JOURNAL OF CATALYSIS **166,** 384–387 (1997)
ARTICLE NO. CA971507

NOTE

Sink Effect in Activated Carbon-Supported Hydrodesulfurization Catalysts

A synergistic effect has been proposed in previous papers (1, 2), attempting to explain the higher activity of activated carbon-supported hydrodesulfurization (HDS) catalysts with respect to conventional alumina-supported catalysts, reported earlier (3). However, activated carbon characteristics can be strongly affected by the raw material and the method of activation. Thus, previous work (2) using Ni–Mo catalysts supported on two different activated carbons (one prepared by "physical" and the other by "chemical" activation) showed different optimal Ni concentrations for higher HDS activity, such difference being attributed to the predominance of Topsøe's Type I "NiMoS" phase (4) in one carbon and the predominance of Type II in the other.

Due to the lack of proper characterization of the activated carbon supported catalysts of the previous work (2), this paper presents further data suggesting that microporosity provided by the activated carbon may be the responsible for the above referred synergism.

Catalyst preparation, sulfidation, and activity test (HDS of thiophene at 400°C and atmospheric pressure) were carried out as before (1, 2). Briefly, the supports were first impregnated with an ammonium molybdate solution at 80°C until the excess solution was evaporated. After drying at 120°C, the same procedure was repeated using nickel nitrate solution. No calcination step was performed before the in situ sulfidation with pure H_2S at 400°C. Thiophene conversions reported were obtained after aparent steady-state activity was attained (3–4 h of reaction). The two activated carbon supported catalysts, named NiMo/CA and NiMo/CB, had compositions of 5/10 and 3/10 wt% NiO/wt% MoO_3, respectively. These were (2) the optimum Ni contents for higher thiophene conversions for the 10 wt% MoO_3 loaded CA and CB activated carbons. These carbons were commercial activated carbons Pica (CA) and Purocarbon (CB) prepared from lignocellulosic raw materials by "physical" and "chemical" activation methods, respectively. A commercial alumina-supported HDS catalyst (named NiMo/Al) with 3/15 wt% NiO/wt% MoO_3 (Cyanamid Aero HDS 3A) was also employed for comparative purposes.

The porosity characteristics of the supports and impregnated catalysts were obtained from N_2 adsorption isotherm at 77 K using a Micromeritic ASAP 2000 apparatus, and the various data reduction methods contained in the equipment software: BET, Harkins and Jura (HJ), Horwarth and Kawazoe (HK), and density functional theory (DFT) methods. These two latter are reported as improved methods, recently introduced for porosity characterization (5). Samples were pretreated under vacuum at 350°C. The results were calculated from data in the range of 0.03 up to 630 Torr pressure.

Oxygen chemisorption was served to estimate the amount of active species available on each catalyst. Oxygen adsorption isotherms were obtained at 25°C using same Micromeritics ASAP 2000 high vacuum system. The dried impregnated sample was first reduced with H_2 at 400°C for 3 h, reaching final temperature at 10°C/min. Then it was evacuated at slightly above reduction temperature (415°C) for 2 h to ensure a complete removal of H_2. Oxygen chemisorption was then performed at 25°C, employing a range of 10 up to 630 Torr pressure. The total amount of O_2 chemisorbed was obtained by extrapolation of the end trend (plateau) of the isotherm to zero pressure intercept. The amount of O_2 thus obtained is directly related to the amount of accessible sites on the catalyst, and we assume that this amount remains proportional to the amount of active species on the sulfided catalyst.

Tables 1 and 2, and Fig. 1 show reproducible data obtained from the adsorption isotherms of N_2 at 77 K of the solid samples. Porosity data should always be taken into account cautiously. For example, both BET and HK methods give values of surface area and pore volume that include both micropores ($<$20 Å) and mesopores (20–500 Å), but HJ gives values corresponding only to micropores. Thus, the HJ surface area for NiMo/Al is negligible with respect to its BET surface area (Table 2), indicating that the alumina catalyst is mainly a mesoporous solid. On the other hand, the HK value of median pore width is a measure of the pore width that contributes most to surface area, but not necessarily to pore volume. Thus, the HK median pore width for CA: 6 Å (Table 1), falling in the "ultra" class of micropores referred to by several authors (6), contributes significantly less to pore volume than other larger micropores. A remarkable difference between CA and CB, even after impregnation, is the presence of mesopores in CB but not in CA.

