EFFECT OF LIQUID SPATIAL VELOCITY ON M_D [M_D = Mn, Fe, Co, Ni, Cu AND Zn]//Mo SYNERGISM IN THE HYDRODESULPHURIZATION REACTION

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ABSTRACT

A study is made of Mn//Mo, Fe//Mo, Co//Mo, Ni//Mo, Cu//Mo or Zn//Mo stacked beds systems, separated by γ -Al₂O₃, in the gas-oil hydrodesulphurization reaction, under experimental conditions similar to those industry. The synergism between these beds is clearly detected, and occurs in the absence of mixed phases. The results show that the promotion effect of the pairs in stacked beds, caused by the spillover hydrogen increases when the liquid spatial velocity decreases.

Keywords: Hydrodesulphurization; Hydrogen Spillover; Synergism; LHsv

INTRODUCTION

In 2003¹ it was shown that in conventional Co-Mo hydrodesulphurization (HDS) catalysts, synergism between the Co₉S₈ and MoS_x phases can exist even in the absence of a mixed phase. In that study the Co-Mo synergism was detected using an experimental system of stacked beds in which the presence of a separator bed between Co and Mo sulphides beds prevents the formation of mixed phases like CoMoS₂.

In the absence of mixed phases this synergism has been accounted by the formation on Co sulphide of active hydrogen which migrates ("hydrogen spillover" or Hso) to MoS_x, increasing the concentration of active sites in the acceptor phase, in accordance with the "remote control theory" proposed by Delmon et al.³. In this model Co₉S₈ and MoS_x are called donor (D) and acceptor (A), respectively. Thus, the stacked [donor metal//separator//acceptor metal] bed is abbreviated as M_D/M_A and the [HDS (%) stacked bed/HDS (%) single bed] ratio was defined as the "spillover factor" and abbreviated Fso¹. In that study Co/SiO₂ was located in the first bed; SiO₂ in the second bed (as separator), and Mo/SiO₂ in the third bed. The Co/SiO₂ and Mo/SiO₂ beds were separated by 5 mm of SiO₂. After that, other supports (γ -Al₂O₃)⁴, other distances (up to 10 mm)⁵, other donors (Mn, Fe, Ni, Cu and Zn)⁶, other separators^{5,7}, and other acceptors (W and Re)^{6,8} have been studied in order to find the variables that improve this synergism via Hso. Moreover, other feed gas oil, dibenzothiophene (DBT)⁹, and 4,6 dimethyldibenzothiophene (4,6 DMBT)¹⁰ have been used. The activities were determined under experimental conditions similar to those of hydrodesulphurization industry.

From these studies it has been concluded that promotion via hydrogen spillover increases by decreasing reaction temperature^{1,4-8}; decreasing the distance between D and A⁵; decreasing the isoelectric point (IEP) of the material used as separator between both beds⁵; avoiding discontinuity between D and A⁵; and supporting phosphorus in the separator⁷. Moreover, it has been shown that Fso defined as $\%HDS_{(stacked\ bed)} / \%HDS_{(acceptor)}$, where $\%HDS_{(stacked\ bed)}$ is the activity of the stacked bed donor//acceptor and $\%HDS_{(acceptor)}$ is the activity of the Hso acceptor, is higher when Co or Ni are used as donors instead Mn, Fe, Cu or Zn⁶. However the effect of (liquid hourly space velocity) LHsv on promotion via "hydrogen spillover" is actually unknown. Thus, the main aim of this study is to know the relation between LHsv and Fso in the hydrodesulphurization reaction in a stacked bed using the Mn//Mo, Fe//Mo, Co//Mo, Ni//Mo, Cu//Mo, or Zn//Mo pairs. This parameter has not yet been studied on stacked systems, where the synergism is explained exclusively via Hso

EXPERIMENTAL

a) Sample preparation

As in previous studies^{1,4-10}, Mo/ γ -Al₂O₃ and M_D / γ -Al₂O₃ [M_D = Mn, Fe, Co, Ni, Cu and Zn] monometallic samples were prepared by wet impregnation, dried overnight at 373 K, and calcined at 823 K for 4.5 h. As precursors, Mn, Fe, Co, Ni, Cu and Zn nitrates and ammonium heptamolybdate (Merck p.a)

were used. The support and the "separator" between the beds was γ -Al₂O₃ (BASF D1010, N₂ BET 213 m²g⁻¹ and pore volume 0.500 cm³g⁻¹). The metal contents were about 2.5 atoms nm⁻² for Mn, Fe, Co, Ni, Cu and Zn, and 2.9 atoms nm⁻² for Mo.

b) Reaction Conditions

The reactions in single and stacked beds were carried out as reported previously in a stainless steel continuous-flow microreactor operated in the down-flow mode^{1,4-10}. The stacked beds arrangement was made as follows: on top, the first bed contained 3 g of promoter (Mn, Fe, Co, Ni, Cu or Zn supported on γ -Al₂O₃); the second bed was 5 mm of γ -Al₂O₃ (separator); the third bed (below the separator) contained 0.5 g of active material (Mo supported on γ -Al₂O₃) diluted 1:1 with γ -Al₂O₃. The remaining space in the reactor was filled with SiC particles. Particle size in all the beds as well as of SiC was 0.84–1.19 mm. Before the reaction, the catalysts were submitted to in situ sulphidation for 4 h at 623 K, using 7% CS₂ dissolved in the gas-oil. The HDS reaction temperature was 623 K; LHsv between 22.2 and 66.7 h⁻¹; gas hourly spatial velocity (GHSV) 3600 h⁻¹; and total pressure 3 MPa. A gas-oil containing 2700 ppm of S was used as reactant. Identical reaction conditions were used for single and stacked beds. Under each reaction condition, almost three samples of the reaction product were collected at 30 min intervals. Consequently, the time to complete each experiment at the three temperatures was more than 8 h.

