JOURNAL OF CATALYSIS 138, 145–149 (1992)

The Synergistic Participation of the Support in Sulfided Ni–Mo/C Hydrodesulfurization Catalysts

J. LAINE, F. SEVERINO, M. LABADY, AND J. GALLARDO

Laboratorio de Fisico-Química de Superficie, Instituto Venezolano de Investigaciones Científicas, Apt. 21827, Caracas 1020-A, Venezuela

Received December 11, 1991; revised May 29, 1992

Carbon-supported Ni–Mo hydrodesulfurization (HDS) catalysts were studied and compared with previously reported results obtained from alumina supports. In contrast to the latter, the nonimpregnated carbon itself behaved as an HDS catalyst. It is suggested that the carbon support functions synergistically in a sulfided state in conjunction with Mo and Ni, so that both Mo and carbon act as sulfur sinks promoting the exposure of active Ni centers. © 1992 Academic Press, Inc.

INTRODUCTION

In the scientific literature (*1*, *2*) potential advantages have been claimed for carbon-supported catalysts over conventional alumina-supported catalysts, both with respect to high hydrodesulfurization (HDS) activity and low carbon deposition. However, these findings have not been completely clarified, especially with respect to the high activity. For example, while some results (*3*) correlate the high HDS activity to a better dispersion of the molybdenum sulfide on the carbon support, other evidence (*4*) suggests that the weak interaction of the active species with carbon promotes sintering during sulfidation, so that three-dimensional MoS_2 crystallites are preferentially formed in contrast to the more dispersed "single slab" MoS_2 formed on alumina supports. The latter tend to also promote the formation of certain amounts of well dispersed but less active phases such as $Al_2(MoO_4)_3$ and Ni (or Co) spinels (*5*). The relationship between dispersion and HDS activity is further complicated if one takes into account that the number of catalytically active sites for HDS is probably small compared to the total number of adsorption sites (*6*).

In this communication, we are presenting evidence suggesting that, in the case of Ni–Mo, the carbon support provides a more active HDS catalyst because, in contrast to an alumina support, it functions synergistically in a sulfided state in conjunction with Mo and Ni.

EXPERIMENTAL

High purity activated carbon (Merck, 750 m^2/g, <1 wt% ash) was employed for the present work. This carbon was impregnated with ammonium molybdate and nickel nitrate solutions. Molybdenum was first impregnated in the case of the bimetallic catalyst. The impregnated samples were dried at 110°C. The dried samples were presulfided *in situ* before either temperature-programmed reduction (TPR), coking tendency, or HDS activity tests were performed. These tests were carried out employing the apparatus and procedures as described in detail previously (*7–9*). The sulfiding procedure consisted in heating (10°C/min) under a pure H_2S flow from ambient to 400°C, remaining at this temperature for 1 h.

In the text that follows, the composition of the catalysts is referred as y/x (= wt% NiO/wt% MoO_3). Note that these oxides are not actually present, but this convention is followed for consistency with previous work (*7–9*).

0021-9517/92 $5.00

TABLE 1

Initial Rate of Carbon Deposition from 1,3 Butadiene and HDS Activity in the Nonimpregnated Carbon

Carbon pretreatment	Coking rate[a] (min^{-1}) × 10^2	Thiophene conversion[b] (%)
Nonpresulfided	0.8	5
Presulfided	0.3	16

[a] Coking conditions: 400°C, 60 ml/min butadiene, 110 ml/min He, 50-mg samples.

[b] Reaction conditions: 400°C, 160 ml/min H_2, 6.8×10^{-5} mol C_4H_4S/min, 500-mg samples.

RESULTS AND DISCUSSION

Properties of Nonimpregnated Carbon

Some properties of the bare—nonimpregnated—carbon support are shown in Table 1. Presulfidation caused both the appearance of significant HDS activity and a decrease in coking tendency. The detection of HDS activity is remarkable, since the aluminas studied previously (*7, 8*) were proven to be essentially inactive.

The decrease of coking tendency after sulfidation (as seen in Table 1) is another interesting property of the carbon support. In contrast, alumina has been shown to produce practically the same coking either with or without presulfiding (*10*).

Therefore, taking into account that presulfidation of HDS catalysts is well known to increase catalytic activity (*7, 9*), and also to decrease coking (*7, 8, 10*), both features (Table 1) suggest that, contrary to other supports, carbon itself behaves as an HDS catalyst.

Temperature-Programmed Reduction

TPR spectra (Fig. 1) indicate a high-temperature signal at about 700°C, attributed to the reduction of carbon surface groups, and another signal, between 350 and 530°C, depending on the sample, assigned to the reduction of sulfided species.

The appearance of the low-temperature signal in the TPR spectrum of the nonimpregnated support after sulfiding differentiates this material from nonsulfidable alumina, and may be correlated to the increase of HDS activity in the support after sulfidation (Table 1). The nature of such incorporated sulfur is believed to be chemically bonded to carbon, and the existence of sulfhydryl groups (-SH) has also been claimed earlier (*11*).

