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RESEARCH NOTE

Compensation Effect and Dual Promotion Effect in Activated Carbon-Supported CoNiMo Hydrodesulfurization Catalysts

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Although scientific evidence for the superior performance of activated carbon-supported Ni(or Co)Mo hydrodesulfurization (HDS) catalysts compared with that of conventional alumina-supported ones does exist (1–6), this superiority appears not to be clearly demonstrated under commercial operation conditions.

Based on activity measurements at atmospheric pressure, a synergism between the active sulfided Ni(or Co)Mo phase and the slit micropores of the activated carbon has been postulated (7–9).

On the other hand, dual promotion (e.g., Co + Ni) in HDS catalysts has been reported to be beneficial when using alumina support (10–14).

Within the above scope, two objectives are pursued in this communication: (1) to investigate the synergy effect of activated carbon when using more realistic HDS commercial conditions, i.e., at high H_2 pressure and (2) to investigate the dual promotion effect in HDS catalysts supported on activated carbon.

Two commercial activated carbons, both prepared from natural lignocellulose raw materials, were used for the present study. Pica carbon (C_A) was manufactured employing the high-temperature "physical" activation and Purocarbon (C_B) employing the phosphoric acid "chemical" activation method. These two carbons have been fully characterized in a previous work (9). Their main differences are that C_A features very narrow micropores (median micropore width = 6 Å; BET surface area = 680 m^2/g) and a solid pH of 10, whereas C_B has wide micropores as well as mesopores (median pore width = 19 Å; BET surface area = 1240 m^2/g) and a solid pH of 5.

The catalysts were prepared by a two-step impregnation method as in previous works (7–9). All samples had Mo loading of 10 wt% (reported as MoO_3) and Co + Ni concentration of 5 wt% (as CoO + NiO), with atomic ratios $r = Co/(Co + Ni)$ varying between 0.0 and 1.0. Oxygen chemisorption reported previously (9) suggested that C_B catalysts have better dispersion of active sites than C_A catalysts, probably as a result of different surface areas and physicochemical characteristics of both carbon surfaces which affect the impregnation phenomena.

The impregnated samples were dried at 110°C, then presulfided *in situ* with H_2S at 400°C before activity tests were performed. Activity tests were carried out in microreactor flow systems at atmospheric and high pressure, and the resulting thiophene conversions are shown in Figs. 1 and 2.

Figure 1 shows that catalysts supported on C_A are more active than catalysts supported on C_B. This is in accordance with the sink effect reported before (9); i.e., catalysts with narrower slit micropores (those supported on C_A) are more active. However, this synergism between the active sulfided Ni(or Co)Mo phase and the slit micropores of the activated carbon (see Fig. 3) has been based only on activity measurements at atmospheric pressure. It was suggested that a driving force (or "sink") functioning from the inside of the slit micropores subtract excess sulfur (this excess remaining at the crystallite edges after S–C bond cleavage), thus, regenerating the sulfur vacancies (i.e., the active sites at the crystallite edges) in the Co(or Ni)MoS phase. This synergism would lead to a faster reaction rate if it is assumed that vacancy regeneration is the slow step in the HDS mechanism. The slit-pore feature of being open along all of the slit perimeter allows the sulfur accumulated between the pore walls to be attacked by hydrogen from any pore side and desorb as H_2S.

When the HDS was carried at 30 atm (Fig. 2), the opposite to that shown in Fig. 1 occurs; i.e., C_B catalysts are now more active than C_A catalysts. This change in activity superiority between C_A and C_B catalysts is most probably a consequence of the high hydrogen partial pressure which produces vacancy regeneration (the slow step in the HDS mechanism) more rapidly than what would be produced by the sink effect of the slit micropores. Therefore, it can be

