

The Role of Group VIII Metal Promoter in MoS₂ Hydrotreating Catalysts

III. Catalytic and Physicochemical Properties of Iron-Molybdenum Sulfide Catalysts

INTRODUCTION

Catalysts used for hydrotreating petroleum crudes are normally based on Group VI-B metals (Mo or W) as active components, promoted by Group VIII metal (Co or Ni) with alumina as a carrier. Several attempts (1-8) have been made to establish correlation between the catalytic and physicochemical properties of these catalysts (supported or unsupported). Four hypothesis, viz., "monolayer model" (1), "intercalation model" (2), "synergy by contact" or "remote-control model" (3, 4), and "Co-Mo-S model" (5), have been proposed to explain the role of promoter in HDS catalysts.

In our earlier work on comacerated Mo- or W-based HDS catalysts (9-14) we showed that addition of Co or Ni modifies the structural and textural properties of MoS₂ or WS₂. These modifications were found to be strongly dependent on the amount of promoter. For example, structural and physicochemical properties of samples containing less than 5% promoter atom ($0.0 < r = \text{Co (Ni)} / \{\text{Co (Ni)} + \text{Mo}\} < 0.05$) were different from those of samples belonging to the range $0.2 < r < 0.4$. The present investigation on Fe-promoted MoS₂ catalysts was undertaken to generalize the role of Group VIII metal promoters in HDS catalysis. Four Fe-Mo samples (each belonging to different composition range) were selected for evaluation of catalytic and structural properties.

EXPERIMENTAL METHODS

The catalysts were prepared by the comaceration method described elsewhere (3, 4, 9-11). Four samples with composition ratios " r " = 0.0, 0.02, 0.25, and 1.00 were prepared. They are denoted by r -0.00, r -0.02, etc. Catalysts used for activity measurements and X-ray diffraction studies were presulfided for 6 h (20% H₂S in H₂) at 400 and 1000°C, respectively. Surface areas of these catalysts were measured by the BET method (nitrogen adsorption) using a Setaram microbalance MTB-10-8. The catalysts were tested for their activity in thiophene HDS and cyclohexene hydrogenation. Reaction conditions are listed in Table 1. Product samples were analyzed every half hour for 6 h. Steady-state specific activities (A = conversion per g catalyst) and rates per unit surface area of catalyst (A^*) are reported here.

X-Ray diffraction patterns were obtained by using Philips X-ray diffractometer Type PW 1010 with CuK α radiation while the crystalline parameters were measured by stepwise scanning the peaks (step = 1° per 4 h) using CGR SIGMA 2080 monochromator with CuK α_1 radiation. Silicon was used an internal standard.

RESULTS

Figure 1 presents X-ray diffraction patterns of Fe-Mo samples presulfided at 1000°C. Mo-Containing samples presulfided

TABLE I

Surface Areas and Specific Activities of Fe–Mo Samples

Catalyst	Surface area (m ² /g)	Reaction conditions				SEL ^c
		Temperature: 305°C		Pressure: 30 bars		
		H ₂ /liq. hydrocarbon (vol): 600		LHSV: 18		
		Weight of the catalyst: 1 g presulfided at 400°C				
		Feed (wt %): 70% cyclohexane + 30% cyclohexene + 5000 ppm thiophene				
		Specific activity ^a		Rate ^b		
		A _{HDS}	A _{HYD}	A* _{HDS} × 10 ⁵	A* _{HYD} × 10 ³	
r-0.00	11.0	9.5	0.3	2.43	0.044	0.550
r-0.02	6.7	3.2	4.0	1.47	1.110	0.013
r-0.25	11.7	15.0	8.0	4.07	1.250	0.032
r-1.00	8.0	1.0	3.1	0.36	0.650	0.006

^a In % conversion g⁻¹ catalyst.

^b In (mol h⁻¹) m⁻² catalyst.

