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Hydrogen Activation on Alumina Supported MoS_2 Based Catalysts: Role of the Promoter

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The properties of alumina-supported Mo and NiMo sulfides toward a hydrogen atmosphere were investigated in order to elucidate if the synergy observed in hydrotreating reactions might be related to the activation of hydrogen. The determination of the amount of adsorbed hydrogen and of the H_2–D_2 exchange rate for various reduced states has evidenced that Ni does not promote the reducibility and the amount of adsorbed hydrogen of the MoS_2 phase while the exchange rate is increased only by factor of 2–3. It is concluded that the synergy observed in hydrotreating reactions does not come from hydrogen activation limitation. © 1999 Academic Press

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Alumina-supported molybdenum sulfide promoted by Co or Ni is an important catalytic material because of its extensive utilization in refinery hydrotreating processes. Such a process refers mostly to hydrogenolysis and hydrogenation reactions, where the first category of reactions concerns hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) which consist in C–S, C–N, and C–O bond cleavage, respectively. As all these C-heteroatom bond scission reactions occur at relatively high temperatures (573–673 K) and high hydrogen pressures (20–60 bars) hydrogenation of unsaturated compounds takes place simultaneously with hydrogenolysis (1). The role of the group VIII metal promoter is to drastically increase the reaction rate of all these reactions. Besides these overall considerations, mechanistic investigations have often proposed that the HDS and HDN of benzothiophene-, pyridine-, or quinoline-type structures require a hydrogenation step prior to the carbon–heteroatom hydrogenolysis because cleavage of the heteroatom–Csp^2 bond is energetically more demanding than that of the heteroatom–Csp^3 one (2). The knowledge of dihydrogen adsorption and activation processes is thus important for a better understanding of the mechanism of the various hydrotreatment reactions.

Hydrogen activation over sulfided materials is a very complex process since hydrogen does not intervene only as a reactant but also in site formation. Indeed, several fundamental studies have shown that the amount of hydrogen adsorbed on transition metal sulfides depends on the S/metal ratio (3). For instance, a fully sulfided particle does not activate hydrogen and hydrogen chemisorption takes place only after solid reduction where the catalyst surface contains enough anionic vacancies. The resulting coordinatively unsaturated sites created upon sulfur removal are also the active centers involved in the chemisorption of the various organic substrates to be transformed during the overall hydrotreating process. Up to now such basic studies were performed on unsupported MoS_2 (4), WS_2 (5), RuS_2 (6), and alumina-supported MoS_2 (7, 8) and no studies were related to the effect of Ni or Co on the properties of the MoS_2 phase toward the activation of the dihydrogen molecule except for the work of Thomas *et al.* (9). In this paper the authors have studied the properties of MoS_2 on alumina catalyst alone or promoted with different amounts of Ni. They have evidenced that the promoter does not affect to a large extent the activity of the sulfided Mo phase toward the H_2–D_2 or the D_2–H_2S exchange reaction. However, in this work the catalysts were not reduced and solid reduction might greatly affect the reactivity of both materials.

The aim of this work was to examine if Ni promotes the properties of the MoS_2 phase toward both the hydrogen chemisorption and the reactivity of hydrogen adsorbed species. The solids studied in this work were a Mo/γ Al_2O_3 and a NiMo/γ Al_2O_3 catalyst containing 9.3 wt% of Mo and 2.4 wt% of Ni, both catalysts having a BET area of 220 m^2/g. They were prepared by impregnation of the alumina carrier with aqueous solutions of ammonium heptamolybdate and nickel nitrate using the pore filling method. The oxidic phases were sulfided at 673 K with a mixture of H_2 (85%)–H_2S (15%) for 4 h. After this sulfidation step, the solids were cooled down to room temperature and flushed with an Ar flow for about half an hour and kept in a sealed bottle. The total sulfur content determined by chemical analysis was 7.2 wt% for the nonpromoted catalyst and 7.7 wt% for the nickel-promoted sample. Both catalysts will be thereafter denoted by Mo/Al and NiMo/Al, respectively, for the nonpromoted and the Ni-promoted sample. In order to control the preparation of these samples, they were tested in the HDS of thiophene at atmospheric pressure using a thiophene partial pressure of 18 Torr and at a reaction temperature of 573 K. In these conditions, the activity of the NiMo/Al was 17 times higher than that of Mo/Al (293 10^{-8} mol s^{-1} g^{-1} and 17 10^{-8} mol s^{-1} g^{-1}).

