JOURNAL OF CATALYSIS 91, 64–68 (1985)

The Role of Nickel in the Initial Transformations of Hydrodesulfurization Catalysts

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Received July 13, 1983; revised May 23, 1984

The initial hydrodesulfurization activity behavior of supported nickel molybdate catalysts has been found to be markedly influenced by the presence of the promoter (nickel). The promoter diminished both the rate and the extent of deactivation of the fresh catalyst when exposed to a mixture of hydrogen and thiophene at atmospheric pressure. Presulfidation of the catalysts with pure H_2S did not affect the optimum nickel concentration but increased the optimum molybdenum concentration. These results together with those obtained on surface acidity, carbon deposition, and sulfidation extent seems to support the idea that the positive influence of the promoter on the initial transformation of the catalyst is to maintain the dispersion of molybdenum during the sulfidation of the catalyst and to diminish carbon deposition. © 1985 Academic Press, Inc.

INTRODUCTION

The structure and mode of operation of hydrodesulfurization (HDS) catalysts is still a puzzle as a result of the great variety of possible morphologies and interactions that may occur between the three species forming the catalyst, namely the support (generally γ-Al_2O_3), the promoter (Co or Ni) and the main active component (generally Mo).

The extensive experimental evidence available on this system has been reviewed several times (*1–5*). The enhancement of HDS activity produced by the promoter is probably the most complex aspect. This has been the subject of a number of theories. The bases of these theories may be grouped into two general postulates: (i) the promoter increases the number of active Mo-sites, or (ii) it increases the activity of the active Mo-sites. In fact, both approaches could be applicable simultaneously in the catalyst operation.

Significant structural differences between oxidic (fresh) and sulfided (used) catalyst states suggest that the transformations occurring during the initial catalyst operation are important in determining the steady-state activity. However, the influence of the promoter on this catalyst state change does not seem to be clearly established.

In this work the involvement of nickel in the initial transformation of molybdate catalysts has been studied by examining a series of alumina-supported catalysts of various Ni and Mo concentrations.

EXPERIMENTAL

The support employed was a γ-alumina (BDH) in the form of powder (150–200 mesh) with an area of approximately 110 m^2/g. Solutions of nickel nitrate and ammonium molybdate of appropriate concentrations to obtain the desired catalyst compositions were mixed with the support while stirring and heating at 80°C. The paste obtained in each case was dried at 120°C overnight and calcined at 500°C for 5 hr. Compositions employed were 0–10 wt% NiO and 0–60 wt% MoO_3.

The HDS activity was measured using a continuous-flow reactor operating at atmospheric pressure and connected to an online gas chromatograph. The activities are reported as the conversion of thiophene as a function of processing time. The reaction

0021-9517/85 $3.00
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conditions were: 3 g of catalyst, 45 mol H_2/mol C_4H_4S, 740 cm^3/min H_2, and 400°C. Prior to activity tests the catalyst sample was heated to the reaction temperature under a nitrogen atmosphere for 20 min. Other tests were carried out presulfiding the sample with pure H_2S at 400°C for 2 hr. In the latter cases the activity was measured at a reaction temperature of 300°C. After use the catalyst sample was allowed to cool to room temperature under a flow of nitrogen before being taken out of the reactor for further analyses.

Fresh (nonpresulfided) and presulfided samples were employed for acidity and carbon-deposition measurements.

Acidity is reported as the amount of ammonia adsorbed. A McBain microbalance was used under high-vacuum conditions. The catalyst samples were first evacuated at 200°C overnight. Two types of acidity were measured, as given by the amount of ammonia adsorbed at 600 Torr and 25°C (a_1) and the amount retained after evacuation at 25°C for 15 hr (a_2). The fraction of acid-active sites is assumed to be reflected by the ratio a_2/a_1.

