

“Effect of Support on NiMo/MnO-Al₂O₃ catalysts: Application on Hydrodesulphurization of dibenzothiophene”.

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Introduction

In order to get diesel and gasoline fuels with ultra-low (10-15 ppm) sulfur content catalysts currently used in hydrodesulphurization processes must be improved. The most used catalyst support in hydrotreating processes is γ -Al₂O₃. This catalyst support offers interesting textural and mechanical properties and it is able to allow formation of well-dispersed MoS₂ nanocrystallites decorated with Co or Ni promoter atoms according to Topsoe's model [1]. Nevertheless, interaction between Ni- or Co- atoms and supports form NiAl₂O₄ (CoAl₂O₄) spinels, leading to activity loss. In addition, Al₂O₃ acid character allows coke formation and consequently, catalytic deactivation. We suggest that addition of MnO to Al₂O₃ could change its acid character and consequently increase activity and selectivity of the catalyst.

Materials and Methods

MnO-Al₂O₃ with 5 and 10 %mol of MnO were prepared by sol-gel method. These supports named: MnAl_(5:95) and MnAl_(10:90) have A_{BET}= 392, PCC = 7.6 and 381 m²g⁻¹, PCC = 8.6, respectively. NiMo catalysts were prepared with 12% w/w of MoO₃ and Ni/(Ni+Mo)=0.3 mol. The support was impregnated with an aqueous solution of ammonium heptamolibdate ((NH₄)₆Mo₇O₂₄·4H₂O) and nickel nitrate (Ni(NO₃)₂), pH of impregnation solution was adjusted to 9, using an aqueous solution of 0.01 M of NH₄OH [2]. Catalysts were dried at 120 °C for 12h and then calcinated at 550 °C for 4h. Catalysts were activated by sulfuration with a gas flow of 4 Lh⁻¹ of 10% v/v H₂S/H₂ and a liquid flow of 1% DMDS/n-heptane at T=300°C and P=30 bar by 4 h. Catalyst evaluation was performed in a fixed bed (0.05 g of catalysts) reactor at T= 300 °C, P= 30 bar. The reactor was fed with a liquid flow of 0.12 cm³min⁻¹ of 0.037 mol DBT/n-heptane and a gas flow of 35cm³min⁻¹ of H₂. Reaction products were analyzed in a Perkin Elmer AUTOSYSTEM XL chromatograph equipped with ionization of flame FID detector and capillary column ULTRA2 (L= 24 m, I. D. = 0,32 mm).

Results and Discussion

Figure 1 shows Raman spectra of NiMo/MnAl_(5:95) and /MnAl_(10:90) calcinated catalysts. Catalysts present bands at 930 and 210 cm⁻¹, associated to Mo₇O₂₄⁶⁻ species and bands at 890, 300 and 312 cm⁻¹ attributed to MoO₄²⁻ species [3]. Comparison of these catalysts with Mo/MnAl_(10:90) suggests that Ni allows a polymerization of MoO₄²⁻ to Mo₇O₂₄⁶⁻ during calcination, probably due to close interaction between Ni and Mo. On the other side, with impregnation at pH=9, the solution precursor is MoO₄²⁻, whereas at pH=7 the solution precursor is Mo₇O₂₄⁶⁻. These species are transformed to Mo₈O₂₆⁴⁻ during calcination. In Table 1 can be observed that dry catalysts impregnated at pH=7 are more active than their calcinated homologues, because of this transformation. In contrast, calcinated catalyst impregnated at pH=9, has a higher rate transformation by formation of NiMoO_x clusters during calcination

and by a promotional effect of nickel. Since calcinated NiMo/MnAl_(5:95) catalyst shows a higher rate of HDS than the reference catalyst, we suggest it could be used as an effective catalyst.

Table 1. Selectivity and rates of HDS of DBT. T=300°C P=30 bar after 8h.

Catalyst	Treatment	pH Impregnation	Conversion (%)	Selectivity (%)		r (E ⁻⁸ mol ⁻¹ g ⁻¹)
				BP	BCH	
Reference	Calcinated	--	86	85	15	37
Mo/MA _(10:90)	Dried	9	29	98	2	12
Mo/MA _(10:90)	Calcinated	9	37	84	16	16
NiMo/MA _(10:90)	Dried	9	48	83	17	20
NiMo/MA _(10:90)	Calcinated	9	80	88	12	34
NiMo/MA _(5:95)	Dried	9	56	88	12	24
NiMo/MA _(5:95)	Calcinated	9	95	96	4	40
NiMo/MA _(10:90)	Dried	7	81	89	11	35
NiMo/MA _(10:90)	Calcinated	7	64	91	9	27
NiMo/MA _(5:95)	Dried	7	76	83	17	33
NiMo/MA _(5:95)	Calcinated	7	65	91	9	28

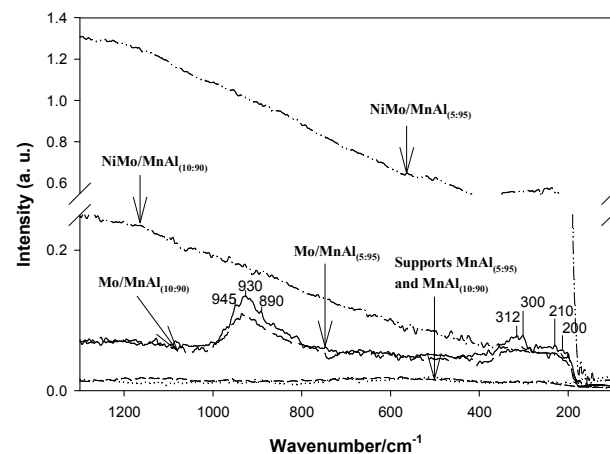


Figure 1. Raman spectra of Mo and NiMo supported on MnAl_(5:95) and MnAl_(10:90) catalysts, calcinated and impregnated at pH 9.

References

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