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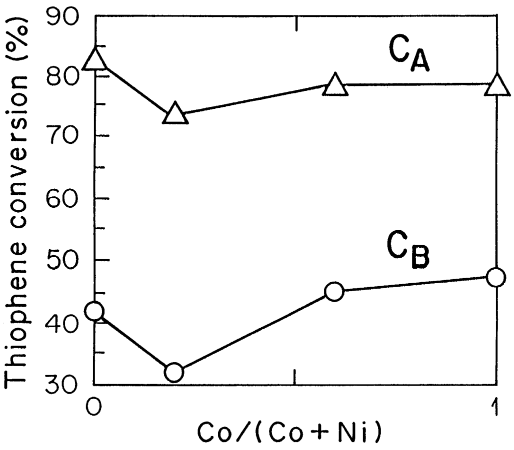
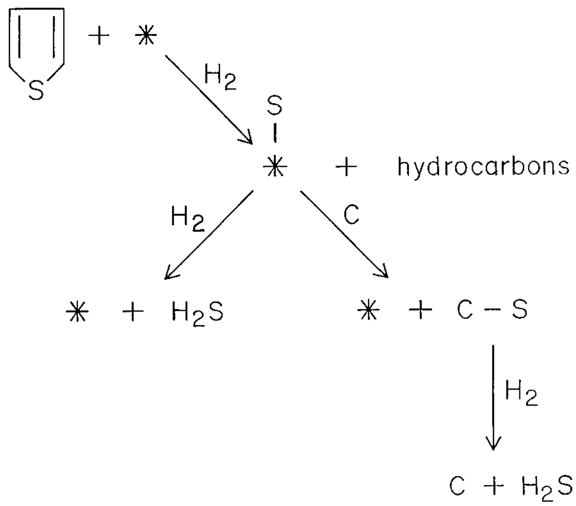


FIG. 1. HDS activity of the CoNiMo/C catalysts at 400°C and 1 atm. Other experimental details as described elsewhere (8).



SCHEME 1

concluded that the sink effect, previously reported (9), is compensated at high pressure.

Accordingly, the mechanism in Scheme 1 is proposed. Hence, two parallel routes are possible for the regeneration of vacancies (i.e., the active sites, denoted by *): one (right), sulfur subtraction by the sink effect, followed by hydrogen attack inside the micropores; and the other (left), sulfur direct hydrogenation by which the rate increases with hydrogen pressure.

Figures 1 and 2 also show minimum HDS activity for an intermediate value of *r*. This result is in contrast with the previous one, where a maximum HDS activity was obtained when using alumina-supported CoNiMo catalysts (13, 14). In that case, IR spectra of adsorbed NO suggested an optimal surface concentration of promoters (13), attributed to the differences in reactivity between Co and Ni with alumina.

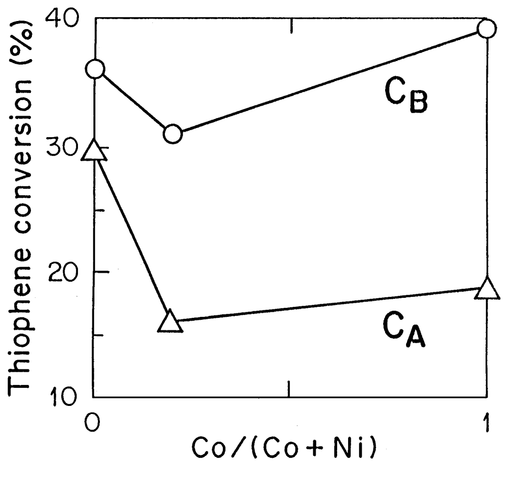


FIG. 2. HDS activity of the CoNiMo/C catalysts at 375°C and 30 atm. Feed of 0.2 ml/min 17 wt% thiophene in cyclohexane. Catalyst sample = 250 mg diluted in carburumdum inside a 10-mm i.d. tubular reactor. Thiophene conversion was calculated from the analysis of sulfur content in the total liquid collected after about 5 h of reaction.

These opposed dual effects when using activated carbon or alumina could be related to the possible presence of Topsøe's Type I or Type II Co(or Ni)MoS active phases (15). As suggested in previous works (8, 9), the weak interaction between the carbon support and the metal species favours the formation of the Type II—fully sulfided—phase, whereas in a support like alumina, where there is a stronger interaction, Type I phase, not fully sulfided with the remaining metal–O–Al linkages, will be favoured.

In the case of silica-supported CoNiMo, a minimum for an intermediate value or *r* has also been found (16). This similarity with the present results could also be related to the weak interaction between the support and the active species. Nevertheless, more evidence is necessary to give a clear explanation for the occurence of such a minimum. One possibility is that the stabilization of the active phase is affected by *r*. To study this aspect, theoretical calculations by quantum mechanical methods are actually performed by our research group.