Weight increases by carbon deposition from 1,3-butadiene (thiophene HDS intermediary) were followed employing also a microbalance but connected to an atmospheric pressure flow system. The following conditions were employed: 50 mg of catalyst, 60 cm^3/min 1,3-butadiene, 110 cm^3/min He or H_2, and 400°C. Prior to deposition, the sample was outgassed under a helium flow and treated with the olefin diluting gas (He, H_2 or H_2 + 5 vol% H_2S) at 400°C for 2 hr.

In the text that follows, the composition of the catalysts will be referred as y/x ($\equiv$ wt% NiO/wt% MoO_3 as deposited on the support).

RESULTS

Activity behavior. Neither the support alone nor the support impregnated with Ni only exhibited detectable activity. The influence of the promoter on the initial activity of the molybdate catalyst is shown in Fig. 1. It is clear that the promoter remarkably affects the initial activity of the molybdate catalyst: while a pronounced drop in activity with respect of time occurred for the unpromoted sample (0/10), the catalysts containing Ni in concentrations near to commercial catalysts (3/10 and 5/15) exhibited a continuous activity increase up to a maximum. Also, the unpromoted catalyst (0/10) has initially (reaction time near zero) larger activity than the promoted catalysts. It is interesting to observe that although the samples with 3/10 and 5/15 have very similar values of the Ni/Mo ratio, the extent of deactivation that follows the activity increase is significantly more pronounced in the first case.

Figure 2 shows an optimum Ni concentration near to values reported elsewhere (*6*). It can be seen that the difference between the maximum activity and the steady-state activity of nonpresulfided samples (i.e., the deactivation extent) decreases as the Ni content increases. It is

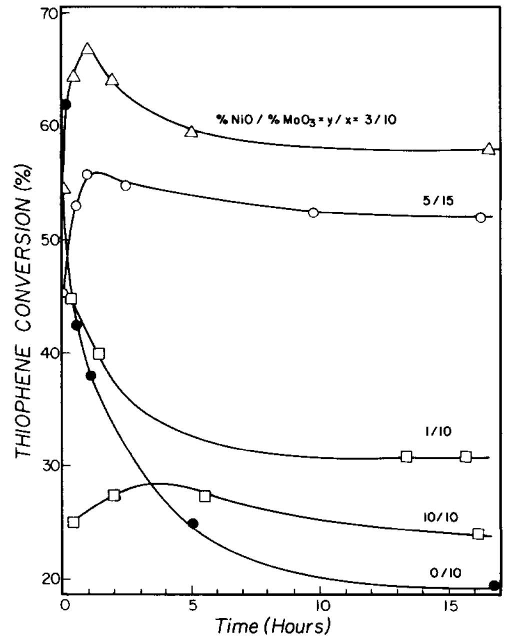

FIG. 1. Activity behavior (400°C) of nonpresulfided catalyst of various compositions.

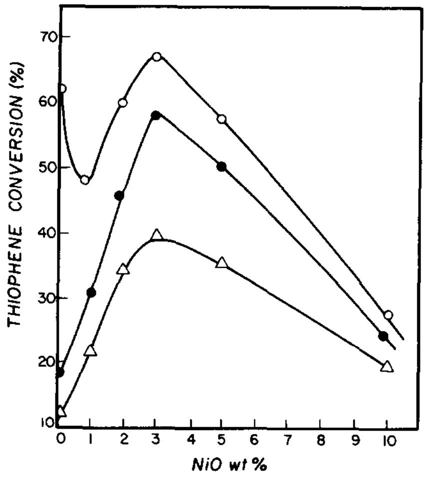

FIG. 2. Effect of nickel content on activity of catalysts with 10% MoO_3. Nonpresulfided samples (reaction temperature: 400°C): (○) activities at the maxima, (●) steady-state activities. Presulfided samples (reaction temperature: 300°C): (△) steady-state activities.