^c SEL = A*_{HDS}/A*_{HYD}.

at 400°C yield only broad X-ray lines due to intense reflections of MoS₂, whereas pure iron sulfide sample (r-1.00) gives X-ray pattern corresponding to Fe_{1-x}S phase at both pretreatment temperatures. The “c” parameter values determined for these samples are slightly higher than literature values (15). Table I compares surface areas, and HDS and hydrogenation activities of various samples.

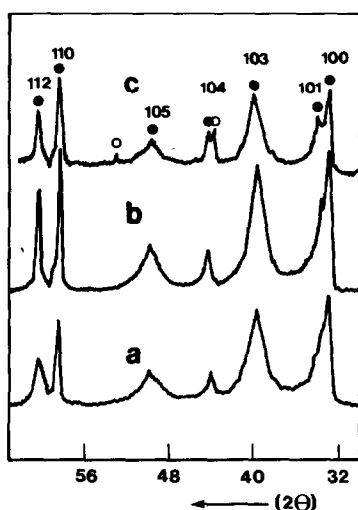


FIG. 1. X-Ray diffraction patterns of Fe–Mo catalysts sulfided at 1000°C. Closed and open circles represent MoS₂ and Fe_{1-x}S, respectively. (a) r-0.00, (b) r-0.02, and (c) r-0.25.

DISCUSSION

X-Ray results show that the X-ray lines corresponding to 10L (L = 1, 2, 3, 5, etc.) and 112 planes of pure MoS₂ (Fig. 1, r-0.00 and r-0.02) gain higher intensities and better resolution by addition of 2% Fe atom to MoS₂. This is accompanied by a decrease in the “c” parameter from 12.406 Å for r-0.00 to 12.304 Å for r-0.02. Further addition of iron (r-0.25) to MoS₂ increases the “c” parameter back to its original value. The presence of Fe_{1-x}S in r-0.25 sample detected by X rays (Fig. 1c) is in accordance with the findings of Vaishnava *et al.* (16) and Qi *et al.* (17), and indicates that this sample is essentially biphasic. The present X-ray results together with earlier results on comacerated Co–Mo (3, 10) and Ni–Mo catalysts (9) suggest that addition of Group VIII metal atom improves the crystallinity of MoS₂. This effect is more pronounced when a small amount of promoter is added. A decrease in surface area (for r-0.02) supports this interpretation. At synergetic promoter concentration r-0.25, one observes an increase in surface area and the presence of two separate phases, viz., MoS₂ and Group VIII metal sulfide.

We shall discuss the promotional effects of iron toward HDS and hydrogenation. Specific activity A_{HDS} goes through a minimum at r-0.02, while A_{HYD} increases contin-

uously with increase in iron content. At synergetic composition, specific activity value (for each function) is larger than the sum of activity values for pure components. Sample *r*-1.00 is more active in hydrogenation than HDS (18). Addition of 2% iron enhances hydrogenation rate (A_{HYD}^*) of MoS_2 by a factor of 25 but suppresses HDS rate (and surface area) by a factor of 2 thus indicating that olefin hydrogenation and thiophene HDS occur on different sites as proposed by Delmon (4) and Clausen *et al.* (5). These results and earlier findings on analogous Ni-Mo (9) and Co-Mo (19) clearly demonstrate that the modifications brought about by incorporating 2% promoter favor the hydrogenation activity in accordance with the remote-control model (4). Addition of 25% iron promotes both HDS and hydrogenation activities of pure MoS_2 . For this composition, Ni was found to promote both functions while Co increased HDS rates relative to hydrogenation (14). Although a comparison of activities of Fe-Mo with Ni-Mo and Co-Mo (14) shows that Fe-promoted catalysts are less active than Ni- or Co-promoted catalysts, the overall trends and selectivity ($\text{SEL} = 0.032$) of Fe-Mo are similar to those exhibited by Ni-Mo ($\text{SEL} = 0.034$). Higher activities and the presence of two separate phases observed for this sample are in favor of the remote-control model.

In conclusion, the present investigation shows that Group VIII metals modify the structural properties of MoS_2 in an identical manner, and that iron behaves like nickel in promoting hydrogenation and HDS activities.

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