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NOTE

Optimum Ni Composition in Sulfided Ni–Mo Hydrodesulfurization Catalysts: Effect of the Support

A synergistic effect of the support in Ni–Mo hydrodesulfurization (HDS) catalysts has been recently proposed (1), suggesting that in the case of a carbon support, this functions in conjunction with molybdenum sulfide to promote the exposure of nickel active centers. This effect is a possible explanation for the higher HDS activity of carbon-supported catalysts with respect to conventional catalysts reported earlier (2); however, there are insufficient clues as to which carbon characteristics are involved in the activity promotion.

Taking into account that a variety of different supports have been studied for HDS catalysts in the past (3), e.g., alumina, silica, titania, zeolites, and carbon, it is interesting to investigate how the intrinsic activity can be affected by the differences in the nature of the support, especially whether the presence of a particular active phase or structure could be promoted by choosing an appropriate support.

In this communication, we present evidence suggesting that two different active Ni–Mo sulfide structures can exist in HDS catalysts, the presence of either one being possibly determined by the nature of the support employed. In addition, the study focusses on the possible properties of carbon supports that may be responsible for the higher activity referred to above.

Two commercial activated carbons with similar B.E.T. surface areas, both prepared from natural ligno-cellulose raw materials, were used for the present study. Pica carbon (C_A, 1280 m^2/g) was manufactured employing the high-temperature "physical" activation, and Purocarbon (C_B, 1330 m^2/g) employing the phosphoric acid "chemical" activation method. Note that "physical" activation should produce a narrower micropore size distribution (most likely featuring slit micropores) than "chemical" activation (4).

These carbons were impregnated with ammonium molybdate and nickel nitrate solutions following the procedure described in detail earlier (1). Samples had Mo loadings of 10 wt% (reported as MoO_3) and Ni concentrations ranging from 0 to 10 wt% (as NiO). The impregnated samples were dried at 110°C and then presulfided *in situ* before either temperature-programmed reduction (TPR) or HDS activity test was performed. These tests were carried out employing apparatus and procedures described in detail previously (5). The sulfidation of the catalyst consisted of heating (10°C/min) under a pure H_2S flow from ambient to 400°C, holding this temperature for 1 hr.

TPR spectra of the nonimpregnated supports (Fig. 1) show that before sulfidation both C_A and C_B present a peak at about 680°C attributed to surface oxygen complexes (6). The larger area of the peak in C_B suggests a larger proportion of such complexes with respect to C_A. The high-temperature negative peak observed in C_B should be attributed to hydrogen evolution (6).

Sulfiding the nonimpregnated carbons produced changes in TPR (Fig. 1), especially in C_A, where the appearance of a new signal at 530°C suggests incorporation of sulfur to the carbon. In contrast, C_B appears to be more resistant to sulfur incorporation, as its TPR spectrum does not change significantly after sulfidation.

TPR spectra of the sulfided catalysts (Fig. 2) show quite different peak temperatures: 430 and 340°C for the samples with $r = 0$ supported on C_A and C_B, respectively, suggesting the presence of two different reducible molybdenum sulfide species. The incorporation of Ni to the catalyst produced changes (not shown) similar to those previously reported (1) for other carbon-supported catalysts: small peak shifts (10–20°C) to lower temperatures and peak intensity increases. Similar sensitivity to Ni presence of TPR spectra has also been noted previously using the same experimental procedure for silica-supported NiMo and CoMo sulfides (5), though in these cases peaks appeared at significantly lower temperatures (around 200°C).

Figure 3 shows that the optimum r value for higher steady-state HDS activity at 300°C is different in each of the supports employed. The optima are located at approximately $r = 1/2$ for C_A and $r = 1/3$ for C_B, i.e., atomic ratios Ni : Mo = 1 : 1 and 1 : 2, almost corresponding to samples with NiO/MoO_3 = 5/10 and 3/10 (wt%/wt%), respectively.

Table 1 shows that the C_A support produces higher activities than C_B, both in the bare-nonimpregnated-car-

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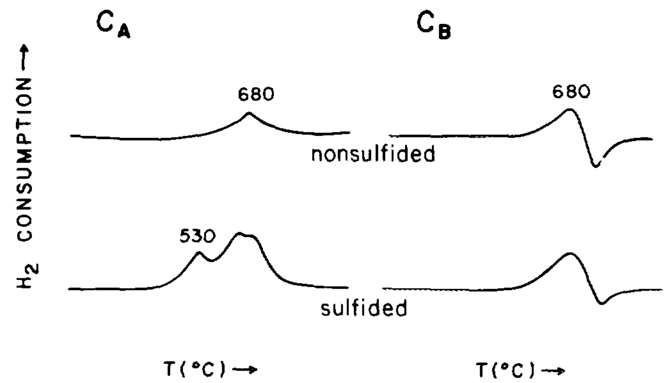

FIG. 1. TPR spectra of the nonimpregnated carbon supports.

bon (0/0) and in the monometallic Ni (5/0) and Mo (0/10) catalyst.

Contrary to previous findings on carbon-supported (1) and alumina-supported HDS catalysts (7) postulating that catalysts from which chemisorbed sulfur is hydrogenated at lower temperatures have higher HDS activities, in the present work the higher activity of the C_A-supported catalyst (Table 1) may be rather related to its higher peak temperature in TPR spectrum with respect to C_B catalyst (Fig. 2). This suggests that the previous postulate is probably valid only for series of catalysts based on the same support. In addition, the relatively lower TPR peak temperature referred to above for the silica-supported sulfides (5) is also in agreement with the lower activity of these catalysts with respect to the present carbon-supported catalysts.