Total sulphur content in the liquid feed (So) and effluents (S) was determined using a LECO S-144DR analyzer. The conversions were expressed as HDS (%) = [(So-S)/So]*100. The precision of the HDS values is better than 2%. Fso was used to quantify the synergism.

RESULTS AND DISCUSSION

Table I shows, first, that none of the metals of the first transition series studied, is active under the reaction conditions employed. It also shows that in the range of LHsv's studied the catalytic activity of the stacked beds is, as expected, higher than the activity of the simple bed. For example, at LHsv = 66.7 h⁻¹, the HDS activity of the single bed //Mo and stacked bed Co//Mo increased from 5.0% to 12.0%, respectively, in close agreement with all the previous studies^{1,4-10}.

The main observation from Table I is that Fso improves greatly if LHsv increases. For example, in the Co//Mo stacked bed Fso changes from 1.28, to 1.68, and 2.40 if LHsv changes from 22.2 to 33.3, and 66.7 h⁻¹, respectively. A quantitative analysis of Co//Mo results shows that in order to double the spillover factor it is necessary to increase the LHsv in 50± 2 h⁻¹; from a quantitative analysis for the Ni//Mo results reached this same value. However, for Mn//Mo, Fe//Mo, Cu//Mo and Zn//Mo pairs in order to double the spillover factor it is necessary to increase the LHsv in 140± 6, 100± 4 140± 6 and 120± 6 h⁻¹, respectively. This improvement can be caused by two phenomena: a) during migration from D to A, Hso concentration decreases by recombination, therefore Fso must improve because increasing the flow decreases the time for recombination; b) increasing LHsv decreases contact time and therefore decreases the activity, and consequently the partial pressure of H₂S in the

reactor also decreases. A lower H_2S concentration can lead to a higher Hso concentration probably by the competition of H_2S for sites active in the dissociation of hydrogen to spillover species, bringing about an inhibitory effect⁵. This hypothesis is supported by the fact that the HDS of dibenzothiophene (DBT) decreases strongly (from 70.9 to 4.2) if the partial pressure of H_2S increases from 0 to 0.1 MPa¹¹.

Table 1: Catalytic HDS activity (%) and spillover factor (Fso), of MD/ γ -Al₂O₃ (MD = Mn, Fe, Co, Ni, Cu, Zn) and Mo/ γ -Al₂O₃ in single bed, and MD/ γ -Al₂O₃// γ -Al₂O₃//Mo/ γ -Al₂O₃ in stacked bed with different LHSV's at 623 K.

System	HDS (%)			Fso		
	LHSV = 66.7 h ⁻¹	LHSV = 33.3 h ⁻¹	LHSV = 22.2 h ⁻¹	LHSV = 66.7 h ⁻¹	LHSV = 33.3 h ⁻¹	LHSV = 22.2 h ⁻¹
M _D / γ -Al ₂ O ₃ (M _D = Mn, Fe, Co, Ni, Cu, Zn) (D = donor)	0	0	0	---	---	---
Mo/ γ -Al ₂ O ₃ (A = acceptor)	5.0	10.0	14.0	---	---	---
Mn//A	7.6	11.4	14.3	1.52	1.14	1.02
Fe//A	8.8	13.0	15.3	1.76	1.30	1.09
Co//A	12.0	16.8	17.9	2.40	1.68	1.28
Ni//A	11.4	17.4	19.2	2.28	1.74	1.37
Cu//A	7.3	12.7	16.0	1.46	1.27	1.14
Zn//A	7.7	13.9	17.8	1.54	1.39	1.27

Figure 1 shows that the behavior described for the Co//Mo pair can be extended to the Mn//Mo, Fe//Mo, Ni//Mo, Cu//Mo, or Zn//Mo pairs. It also shows that Fso changes with the position of the metal in the periodic table according to a volcano type curve, in close agreement with previous results⁶.

Figure 1. LHSV effect of M_D//Mo (M_D = Mn, Fe, Co, Ni, Cu or Zn) on Fso using stacked beds at 623 K.

CONCLUSION

In the hydrodesulphurization reaction under experimental conditions similar to those of industry, promotion via Hso of Mn//Mo, Fe//Mo, Co//Mo, Ni//Mo, Cu//Mo, or Zn//Mo pairs located in a stacked bed improves if liquid hourly spatial velocity increases. The promotion Co//Mo and Ni//Mo via Hso doubles if LHSV increases in 50±2 h⁻¹.

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