conversion value of 55%. Monometallic molybdenum oxide catalyst did not showed activity under the same conditions. While, bimetallic catalyst showed a HDO conversion value near 80% at 15 bar. Important conclusions can be extracted from this graph: although molybdenum oxide alone did not presented catalytic activity, it plays an important role when added to a noble metal catalyst. Thus, in bimetallic catalyst the HDO capability improved if compared to the monometallic ones. Therefore it can be thought that Mo promotes the hydrogenolysis reaction.

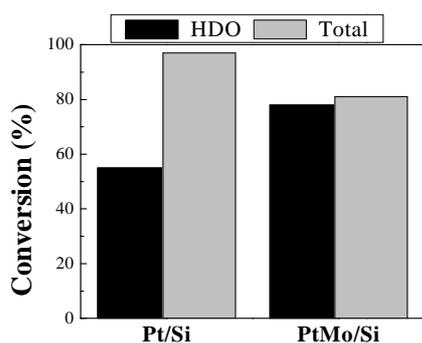


Figure 1. Conversion values after 6 hours on stream for mono and bimetallic catalysts.. Reaction conditions: T = 275 °C, P: 15 bar, LHSV = 3.6 h⁻¹, GHSV = 7200 Ncc/g_{cat}h, H₂ contact time = 6 s, H₂/DBF=69.1.

Sample	S _{BET} (m ² g ⁻¹)	Acidity (μmol NH ₃ g ⁻¹)			
		Weak	Medium	Strong	Total
SiO ₂	217	-	-	-	-
Mo/SiO ₂	161	434	78	0	512
Pt/SiO ₂	188	30	33	4	67
PtMo/SiO ₂	192	61	35	19	115

Table 1. Textural and acidic properties of the different samples prepared.

4. Conclusions

Experimental results showed that the active phase had much influence on the activity and selectivity to the different reaction products, although, in all cases. Molybdenum played a very important role in the case of bimetallic catalyst. Molybdenum species improved the selectivity to O-free products and related to its capacity to break the C-O bond. However, molybdenum activity was nil in absence of noble metal.

References

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