0021-9517/97 $25.00

TABLE 1

Porosity Data from the Isotherm of Adsorption of N_2 at 77 K of the Activated Carbon Supports

	BET	HJ		HK		DFT	
Support	Total surface area m^2/g	Micropore surface m^2/g	Micropore volume cc/g	Max. pore vol. cc/g	Median pore width Å	Volume in pores <8.04 Å cc/g	Total volume in <634 Å cc/g
C_A	680	655	0.39	0.43	6.0	0.24	0.34
C_B	1240	725	0.42	1.1	19	0.11	0.90

Impregnation of the Ni and Mo precursor salts did not essentially change the pore size distribution in CA: the almost uniform decrease in pore volume along all pore sizes observed after impregnation of CA (Fig. 1A) may be attributed to dilution of the support by the presence of Ni and Mo. Contrarily, impregnation did produce more significant changes in CB (Fig. 1B): the volume of micropores and of small mesopores, was reduced not only by support dilution, but also probably by either pore plugging or filling by the precursor salt aggregates, which caused a significant decrease of total surface area, i.e., BET decreased from 1240 (Table 1) to 730 m^2/g (Table 2) after impregnation.

Table 3 shows the uptake of O_2 at 25°C, and the catalyst activity, expressed as the fraction of thiophene converted, refers to the respective O_2 uptake. This latter is assumed to be proportional to the number of active sites. It can be seen that the activated carbon-supported catalysts are about 2 to 3 times more active than the alumina-supported catalysts.

Typical differences between physical and chemical activation suggest that slit pores in CA should have larger polyhexagon planar areas and, consequently, narrower widths than slit pores in CB (7, 8). This fact is confirmed by the pore size distributions obtained for CA and CB, where the shift of maximum pore volume towards ultramicropores (Fig. 1A) suggests the presence of very narrow slit micropores in CA, whereas CB distribution (Fig. 1B) indicates a wider, probably more tortuous, pore structure. In the case of the alumina catalyst (Fig. 1C) micropores are not present and the pore volume (mostly large mesopores) is probably constituted by the void spaces among very small Al_2O_3 crystallites or amorphous aggregates.

The different changes in pore size distribution and in surface area after impregnation of CA and CB (Tables 1, 2 and Fig. 1) are probably consequences of the differences in porosity, as well as the differences in surface functionality of the carbon supports. CB has been shown to be

TABLE 2

Porosity Data from the Isotherm of Adsorption of N_2 at 77 K of the Catalysts

	BET	HJ		HK		DFT	
Catalyst	Total surface area m^2/g	Micropore surface m^2/g	Micropore volume cc/g	Max. pore vol. cc/g	Median pore width Å	Volume in pores <8.04 Å cc/g	Total volume in <634 Å cc/g
NiMo/C_A	540	530	0.30	0.34	6.0	0.23	0.30
NiMo/C_B	730	370	0.22	0.78	30	0.11	0.54
NiMo/Al	164	<1	0.001	0.47	162	0.01	0.44