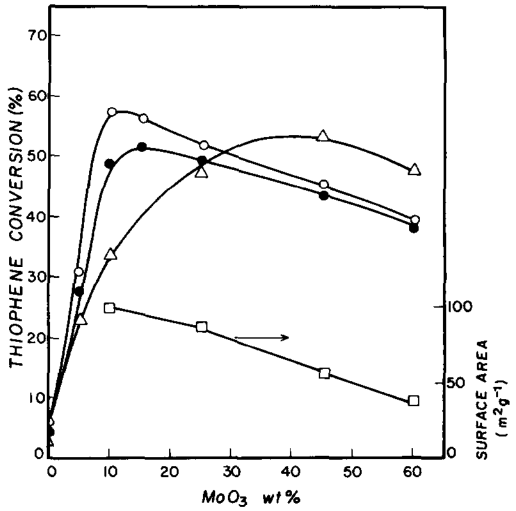

FIG. 3. Effect of molybdenum content on activity of catalysts with 5% NiO (symbols as in Fig. 2).

also shown that the optimum is not changed by presulfiding. In contrast, the optimum molybdenum concentration is affected by presulfiding (Fig. 3), i.e., the optimum MoO_3 concentration is increased from 10–15 wt% to about 35 wt% by presulfiding.

Acidity measurements. From the results summarized in Table 1 it can be concluded that the incorporation of nickel in the supported molybdate catalyst reduces the fraction of acid-active sites (a_2/a_1). Sulfidation of the catalysts produces an increase in the fraction of acid-active sites of the promoted catalyst, but a significant decrease in the case of the unpromoted catalyst.

Sulfur and carbon analyses. Sulfur and carbon content of nonpresulfided catalysts used for 17 hr are shown in Fig. 4. It can be seen in this figure that there is a maximum

TABLE 1

Acidities of Promoted and Nonpromoted Catalysts

Catalyst		Acidity (mmol NH_3/g)		
		a_1	a_2	a_2/a_1
0/10	Nonpresulfided	1.80	0.74	0.41
	Presulfided	1.34	0.20	0.15
3/10	Nonpresulfided	1.78	0.46	0.26
	Presulfided	1.30	0.42	0.32

Note. a_1, ammonia adsorbed at 600 Torr and 25°C; a_2, ammonia retained after evacuation; a_2/a_1, fraction of acid-active sites.

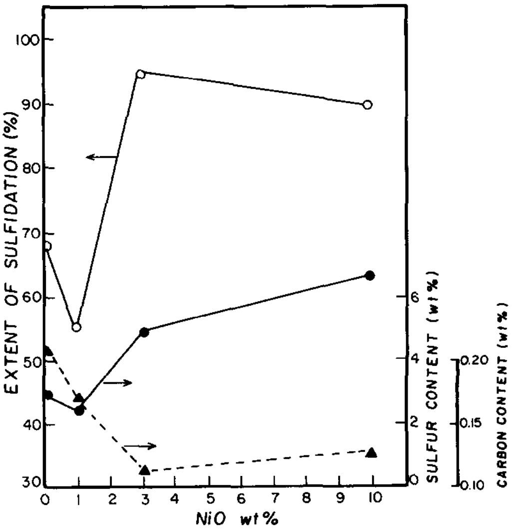

FIG. 4. Sulfur (●) and carbon (▲) content of nonpresulfided used catalysts. The extent of sulfidation (○) was calculated assuming that MoO_3 passes to MoS_2 and that NiO passes to Ni_3S_2.

TABLE 2

Initial Rate of Carbon Deposition from 1,3-Butadiene Using He, H_2, or H_2 + H_2S Atmospheres

Catalyst	Rate of deposition $(min^{-1}) \times 10^2$		
	He[a]	H_2[a]	H_2 + H_2S[b]
0/10	1.40	0.85	0.10
3/10	1.75	0.40	0.06

[a] Deposition on nonpresulfided catalysts.
[b] Deposition on presulfided catalysts.

in sulfidation extent for a Ni concentration that coincides with the optimum Ni concentration for maximum HDS activity (Fig. 2).

Results on carbon deposition from 1,3-butadiene (Table 2) show that the presence of the promoter reduces the rate of carbon deposition when this is carried out under a reducing atmosphere (H_2 or H_2 + H_2S). This observation is consistent with the results on carbon content in Fig. 4.

