TEXTURE EFFECT IN ACTIVATED CARBON BASED HDS CATALYSTS

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INTRODUCTION

Higher hydrodesulfurization (HDS) activity and lower coke deposition have been claimed for activated carbon-supported Co(or Ni)-Mo catalysts with respect to conventional alumina-supported catalysts (1). However, these findings have not been completely clarified, for example, carbon support interaction with the active phase is weak promoting sintering during catalyst 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.

As a possible explanation for the higher activity, a synergistic efect of the activated carbon support in Ni-Mo HDS catalysts has been recently proposed (2,3), suggesting that the carbon support functions in conjunction with molybdenum sulfide to promote the exposure of nickel active centers; however, there are insufficient clues as to which activated carbon characteristics are involved in the activity promotion.

In this communication we show evidence suggesting that the synergistic effect of the activated carbon may be assigned to the presence of slit micropores that function as sulfur sinks.

EXPERIMENTAL

Catalyst preparation, sulfidation and activity test (HDS of thiophene at 400°C and atmospheric pressure) were carried out as before (2,3). 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 (3) the optimum Ni contents for higher HDS activity for the 10 wt% MoO_3 loaded CA and CB activated carbons respectively. These carbons were commercial activated carbons Pica (CA) and Purocarbon (CB) prepared from lignocellulosic raw materials by "physical" and "chemical" activation, respectively.

The textural characteristics of the supports and catalysts were obtained from nitrogen adsorption isotherm at 77 K using a Micromeritic 2000 apparatus, and the various data reduction methods contained in the equipment software: BET, Harkins & Jura (HJ) t-plot, and Horuwath & Kawazoe (HK).

RESULTS AND DISCUSSION

The textural differences observed in Table 1 sugest that NiMo/CB is a meso+microporous catalyst, and that NiMo/CA is a micro+ ultramicroporous catalyst. This classification is closely related to HDS activity (Table 1), so that the catalyst having narrower pore sizes, and thus, larger diffusional resistance, has higher activity. This is unexpected because larger diffusion resistance should imply smaller global reaction rates, if intrinsic activity is the same. Therefore, the narrower texture provided by CA is probably playing a positive role in the HDS reaction mechanism, by promoting a higher intrinsic activity that compensates for its larger diffusion resistance.

The promotion of HDS activity by micropores, in particular by slit-shaped micropores as normally found in activated carbons (4), may be attributed to a sulfur sink effect of the slit micropores that favor the generation of sulfur vacancies on the sulfided Ni-Mo active phase.

Topsøe active phase (5), generally referred to as "NiMoS" (or "CoMoS)", is probably present in both CA and CB as suggested previously (3). 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 atomic ratio Ni/Mo may vary between 1/2 and 1 (3) depending on the planar size of the slab and on the occurrence of multiple slab crystallites , where the sulfur planes of different slabs sit one over the other, as a result of weak van der Waals attraction forces, forming tetra- and octahedral holes. The NiMoS phase is complicated by the introduction of Type I (not fully sulfided) and Type II (fully sulfided), and by the occurrence of multislabs where intercalation sites are also possible for Ni location. The predominant presence of Type I in CB and Type II in CA reported earlier (3) is probably a consequence of the differences in surface functionality and texture between CA and CB discussed above.

The ionic thickness of a simple NiMoS slab is probably twice the ionic diameter in sulfur, i.e., 2x3.2=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, slit borders holding the active phase are probably a better model than the active phase laying on the flat surface. Indeed a more stable linking between the support and the active phase probably results in less free energy and thus, less activity, than if the active phase is loosely connected to the support.

According to Jagiello and Schwartz (6), 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. Accordingly, assuming that NiMoS is next to the micropores, a driving force may be functioning from the micropores to subtract excess sulfur from NiMoS (remaining after S-C bond cleavage following thiophene adsorption), regenerating the active sulfur vacancies over the Ni (or Mo) site at the slab border. Therefore, a faster reaction rate should be expected if vacancy regeneration is the slow step in the HDS mechanism.

It is remarkable that other high surface area supports having micropores that are not slit-shaped, such as silica, have been shown (7) not to promote a synergistic effect as found in activated carbons. Thus, pore shape appears to be a necessary condition for the above proposed synergism. This condition probably arises from qthe slit pore feature of being open at rear and/or lateral sides, allowing the sulfur accumulated between the pore walls to be attacked by hydrogen from either pore side.

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Table 1: Textural data and activity of the catalysts.

| Catalyst | BET Surface Area (m^2/g) | HJ Micropore | | HK | | Thiophene Conversion (X) (%) | Relative Diffusion Resistance* |
		Surface m^2/g	Volume cc/g	Max. Pore Vol. cc/g	Median Pore Width Å		
NiMo/C$_A$	540	530	0.30	0.34	6.0	67	14
NiMo/C$_B$	730	370	0.22	0.78	30	58	9

* Defined as (Xo-X), where Xo was measured maintaining same contact time as for X but at a higher flux.