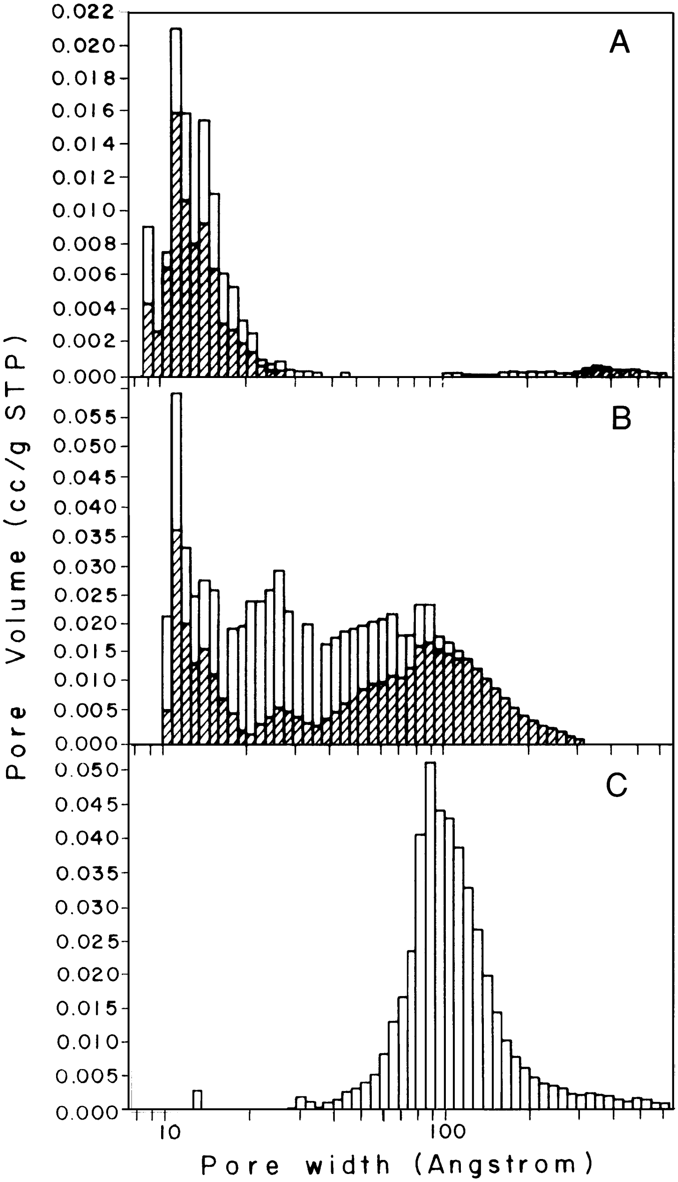

FIG. 1. Pore size distribution from isotherms of adsorption of N_2 at 77 K (DFT method): (A) white columns: CA, shade columns: NiMo/CA; (B) white columns: CB, shade columns: NiMo/CB; (C) NiMo/Al.

TABLE 3

Data from Adsorption of O_2 at 298 K and HDS Activity of the Catalysts

Catalyst	Volume of O_2 adsorbed (cc/g)	Activity[a]
NiMo/CA	8.2	10
NiMo/CB	9.8	7
NiMo/Al	3.3	3

[a] Fraction of thiophene converted at 400°C per gram of catalyst divided by volume of O_2 adsorbed.

more acidic than CA; solid pH is about 10 for CA and about 5 for CB (9). Therefore, the impregnating solution may interact with acidic complexes located at slit edges blocking the access to the slit volume, thus decreasing total surface area. In contrast, the less acidic-hydrophobic-CA, also having a large proportion of less accessible ultramicropores, probably difficult the penetration of the impregnating solution leading to the accumulation of aggregates outside the smallest micropores, resulting in a smaller dispersion (i.e., smaller O_2 adsorption) compared with CB (Table 3).

The results in Table 2 and in Fig. 1 suggest that NiMo/Al is a mesoporous, NiMo/CB is a meso + microporous, and NiMo/CA is a micro + ultramicroporous catalyst. Interestingly, this classification is closely related to HDS activity (Table 3), so that catalysts having narrower pore sizes produce larger activities. However, HDS activity is inversely related to the amount of O_2 chemisorbed (i.e., the number of active sites) when comparing CA with CB catalysts (Table 3). Therefore, some porosity factor provided by the activated carbons, particularly by CA, is probably playing a positive role in the HDS reaction mechanism enhancing catalytic activity.

Topsøe's active phase (4), generally referred to as "NiMoS" (or "CoMoS"), is probably present in both CA and CB as suggested previously (2). In general, NiMoS could be considered as "sandwiches" or slabs where two sulfur compact planes (i.e., each sulfur coordinated to other six sulfurs in the same plane) are placed one over the other forming trigonal prismatic holes, half of these holes being occupied by Mo, whereas Ni is "decorating" the borders of the slab in the same plane formed by Mo.