It may be interesting to remark that though activated carbon and silica have given similar results as discussed above, the HDS activities at atmospheric pressure reported previously for the case of the silica support (16) are considerably lower in comparison to those obtained presently with activated carbon. This could be due to the fact that the sink effect probably does not occur in the silica-supported catalysts because the presence of slit micropores (present in activated carbon but not in silica) appears to be a necessary condition for the occurrence of such an effect (9).

In summary, measurements of HDS activities at both atmospheric and high pressures demonstrated that the synergy effect of the activated carbon support postulated in previous works is compensated by the hydrogen pressure.

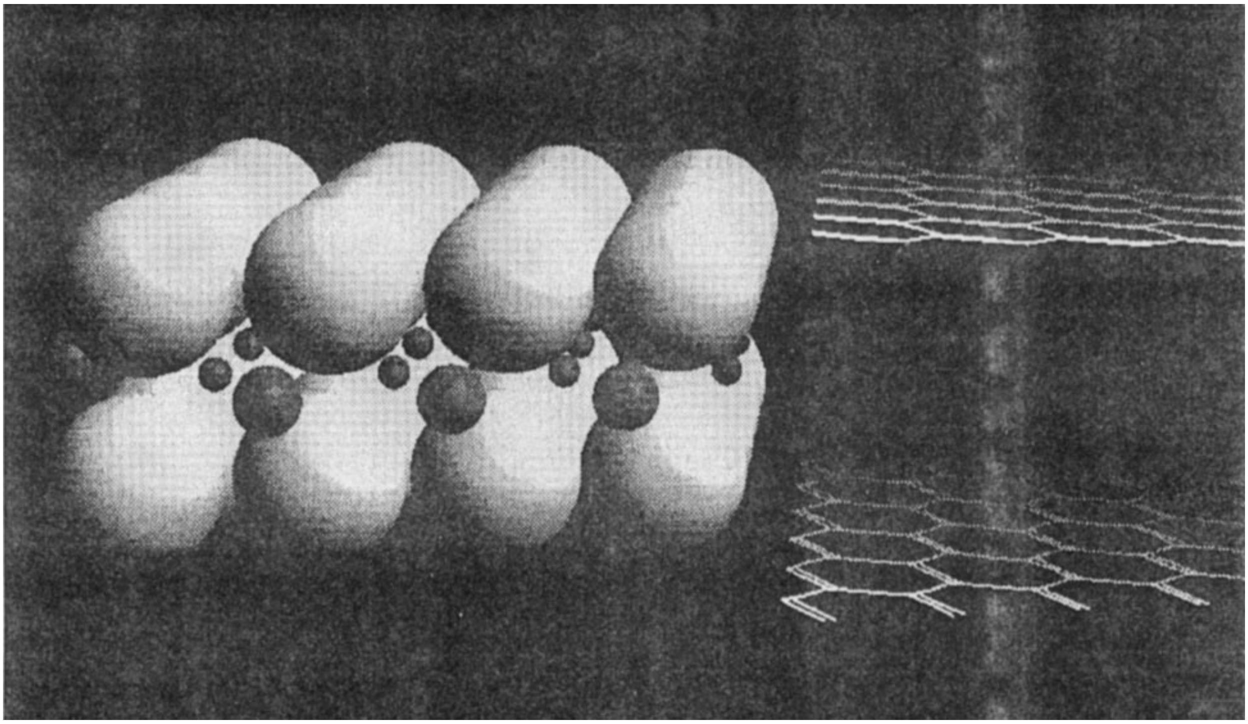


FIG. 3. Model of the synergism between the activated carbon and the Co(or Ni)MoS phase, showing a slit micropore of about 6–7 Å. Mo atoms are located inside trigonal prismatic holes formed between two sulfur compact planes, whereas Co (or Ni) atoms are "decorating" the edges of the slab crystallite.

Minimum HDS activity for the intermediate value of $r = \text{Co}/(\text{Co} + \text{Ni})$ was found, contrasting with previous findings reporting a maximum for alumina-supported CoNiMo catalysts.

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