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Preparation Characterization and Catalytic Properties of Unsupported and Molybdenum-Promoted Vanadium Sulfides

Hydrotreating of light and crude petroleum feedstocks involves hydrogenation of unsaturated materials and sulfur, nitrogen, or oxygen heteroatom removals. These main reactions are catalyzed by Co or Ni-promoted molybdenum or tungsten sulfides supported on alumina. Such catalysts may also be required for treating heavier feedstocks containing organically combined metals. Among the different metals present in the feed, Ni and V are the most important ones, which are mainly associated with naphtenates and porphyrins complexes. Sulfide catalysts can break up these organic complexes but unlike the heteroatom removals, the Ni and V are deposited on the catalyst surface. The hydrodesulfurization (HDS), cracking (CK), and hydrodemetallation (HDM) activities decrease as a function of the extra metal loading (*1*). This work has shown that the vanadium concentration may reach 50 wt% and despite this high metal level, the catalyst retains a nonnegligible activity. Chemical and physicochemical analysis of spent hydrotreating catalysts have evidenced that during the HDM process, the deposited nickel metal is in a sulfided form (*2, 3*). Concerning the nature of the deposited vanadium, several species seem to coexist on the surface of used NiMo or CoMo catalysts. In addition to vanadium sulfide, several oxidized vanadium species have been evidenced in the literature (*4–7*). The presence of VO entities is not surprising since Guillard *et al.* (*8*) have underlined the highly oxophilic character of pure and nonsupported vanadium sesquisulfide. Another interesting result concerns the distribution of the different species present on the surface of used catalysts. It has been observed that the Ni atoms initially located in decoration position of the lamellar structure of supported MoS_2 are progressively removed from the edge position upon vanadium deposit (*9, 10*). These studies tend to show that the residual activity of spent hydrotreating catalyst may be related to the presence of a mixture of vanadium and molybdenum sulfides with a possible influence of a sublayer of Co or Ni chalcogenides.

The aim of this work was to investigate the catalytic properties of molybdenum-promoted vanadium sulfide. Special attention was devoted to the preparation and the characterization of the precursor, as well as of the resulting catalysts.

In this study, all the catalysts were prepared using ammonium thiosalts as precursors. The synthesis of pure $(NH_4)_2MoS_4$ and $(NH_4)_3VS_4$ has been already described in the literature (*11, 12*). Molybdenum-promoted vanadium precursors have been prepared by "cocrystallization" of their thiosalts. For this, an aqueous solution of ammonium pyrovanadate and molybdate is added to a freshly prepared ammonium sulfide solution at 0°C. A H_2S flow was kept bubbling through the solution for a few hours to initiate the crystals precipitation and the flask was left in the refrigerator for several days in order to increase the crystals yield. Then to avoid oxidation, the resulting crystals were filtrated, washed with ethanol, and stored in an inert and dry atmosphere. For all the promoted vanadium samples, the composition was defined by the atomic ratio $r = Mo/(Mo + V)$.

The XRD patterns of pure vanadium and molybdenum thiosalts and those of the MoV ($r = 0.3$) precursor are represented in Fig. 1. The obtained diffracting lines

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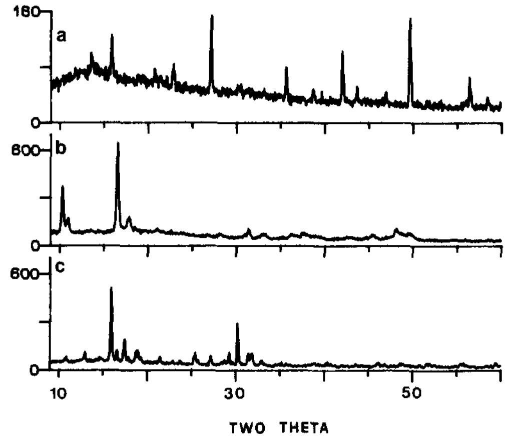

FIG. 1. XRD diffraction patterns of pure $(NH_4)_3VS_4$ (spectrum a); of $(NH_4)_2MoS_4$ (spectrum b); and of the MoV catalyst precursor with $r = 0.3$ (spectrum c). The diffraction patterns were recorded with a Siemens D 500 diffractometer equipped with an automatic identification of phases according to the JCPDS index (scan speed: 1°/min and Cu$K\alpha$ radiation).

of $(NH_4)_2MoS_4$ are in agreement with those reported in the JCPDS index. According to Schafer *et al.* (*13*), ammonium tetrathiovanadate crystallizes in the orthorombic system (D_{2h}^{16}, *Pnma*) with the following cell parameters: $a = 9.4$ Å; $b = 10.79$ Å; and $c = 9.31$ Å. As the diffractogram of $(NH_4)_3VS_4$ has not been recently published in the literature, we have compared our experimental results with those calculated taking into account Shafer's data and Appleman's program (*13, 14*) and both spectra fit fairly well. The X-ray pattern of the mixed MoV precursor does not resemble to the corresponding spectra of pure components. As a matter of fact, the diffracting lines do not consist in the superposition of the patterns of both molybdenum and vanadium thiosalts and the data reported in Table 1 do not correspond to any referenced vanadium–molybdenum–sulfur phase.