The location of the first peak in the TPR spectra may be related to the sulfide bond (-S) strength against hydrogen reduction, this feature decreasing in the order C–S > Ni–S > Mo–S > NiMo–S. Note that this is the same order for increasing HDS activity in the present catalyst series, confirming previous results by Moulijn and co-workers using sulfided HDS catalysts supported on alumina (*12*) suggesting that catalysts from which chemisorbed sulfur is hydrogenated at lower temperatures have higher HDS activities.

Catalytic Activities

A comparison of the HDS steady-state activity of the present carbon-supported Ni–Mo catalyst with an available commercial (3/12) Ni–Mo on alumina (Cyanamid

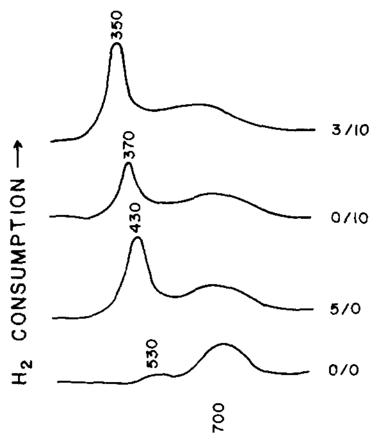

FIG. 1. TPR spectra of presulfided samples (0/0*: nonsulfided support).

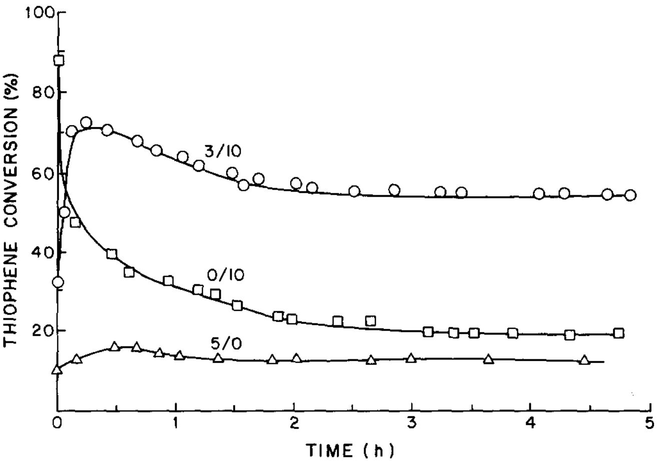

FIG. 2. HDS activity behavior of presulfided samples. Reaction conditions as in Table 1. Sample weight: 50 mg.

Aero 3A, 180 m^2/g) presulfided and tested under the same experimental conditions indicated that the former was seven and three times more active on a weight and surface area basis, respectively. Similarly, van Veen *et al.* (*13*) have shown that the activity per Co atom in CoMoS phase supported on carbon is about 2.5 times higher than that of same phase supported on alumina.

It should be remarked that contrary to alumina-supported catalysts, the surface area of the present catalysts was significantly smaller (about 40% less) than that of the nonimpregnated carbon support, suggesting that active species were forming aggregates plugging small pores. This is probably a consequence of both the weak interaction of the active species with the carbon support referred to above (*4*), and to the narrow micropore distribution of the activated carbon.

Activity behavior (Fig. 2) shows that while a pronounced drop in activity with respect to time occurred for the supported Mo sample (0/10), the catalyst containing Ni and Mo (3/10) exhibited an initial activity increase up to a maximum. Also, the 0/10 catalyst has initially (reaction time near zero) a higher activity than the 3/10 catalyst. Such differences in activity behavior between Mo- and Ni–Mo supported catalysts have also been found previously employing various aluminas as support (*7*, *8*). However, in these cases the samples were not presulfided as in the present work, but were subjected to reaction starting from calcined (oxidic) precursors. Therefore, as long as similar activity behavior occurred when starting either with oxidic (*7*, *8*) or sulfided (this work) precursors, it can be suggested that such behaviors were most likely due to processes involving either coking (activity decrease) or the uncovering or exposure (activity increase) of the active species.

Note also in Fig. 2 that the supported Ni sample (5/0) displays a trend in activity behavior similar to but less pronounced than that of the 3/10 sample: an initial activity increase to a maximum. The remarkable high activity of carbon-supported Ni confirms earlier results by Duchet *et al.* (*14*). Nickel on alumina, on the other hand, is known to be practically inactive for HDS (*7*).

Since the (most active) bimetallic catalyst (3/10) follows an activity behavior similar to that of the 5/0 sample (Fig. 2), the responsibility for the activity behavior in the bimetallic catalyst may be assigned to Ni, rather than to Mo. Hence, the active sites should be intimately related to Ni (viz., Ni accelerates the HDS reaction limiting step), probably involving exposed Ni atoms located (and thus stabilized) at edges of MoS_2 layers conforming the NiMoS (or CoMoS) phase previously proposed by Topsøe *et al.* (*15*). In addition, Ni atoms or clusters (e.g., Ni_xS_y clusters) may be connected to the carbon support so that the exposed Ni is stabilized by carbon similar to that occurring in the case of Ni associated to MoS_2. Indeed, layers and edges are also features in activated carbons, the structure of which is assumed to have reactive sites (where Ni could be also located) at the edges of twisted aromatic sheets forming slit-shaped micropores (*16, 17*).