The ionic thickness of a simple NiMoS slab is probably twice the ionic diameter of sulfur, i.e., $2 \times 3.2 = 6.4$ Å. Thus, such a slab would not fit inside the most abundant pores found in CA: those having widths around 6 Å (Table 1). Accordingly, most of the surface area of CA is probably not completely supporting the active Ni–Mo phase; therefore, in the case of CA slit borders holding the active phase is probably a better model than the active phase laying on the flat surface.

According to Jagiello and Schwartz (10), slit micropores of activated carbons may produce adsorption forces that may be as high as twice the adsorption force found at the surface of larger pores. On the other hand, the above discussion suggests that NiMoS may be outside but next to the micropores. Accordingly, the above cited synergistic effect of the support could consist of a driving force (or "sink") functioning from the inside of micropores that subtract excess sulfur of NiMoS (such excess remaining after S–C bond cleavage following thiophene adsorption), regenerating the sulfur vacancies over the active Ni (or Mo) site at the slab border. Thus, a faster reaction rate should be expected if vacancy regeneration is the slow step in the HDS mechanism.

Vacancy regeneration is probably a function of the strength of sulfur adsorption, and temperature-programmed reduction reported previously (2) suggested a weaker S-binding in Topsøe's Type I phase with respect to Type II. Therefore, the sink effect proposed above will favor the activity of Type II phase, whereas Type I phase will probably be the most active on alumina supports.

It is remarkable that other high surface area supports having micropores that are not slit-shaped, such as silica, have been shown (11) not to produce a synergistic effect in HDS as found in activated carbons, even though enhanced adsorption in micropores has been suggested for other pore geometries different from slit pores (12). Therefore, pore shape appears to be a necessary condition for the above-proposed synergism. This condition probably arises from the slit-pore feature of being open along all the slit perimeter, allowing the sulfur accumulated between the pore walls to be attacked by hydrogen from any pore side to desorb as H_2S.

CONCLUSION

The synergistic effect of the activated carbon support in HDS catalysis is assigned to the presence of slit micropores that function as sulfur sinks to promote the activity of the sulfide catalyst.

ACKNOWLEDGMENT

The authors thank CONICIT for financial assistance.

REFERENCES

1. Laine,, J., Severino,, F., Labady, M., and Gallardo, J., *J. Catal.* **138**, 145 (1992).
2. Laine, J., Severino, F., and Labady, M., *J. Catal.* **147**, 355 (1994).
3. van Veen, J. A. R., Gerkema, B., van der Kraan, A. M., and Knoester, A., *J. Chem. Commun.*, 1684 (1987).
4. Candia, R., Sorensen, O., Villadsen, J., Topsøe, N., Clangen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93**, 763 (1984).
5. Olivier, J. P., Conklin, W. B., and Szombathely, M. V., "Characterization of Porous Solids III" (J. Rouquerol *et al.*, Eds.), p. 81, Elsevier, Amsterdam, 1994.

6. Kaneko, K., Setoyama, N., and Susuki, T., “Characterization of Porous Solids III” (J. Rouquerol *et al.*, Eds.), p. 593, Elsevier, Amsterdam, 1994.
7. Laine, J., and Yunes, S., *Carbon* **30**, 601 (1992).
8. Rodríguez, J., Ruette, F., and Laine, J., *Carbon* **32**, 1536 (1994).
9. Laine, J., Calafat, A., and Labady, M., *Carbon* **27**, 191 (1989).
10. Jagiello, J., and Schwarz, J. A., *J. Coll. Interface Sci.* **154**, 225 (1992).
11. Laine, J., Brito, J. L., and Severino, F., *J. Catal.* **131**, 385 (1991).
12. Everett, D. H., and Powl, J. C., *J. Chem. Soc., Faraday Trans.* **1**, 72, 619 (1976).

J. Laine*,[1]
M. Labady*
F. Severino*,[2]
S. Yunes†

**Laboratorio de Físico-Química de Superficie*
Instituto Venezolano de Investigaciones Científicas
Apt. 21827
Caracas 1020-A
Venezuela; and
†*Micromeritics*
One Micromeritics Drive
Norcross, Georgia 30093

Received May 7, 1996; revised September 25, 1996; accepted October 30, 1996

---

[1] To whom correspondence should be addressed. E-mail: jlaine@quimica.ivic.ve.

[2] Deceased.