The S 2*p* binding energies (BE) of $(NH_4)_2MoS_4$, $(NH_4)_3VS_4$, and MoV catalyst precursors were found at 162.2 eV. These BE values are consistent with the presence of S^{2-} species. When identical vanadium BE were observed for both the VS_4^{2-} and the MoV precursor, important variations of Mo BE were detected (Fig. 2). For ammonium thiomolybdate, the Mo $3d_{3/2}$ and Mo $3d_{5/2}$ were found at 230.4 and 233.6 eV. With respect to MoS_2, these BE are shifted to the highest energies, which is in agreement with a highest oxidation state. On the contrary, the molybdenum BE of the MoV precursor are considerably lowered since a shift of about 2 eV (228.5 and 231.7 eV) was observed by comparison with the pure molybdenum thiosalt, and the resulting BE values are even lower than those of pure molybdenum sulfide (229.5 and 232.6 eV). Therefore, the addition of vanadium into the MoS_4^{2-} salt provokes a drastic reduction of the average oxidation state of molybdenum, which is probably due to an important interaction between both metals. Therefore, these physicochemical characterizations suggest that the employed preparation

TABLE 1

XRD Data of the $r = 0.3$ MoV Precursor

2θ	*d* (Å)	Relative intensities (%)
10.827	8.164	12.7
12.971	6.819	19.1
15.944	5.553	100
17.471	5.071	38.1
18.732	4.733	7.2
19.314	4.592	5.3
21.447	4.139	9.1
23.716	3.748	7.6
25.416	3.501	17.8
27.164	3.280	15.2
29.266	3.049	14.8
29.625	3.012	2.2
30.217	2.955	50.8
31.430	2.844	17.1
31.853	2.807	26.3
32.921	2.718	13
34.415	2.603	4.1
41.237	2.187	4.3
43.617	2.073	5.1
46.126	1.966	17.9
46.875	1.936	6.2
51.627	1.769	4.4
51.927	1.759	3.2
59.406	1.554	9.7

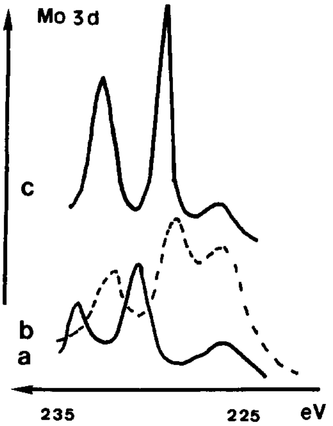

FIG. 2. Mo 3*d* binding energies of pure $(NH_4)_2MoS_4$ (spectrum a); of the MoV precursor $r = 0.3$ (spectrum b); and of MoS_2 (spectrum c). The XPS characterization was performed in a AEI ES 200 B spectrometer having an Al$K\alpha$ X-ray source (reference: C 1*s* level at 285.0 eV).

method leads to a new compound, which could be a mixed ammonium tetrathiovanadomolybdate. As a matter of fact, UV–VIS spectroscopy examination of this compound contains only the strong absorption bands ascribed to both S → Mo and S → V charge transfers. No bands corresponding to oxothioanions $(MO_xS_y)^{n-}$ have been detected. Moreover, by comparison with the decomposition of pure Mo and V thiosalts, the DTA study of the decomposition of these MoV catalyst precursors have also evidenced the presence of some extra peaks, which cannot be related to the transformation of oxothio species.

The catalysts were prepared by thermal decomposition of the precursors for 4 h at 400°C in an inert atmosphere. The X-ray diffraction patterns of the resulting solids exhibit only the presence of MoS_2 and V_5S_8 in agreement with the electron microscopy observation presented in Fig. 3. This photograph reveals the presence of both V_5S_8 and MoS_2 phases. The vanadium sulfide crystallites appeared to be formed by an assembling of particles having a hexagonal plate shape with an average length of about 1800 Å. In contrast, the layered molybdenum phase presents a smaller particle size since most of them have 4–5 slabs with an average length of 40 Å. Interestingly, the MoS_2 phase is mainly localized around the vanadium phase meaning that the vanadium sulfide acts mostly as a support of the molybdenum sulfide. STEM analysis has shown that the system is rather heterogeneous, because domains having only vanadium and sulfur were observed as well as domains containing vanadium and molybdenum sulfides. However, no particles without vanadium were found meaning that MoS_2 was always associated with a vanadium sulfide phase. These particles with an r value lying between 0.2 and 0.4, as well as others having a highest Mo/(Mo + V) ratio ($0.7 < r < 0.9$), were found.