Accordingly, it can be suggested that both Mo and carbon in their sulfided states act as sulfur sinks to maintain the active—exposed—Ni centers.

Note that contrary to many other works, we have carried presulfidation with pure H_2S instead of with an H_2S/H_2 mixture. This was most likely the reason for the initial activity increase to a maximum observed in both the 5/0 and 3/10 samples (Fig. 2), which probably reflected the uncovering of the active Ni centers, by the hydrogenation of chemisorbed S linked to these centers. To confirm this, we carried out another experiment (Fig. 3) in which the presulfidation of sample 3/10 was with a mixture of 5% H_2S in H_2. Indeed, there was not an initial activity increase in the sample presulfided with the mixture H_2S/H_2, but an initial activity decay similar to that occurring after the maximum. A similar but less pronounced effect was also found (not shown) for the 5/0 sample. Coincidentally, Louwers and Prins have shown very recently using EXAFS (*18*) that the Ni–S coordination number decreased when using lower H_2S/H_2 ratios for presulfiding, indicating that the Ni atoms become uncovered and available for catalysis.

CONCLUSION

According to the above results and discussion, we generalize that carbon support produce more active HDS catalysts than alumina support since the synergism arising in the former from the three active components (C + Mo + Ni) should be higher than the resulting from two of those components (Mo + Ni) as occurs on alumina.

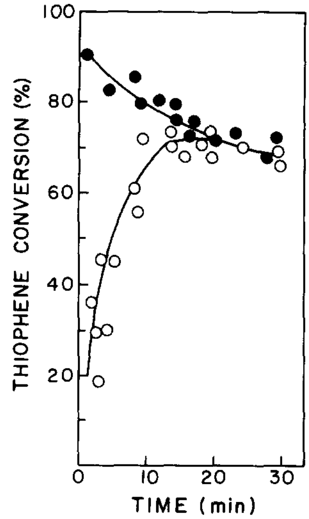

FIG. 3. Effect of presulfidation atmosphere on initial HDS activity behavior. Data is from repeated runs. Presulfidation with: ○, pure H_2S; ●, 5% H_2S in H_2.

ACKNOWLEDGMENTS

Financial support from the Venezuelan Consejo Nacional de Investigaciones Cientificas (CONICIT) is gratefully acknowledged. Many thanks to Dr. Joaquin Brito and Dr. John Labrecque for their collaboration.

REFERENCES

1. Abotsi, G. M. K., and Scaroni, A. W., *Fuel Process. Technol.* **22,** 107 (1989).
2. Solar, J. M., Derbyshire, F. J., de Beer, V. H. J., and Radovic, L. R., *J. Catal.* **129,** 330 (1991).
3. Reddy, B. M., and Subrahmanyam, V. S., *Appl. Catal.* **27,** 1 (1986).
4. Vissers, J. P. R., Scheffer, B., de Beer, V. H. J., Moulijn, J. A., and Prins, R., *J. Catal.* **105,** 227 (1987).
5. Laine, J., and Pratt, K. C., *Ind. Eng. Chem. Fundam.* **20,** 1 (1981).
6. Massoth, F. E., and Miciukiewciz, J., *J. Catal.* **101,** 505 (1986).
7. Laine, J., Brito, J., Gallardo, J., and Severino, F., *J. Catal.* **91,** 64 (1985).
8. Laine, J., Brito, J., and Severino, F., *Appl. Catal.* **15,** 333 (1985).

9. Laine, J., Brito, J. L., and Severino, F., *J. Catal.* **131,** 385 (1991).
10. Brito, J., Golding, R., Severino, F., and Laine, J., *Prepr. Am. Chem. Soc. Div. Pet. Chem.* **27,** 762 (1982).
11. Sykes, K. W., and White, P., *Trans. Faraday Soc.* **52,** 660 (1956).
12. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121,** 31 (1990).
13. van Veen, J. A. R., Gerkema, E., van der Kraan, A. M., and Knoester, A., *J. Chem. Soc. Chem. Commun.,* 1684 (1987).
14. Duchet, J. C., Van Oers, E. M., de Beer, V. H. J., and Prins, R., *J. Catal.* **80,** 386 (1983).
15. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Morup, S., *J. Catal.* **68,** 433 (1981).
16. Stoeckli, H. F., *Carbon* **28,** 1 (1990).
17. Laine, J., and Yunes, S., *Carbon* **30,** 601 (1992).
18. Louwers, S. P. A., and Prins, R., *J. Catal.* **133,** 94 (1992).