As mentioned above, the reactivity of a transition metal sulfide depends on its composition. Therefore, the first step of our study was to examine the reducibility of both catalysts in the presence of a hydrogen atmosphere. Solid reductions were performed in an open flow reactor, which allowed the measurement of the amount of H_2S removed under hydrogen by the use of a specific UV photodetector (hν photoionization detector equipped with a 10.2-eV UV light source). The detector was calibrated before each experiment with a H_2S/H_2 mixture of known composition. The samples were flushed with nitrogen and then contacted with a hydrogen flow of 40 cm^3/min at room temperature. The temperature was linearly raised at a rate of 2 K/min from room temperature (RT) up to the desired temperature. The degree of reduction (α) was defined as the ratio between the amount of H_2S eliminated upon reduction at a given temperature and the total sulfur content. Figure 1A reports the TPR patterns of both catalysts. Between RT and 600 K, the reduction of the NiMo/Al sample is somewhat easier than the nonpromoted Mo/Al catalyst since peak positions are shifted toward the low temperature side. For temperatures ranging from 600 to 800 K, a continuous H_2S production is observed with comparable signal intensity for both solids while at high temperatures the reduction of the Ni-containing catalyst occurs at a higher rate. This result is in fairly good agreement with TPR experiments performed on the CoMo/Al system either at subatmospheric hydrogen pressure (10) or at hydrogen pressures ranging from 10 to 40 bars (11). However, if TPR is a convenient tool for studying the reducibility of a solid, transient data might be obtained because the reactor temperature is continuously increased and the solid may not be in complete equilibrium with the gas phase. For this reason, solid reduction has also been investigated in isothermal conditions. The small inset included in Fig. 1A shows the evolution at 673 K of α of the Mo/Al_2O_3 sample as a function of time. The arrow points for the time required to reach 673 K. The observed S-shaped curve indicates that H_2S is mostly produced during heating since its amount rapidly levels off when the reduction proceeds in isothermal conditions. This behavior observed for both catalysts whatever the selected reduction temperature shows that solid composition expeditiously equilibrates with the reducing atmosphere and suggests that the S/metal ratio is mostly controlled by the temperature rather than by the time on stream. Figure 1B reports the α values determined for both samples after 2 h time on stream at various temperatures. By contrast to previous data reported for CoMo catalysts (1, 10), the presence of Ni does not greatly affect the reduction state achieved at a given temperature.

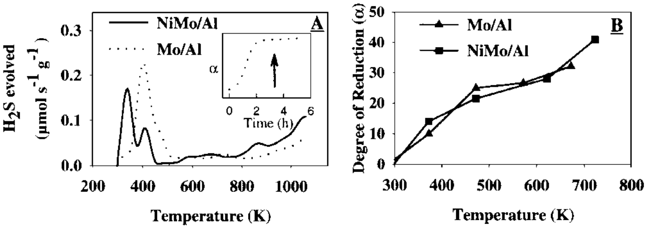

FIG. 1. (A) TPR profiles of the Mo/Al and of the NiMo/Al catalysts (heating rate, 2 K/min). (Inset) Evolution of the degree of reduction (α) at 673 K as a function of time for the Mo/Al catalyst (heating rate, 2 K/min). (B) Evolution of the degree of reduction (α) of the Mo/Al and of the NiMo/Al catalysts as a function of the reduction temperature.

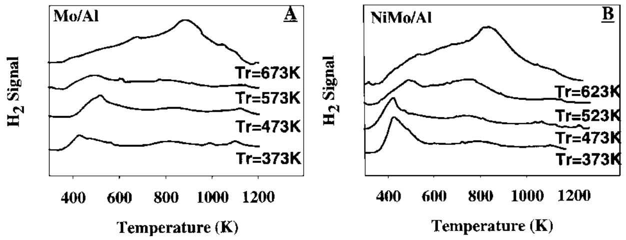

FIG. 2. Hydrogen thermodesorption profiles recorded on Mo/Al (A) and on the NiMo/Al catalyst (B) for various reduction temperatures (T_r).

After the reduction step, the catalysts were cooled from the reduction temperature down to RT in the presence of the hydrogen flow. The amount of hydrogen retained by the reduced surfaces was determined by thermodesorption. The TPD profiles were recorded using He as carrier gas, a TCD detector, and a heating rate of 15 K/min. The obtained data for both catalysts are reported in Figs. 2A and 2B. The recorded H_2 signals are relatively complex and several maxima seem to exist independent of the nature of the catalyst. Unfortunately, an increase of the heating rate does not improve the resolution of the different peaks, it was thus difficult to properly quantify the individual components of the TPD patterns. From a qualitative point of view it appears that the desorption of dihydrogen occurs in two temperature domains, i.e., between RT and ~600 K for the most weakly bonded species and at higher temperatures (600–1100 K) for the strongly attached hydrogen species. These results are different from those already reported for RuS_2 based catalyst for which two defined peaks desorbing at a temperature lower than 573 K were clearly identified (3). Therefore it could be concluded that at least part of the hydrogen adsorbed on