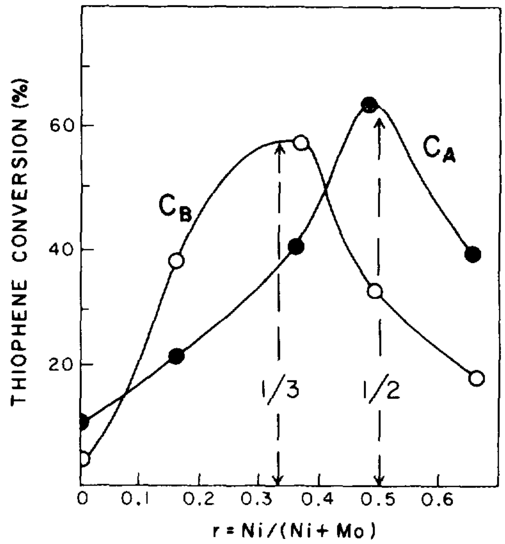

FIG. 3. HDS steady-state activities at 300°C. Flow conditions as in Table 1. Sample weight: 75 mg.

The remarkable differences in TPR spectra (Fig. 2) and in optima r-values (Fig. 3) suggest the presence of quite different active Ni–Mo sulfide species on each support. Different characteristics of the two supports employed are probably responsible for the occurrence of the two optima. For example, TPR (Fig. 1) suggested that C_A support has more affinity for sulfur than C_B, whereas this latter has probably more surface complexes including O and H.

One may consider, on one hand, that the surface of carbon C_B resembles more an alumina surface as a result of the presence of a significant proportion of nonsulfidable oxygen surface complexes than that of C_A. This may explain why the optimum r for C_B ($r = 0.33$, Fig. 3) corresponds to the composition normally found in conventional

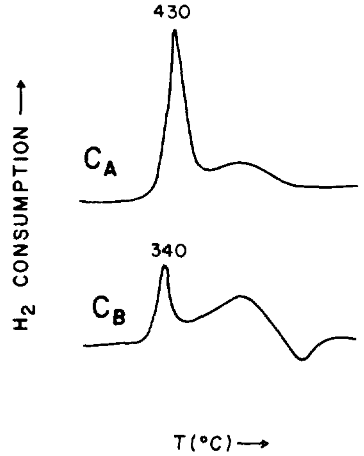

FIG. 2. TPR spectra of molybdenum sulfide catalysts ($r = 0.0$) supported on C_A and C_B.

TABLE 1

Steady-State Thiophene Conversion Rates at 400°C of Presulfided Samples

NiO/MoO_3 (wt%/wt%)	Reaction rate[a] (mol/min g) × 10^5	
	C_A	C_B
0/0[b]	2	<1
5/0	41	29
0/10	50	35

[a] Flow conditions: 160 ml/min H_2, 6.8 × 10^{-5} mol C_4H_4S/min; sample weights: 500 mg for 0/0, 50 mg for others.

[b] Nonimpregnated support.

Ni(or Co)–Mo HDS catalysts supported on alumina. For example, an examination of seven commercial HDS catalysts indicates an average composition (8): NiO(or CoO)/MoO_3 = 3.1/14.3 ± 0.2/1.0 wt%/wt%, i.e., $r = 0.30 \pm 0.02$. In the case of C_A, on the other hand, the active species most likely resembles unsupported Ni–Mo sulfide. Indeed, the optimum r for the latter is reported (9) to be near to the same value obtained for C_A: $r = 1/2$.

The above two resemblances may well relate to type I and II active structures supported on alumina, as reported by Candia *et al.* (10), where the differences between type I and II were supposed to be the existence, in the first case, of remaining Mo–O–Al linkages, while type II structure was fully sulfided. Indeed, C_A catalysts produced a larger TPR signal located at a higher temperature with respect to C_B catalysts (Fig. 2), while in the latter, weakening of sulfur bonds by the occurrence of oxygen linkage between Mo and C_B support probably produced the smaller TPR signal located at lower temperature.

The relation of the support affinity for sulfur with higher catalyst activity (Fig. 1, Table 1) can also be correlated with the synergistic effect of the support recently proposed (1) which suggests that carbon may act as a "sulfur sink" under steady-state HDS reaction conditions, promoting the exposure of the active sites, probably by the operation of a mechanism involving transfer of sulfur trapped by the active sites to neighboring sulfur vacancies.

One may also consider that under HDS reaction conditions, the narrow slit micropores of activated carbons could diminish sulfur vapor pressure to such an extent as to create a driving force for sulfur transfer from the active compound to the micropores (thus, generating active vacancies). In fact, a significant proportion of the slit micropores, the ultramicropores < 7 Å, may well be inaccessible to the active phase, but accessible to sulfur to accomplish the sink effect.

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REFERENCES

1. Laine, J., Severino, F., Labady, M., and Gallardo, J., *J. Catal.* **138,** 145 (1992).
2. van Veen, J. A. R., Gerkema, E., van der Kraan, A.M., and Knoester A., *J. Chem. Soc., Chem. Commun.*, 1684 (1987).
3. Breysse, M., Portefaix, J. L., and Vrinat, M., *Catal. Today* **10,** 489 (1991), and references therein.
4. Laine, J., and Yunes, S., *Carbon* **30,** 601 (1991).
5. Laine, J., Brito, J. L., and Severino, F., *J. Catal.* **131,** 385 (1991).
6. Laine, J., Calafat, A., and Labady, M., *Carbon* **27,** 191 (1989).
7. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121,** 31 (1991).
8. Laine, J., Severino, F., and Golding, R., *J. Chem. Technol. Biotechnol.* **34A,** 387 (1984).
9. Pratt, K. C, Sanders, J. V., and Tamp, N., *J. Catal.* **66,** 82 (1980).
10. Candia, R., Sorensen, O., Villadsen, J., Topsøe, N., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93,** 763 (1984).

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