DISCUSSION

An explanation of the activity behavior observed (Fig. 1) may be advanced in terms of the various surface processes that can occur during the transformation of the fresh catalysts under the HDS reaction conditions. Two of the most plausible processes are sulfidation of Ni and Mo oxide species and carbon deposition.

Table 1 clearly demonstrates that the presence of Ni hinders a decrease in the number of active sites when the catalyst is submitted to sulfidation, i.e., the unpromoted catalyst (0/10) suffered a decrease of about 60% in the fraction of active sites (a_2/a_1 decreased from 0.41 to 0.15), whereas for the promoted catalyst (3/10) it increased about 20% (a_2/a_1 increased from 0.26 to 0.32). This result is consistent with the suggestion that the promoter maintains (or even improves) the dispersion of molybdenum when the catalyst is transformed from the oxide to the sulfide form. A relation between the deactivations observed in Fig. 1 and the above proposed Ni effect of maintaining dispersion can be established considering the larger deactivation experienced by the catalysts when the Mo concentration decreases down to the monolayer concentration (about 10 wt%, Fig. 3), or by taking into account the larger deactivation experienced by the 3/10 sample with respect to the 5/15 sample (Fig. 1). That is, the sample with high Mo content (5/15) does not experience as large a deactivation as does the sample with low Mo content (3/10) since in the former there is a larger source of bulk MoO_3 to provide more sites after the sulfide aggregation which impairs dispersion has occurred. In agreement with this, the optimum MoO_3 concentration was markedly increased by pretreating the catalysts with pure H_2S (Fig. 3). Indeed, pure H_2S should produce a larger sulfidation extent than using the HDS reaction mixture, especially for the high-Mo-content samples.

The above results on acidity reinforce previous findings of Sanders and Pratt (*7*) for Ni–Mo catalysts, and of Vrinat and de Mourgues (*8*) for Co–Mo catalysts, who, employing transmission and scanning electron microscopy, respectively, found that the most active catalysts had the smallest particles (*8*) and the most disordered morphology (*7*).

That the maximum in sulfidation extent (Fig. 4) is observed at the same optimum Ni concentration as the one observed in Fig. 2 establishes a correlation similar to that found recently by Boudart *et al.* (*9*) employing EXAFS. They reported that the optimum promoter concentration for higher HDS activity is also an optimum for the largest number of sulfur first neighbors of Mo.

At processing times tending to zero (Fig. 1), the smaller activity of promoted samples (e.g., 3/10, 5/15) when compared with the unpromoted catalyst (0/10) can be related to the neutralizing effect of Ni on the acid active sites present in the fresh molybdate catalyst (Table 1). The acid sites generated by the presence of molybdenum oxide on the support are also active sites for cracking reactions which favor carbon formation (*10*). The presence of Ni neutralizing acid sites on the oxide catalyst may therefore inhibit the initial deactivation by carbon deposition. The results on carbon formation shown in Table 2 and Fig. 4 agree with these suggestions. It is interesting to notice that carbon deposition may compete with sulfidation of the oxide surface, and this may obstruct sulfidation because of coverage of Mo by carbon. Indeed, presulfiding with H_2S has been shown to render higher HDS activity than treating with the thiophene HDS reaction mixture (*11*).

The larger sulfidation extent attained by the introduction of the promoter also implies less carbon deposition, since the oxide promotes more carbon deposition than the corresponding sulfide catalyst (*12*). This latter statement is confirmed by the results of Table 2 which show that treating the catalysts with an H_2S atmosphere diminishes the rate of deposition by almost an order of magnitude.

The proposed role of nickel in the deactivation by carbon deposition may also be related to the role attributed to nickel which involves a mechanism of hydrogen spillover (*1*), since this would enhance not only C–S bond scission but also hydrogenation of olefinic intermediaries (e.g., 1,3-butadiene), which are carbon-deposition precursors.

ACKNOWLEDGMENTS

The authors thank the Venezuelan Gran Mariscal de Ayacucho Foundation and the Consejo Nacional de Investigaciones Científicas y Tecnológicas for financial assistance.

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