XPS experiments performed on this catalyst have evidenced only the presence of photopeaks corresponding to MoS_2 and V_5S_8.

These observations suggest that the vanadium phase acts mainly as a support of the layered phase. This evidence of the presence of a MoS_2-like structure supported on the other sulfided phase have been already reported for unsupported NiMo sulfide catalysts (*15*).

The catalytic properties of the obtained catalysts have been determined in the biphenyl hydrogenation (HN) as a model reaction. The experimental conditions used for these studies have been detailed elsewhere (*16*). In these experimental conditions, the biphenyl conversion test gives, in addition to the HN properties, some indications about the cracking function since benzene and cyclohexane formation can be observed.

Table 2 summarizes the hydrogenating properties of a series of MoV catalysts. These results show that the catalytic activity of pure vanadium sulfide is much higher than that of molybdenum sulfide. The variation of the catalytic activity with r reaches a maximum around $r = 0.35$. This maximum in activity cannot be related to the variation of specific area since the results reported in

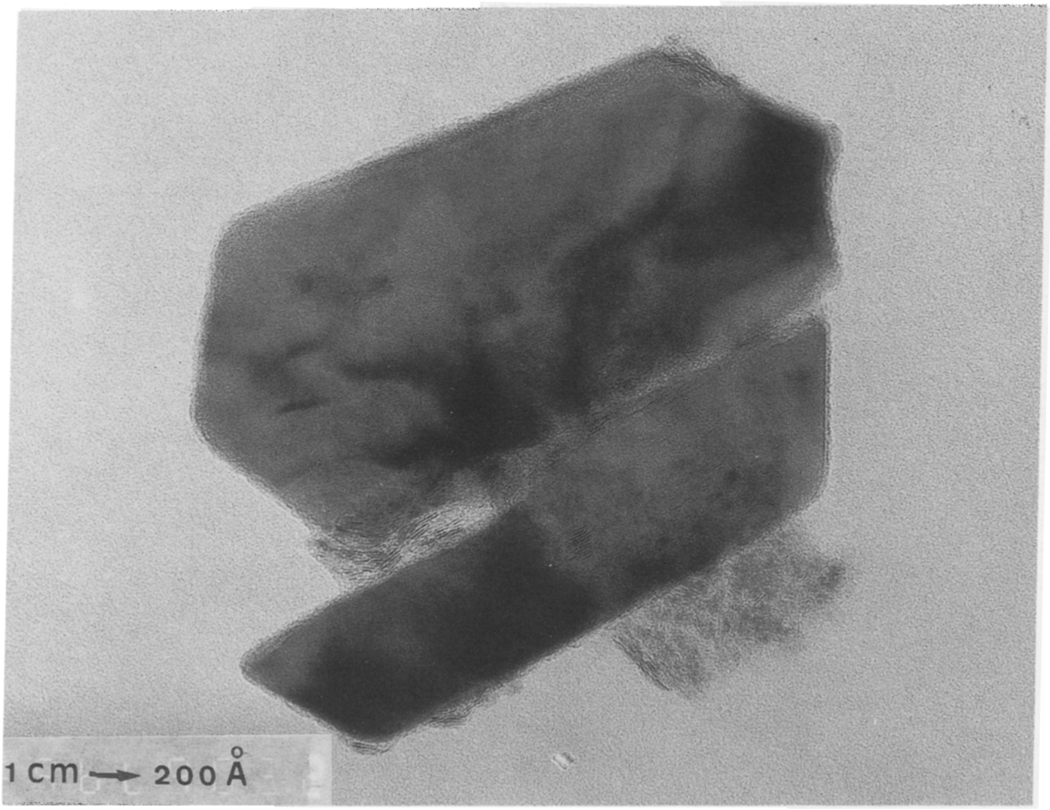

FIG. 3. HREM micrograph of an r = 0.3 MoV catalyst.

Table 2 evidenced a continuous decrease in BET area as far as the molybdenum content is increasing. Consequently, molybdenum can be considered a promoter of vanadium sesquisulfide. In addition to this small synergetic effect, the introduction of molybdenum induces an important modification of the catalyst properties leading to an increase of the CK selectivity. When the precursors are decomposed in a H_2-15% H_2S