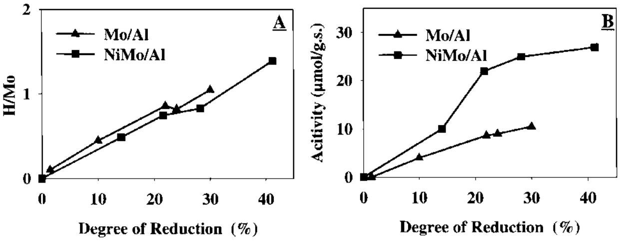

FIG. 3. Evolution of the H/Mo ratios (A) and of the H_2–D_2 exchange activities (B) of the Mo/Al and of the NiMo/Al catalysts as a function of the degree of reduction of the solids (α).

alumina-supported Mo/Al and NiMo/Al catalysts is less mobile than that over RuS_2 systems.

The overall amount of hydrogen was calculated by integrating the area underneath each profile. The obtained values are reported in Fig. 3A, by plotting the H/Mo ratio as a function of the degree of reduction of the catalysts. As shown in this figure the amount of adsorbed hydrogen depends on the solid composition since the nonreduced solid does not contain an appreciable amount of sorbed species which may desorb as dihydrogen. In agreement with data reported in the literature for model unsupported sulfides, hydrogen chemisorption requires the presence of anionic vacancies (3, 4). The comparison of the results observed on both samples evidences a similar variation of the H/Mo ratio with the reduction temperature. Therefore Ni does not increase the adsorptive capacity of the MoS_2 phase, indicating that at a given reduction temperature the amount of chemisorbing sites is roughly the same for the two catalysts investigated. However, it is well established that a reaction rate does not depend only on the number of active sites but also on their quality. For that reason we have determined their catalytic properties using the H_2–D_2 exchange reaction. This model reaction which involved hydrogen activation was chosen because it proceeds at a temperature lower that the one required for solid reduction. In a typical run, the catalyst was reduced at a given temperature and then cooled down to 273 K in the presence of the reducing atmosphere. The reactor was then flushed with nitrogen and the catalyst was thereafter submitted to an equimolar mixture of H_2 and D_2 diluted in Ar. The H_2 and D_2 partial pressures were 76 Torr. The variation of the H_2 and D_2 composition was analyzed by means of a mass spectrometer (FISONS Instrument) equipped with a quadrupole analyzer working in a Faraday mode. A silica capillary tube heated at 453 K continuously bled off a small fraction of the gas phase close to the reactor outlet into the spectrometer. Conversions were calculated either with respect to the decrease of the D_2 or H_2 signals and they were kept lower than 20% for all the solids irrespective of their compositions by adjusting the contact time. It should be mentioned that under these experimental conditions, no H_2S, HDS, or D_2S was released during the reduction course, indicating that sulfur to metal ratios were stable during a catalytic run.

The catalytic properties of both catalysts plotted as a function of the degree of reduction are illustrated in Fig. 3B. Preliminary experiments have shown that the alumina support is not active in this reaction. For both solids, the activity increases upon sulfur removal, demonstrating that the reaction requires the presence of coordinatively unsaturated sites to proceed. The activity of the NiMo/Al catalyst is ca. twice higher than that of the nonpromoted one independent of the reduction temperature. Therefore the addition of Ni slightly increases the hydrogen activation process. However, this augmentation of activity is much less than the synergy observed in hydrotreating type reactions where the synergetic factor might reach one order of magnitude.

To sum up this preliminary work devoted to the understanding of the promoting effect it appears that the addition of Ni to the MoS_2 phase does not affect to a large extent the properties of the MoS_2 phase toward:

1. solid reducibilities because similar degrees of reduction are obtained in both systems,
2. the H-surface bond strength since the TPD profiles are rather similar on both catalysts,
3. the amount of hydrogen retained by the catalysts for different stages of reduction,
4. the ability of the surface to activate the dihydrogen molecule because the H_2–D_2 exchange activity of the Ni-promoted catalysts is only 2–3 times higher than that of Mo/Al irrespectively of the solid composition.

The slight synergy observed in hydrogen activation is somewhat similar to the one reported by Delmon *et al.* using mechanical mixtures (12) but remains very small by comparison to the synergy generally observed in HDS and checked in the present study (ca. 17). This suggests that the synergy observed in hydrotreating reactions does not come mainly from a hydrogen activation limitation or from a modification of the catalysts surface toward hydrogen chemisorption. However, the mechanism of the HDS reaction proceeds via several steps, i.e., hydrogen and hydrocarbon adsorptions, hydrogenation, and C–S bond cleavage steps. Recent studies have shown that the promoter affects the acidic and basic properties of the Mo phase, which should influence the C–S bond breaking step (13).

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