TABLE 2

Hydrogenation Properties of a Series of MoV Catalysts

r Mo/(Mo + V)	BET area (m^2 g^{-1})	As (10^{-8} mol s^{-1} g^{-1})	Ai (10^{-8} mol s^{-1} m^{-2})	S_{CK} (%)
0	26	6.2	0.24	3
0.11	20	5.9	0.29	13
0.25	21	7.6	0.35	18
0.28	17	8.2	0.48	13
0.35	17	9.5	0.56	43
0.40	15	5.6	0.37	40
0.72	14	4.1	0.29	18
0.94	13	3.9	0.29	17
1	7	0.3	0.04	19

atmosphere, the syngery is slightly lower but the resulting catalysts retain their CK properties. These results suggest a modification of the nature of the active sites, which can probably be related to an interaction between molybdenum and vanadium in the sulfided phase. In a thorough theoretical study of the promoting effect of the first row of transition metal sulfides on the properties of MoS_2, Harris and Chianelli (*17*) have predicted only a small synergetic effect for the system MoVS. They have ascribed this synergetic effect to a local reduction of molybdenum by the promoter. Experimentally, this local reduction of molybdenum by the promoter has already been evidenced by XPS for NiMo or NiW catalysts (*18, 19*). Our experimental work is in good agreement with Harris' hypothesis and could explain the modification of the cracking selectivity. However, the amount of vanadium atoms involved in this mixed MoVS site would be extremely small by comparison to the total vanadium content and therefore these vanadium species could not be detected by XPS. In comparison to those of other sulfides, these cracking properties appear to be a characteristic of the MoVS system. Such important cracking properties have never been observed over sulfided catalysts (*16*) except for the NbS_x system. Recent work on the NbS_x system, however, has not revealed the exact nature of the acidic sites of niobium sulfides, the adsorption of H_2S on a Lewis site, or the proton acidic properties of SH groups attached in some particular structural position (*20*). In the case of MoV catalysts, the electron transfer from V species to the surrounded Mo ion may have modified the vanadium–sulfur bonding and conferred an acidity to the mixed site.

(i) The method employed for the preparation of a mixed MoV precursor leads to a new compound, which could be an ammonium tetrathiovanadomolybdate.

(ii) The catalyst obtained by decomposition of such a precursor could be described as a well-dispersed MoS_2-like structure supported on V_5S_8.

(iii) Compared with MoS_2, the MoV catalysts present higher hydrogenating and cracking properties. These HN properties are smaller than those of a NiMo catalyst. Nevertheless, these results may explain the residual activity of spent HDM industrial catalysts.

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REFERENCES

1. Takeuchi, C., Nakata, S., and Shiroro, Y., *ACS Symp., Div. Petrol. Chem. Prep.* **96** (1985).
2. Rankel, L. A., and Rollmann, L. D., *Fuel* **62** (1985).
3. Fleish, T. H., Meyers, B. L., Hall, J. B., and Ott, G. L., *J. Catal.* **86,** 147 (1984).
4. Silbernagel, B. G., *J. Catal.* **56,** 315 (1979).
5. Rankel, L. A., *Am. Chem. Soc., Div. Petrol. Chem.* **26,** 689 (1981).
6. Mitchell, P. C. H., and Valero, J. A., *React. Kinet. Catal. Lett.* **20,** 219 (1982).
7. Loos, M., Ascone, I., Goulon Ginet, C., Goulon, J., Guillard, C., Lacroix, M., Breysse, M., Faure, D., and des Courières, T., *Phys. B* **158,** 145 (1988).
8. Guillard, C., Lacroix, M., Vrinat, M., Breysse, M., Mocaer, B., Grimblot, J., des Courières, T., and Faure, D., *Catal. Today* **7**(4), 587 (1990).
9. Dejonghe, S., Hubaut, R., Grimblot, J., Bonnelle, J. P., des Courieres, T., and Faure, D., *Catal. Today* **7**(4), 569 (1990).
10. Jacobsen, A. C., *in* "29th Petr. Conf., Bratislava, Sept., 1984."
11. Jacobson, A. J., and Rich, S. M., *J. Electrochem. Soc.* **127**(4), 779 (1980).
12. Diemann, E., and Müller, A., *Coord. Chem. Rev.* **10,** 79 (1973).
13. Schafer, H., Moritz, P., and Weiss, A., *Z. Naturforsch. B* **20,** 206 (1965).
14. Appleman, D., *in* "USGS, Aca. meeting Cambridge, 1963."
15. Garreau, G. F., Toulhoat, H., Kasztelan, S., and Paulus, R., *Polyhedron* **5**(12), 211 (1986).
16. Lacroix, M., Boutarfa, N., Guillard, C., Vrinat, M., and Breysse, M., *J. Catal.* **120,** 473 (1989).
17. Harris, S., and Chianelli, R. R., *J. Catal.* **86,** 275 (1986).

18. Eltzner, W., Breysse, M., Lacroix, M., and Vrinat, M., *Polyhedron* **5**(1–2), 203 (1986).
19. Blanchard, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **98,** 229 (1986).
20. Danot, M., Afonso, J. C., Portefaix, J. L., Breysse, M., and des Courières, T., *Catal. Today,* in press.

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