Deuterium tracer studies on hydrotreating catalysts. 3. Influence of nickel on the rates of H_2–D_2 and H_2S–D_2 isotopic exchange

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The H–D isotopic exchange between H_2 and D_2 and between H_2S and D_2 was carried out at 80 °C in a recycling reactor over a series of presulfided Mo/Al_2O_3 catalysts containing different amounts of nickel. Whatever the pretreatment procedure, it was found that the promoter had no significant effect on the rate of H–D exchange or on the amount of exchangeable hydrogen present on the catalysts.

Keywords: sulfided molybdenum-on-alumina, nickel promoter, H–D isotopic exchange, H_2–D_2, H_2S–D_2, promoting effect, effect of pretreatment

1. Introduction

It is well known that group VIII metals (Co or Ni) have a promoting effect on the activity of supported Mo (or W) sulfide catalysts in hydrotreating reactions [1]. The origin of this synergy is still largely debated in the literature [1–3]. Numerous proposals have been made to explain this phenomenon. One of them is the contact synergy (or remote control) model which accounts for the promoting effect by supposing that Co_9S_8 provides (through spill-over) activated hydrogen to MoS_2 or "CoMoS" [2,3]. This proposal makes dihydrogen activation and transport of H species on the catalyst surface of key importance in hydrotreating reactions.

In our previous work on sulfided NiMo and Mo/Al_2O_3 catalysts [4,5], we showed by using H_2/D_2, D_2S/H_2 and D_2/H_2S mixtures that there was an exchange of hydrogen between H_2 and H_2S. The existence of this exchange reaction seems to indicate there is a common mode of dissociation, presumably heterolytic, for both reactants on the same catalytic centers. Moreover, H_2–D_2 experiments allow one to measure by isotopic dilution the amount of hydrogen adsorbed on the sulfided catalysts, including the alumina support.

The aim of this work is to show the influence of the Ni promoter on the exchange reactions between H_2 and D_2 and between D_2 and H_2S, after two discrete pretreatments of sulfided catalysts.

2. Experimental

A series of $NiMo/Al_2O_3$ catalysts containing the same amount of molybdenum (8 wt%) and different nickel loadings were prepared by incipient wetness impregnation using ammonium heptamolybdate and nickel nitrate. First, the molybdenum was deposited on the alumina. The 8Mo catalyst was obtained and after drying and calcination at 500 °C, the nickel was impregnated and the sample was again dried and calcined at 500 °C for 2 h. A commercial $NiMo/Al_2O_3$ catalyst was also used as a reference. Table 1 gives the nickel and molybdenum content of the catalysts.

The catalysts were sulfided *in situ* in a flow of H_2 (90%) and H_2S (10%) at 400 °C for 15 h under atmospheric pressure. After sulfidation the catalysts underwent two different pretreatments:

1. the catalysts were cooled down to the exchange reaction temperature (80 °C) under the sulfidation flow and treated under flowing helium (1 bar), the diluting gas, for 1 h.
2. the catalysts were cooled down to 350 °C under the sulfidation flow and treated under flowing helium (1 bar) for 1 h and cooled down to the exchange reaction temperature (80 °C) under flowing helium.

It should be noted that no. **2** is more representative of the conventional pretreatment under practical hydrotreatment conditions than no. **1**.

Table 1
Chemical composition of the catalysts.

Catalyst	Mo (%)	Ni (%)	Ni/(Ni + Mo)
8Mo	7.9	–	–
0.1NiMo	7.9	0.55	0.102
0.3NiMo	8.0	2.2	0.308
0.4NiMo	8.2	3.2	0.393
$NiMo^c$ [a]	8.3	2.3	0.309

[a] $NiMo^c$: $NiMo/Al_2O_3$ commercial catalyst.

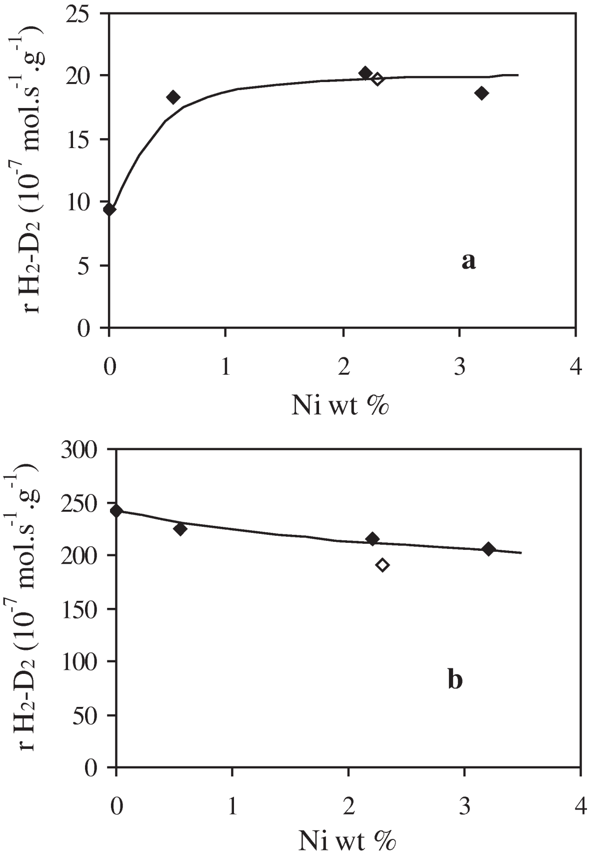

Figure 1. Influence of Ni loadings on the initial rates of the exchange reaction between H_2 and D_2 (80 °C; recycling reactor): (a) after pretreatment **1**, (b) after pretreatment **2**. ((◇) Commercial catalyst.)

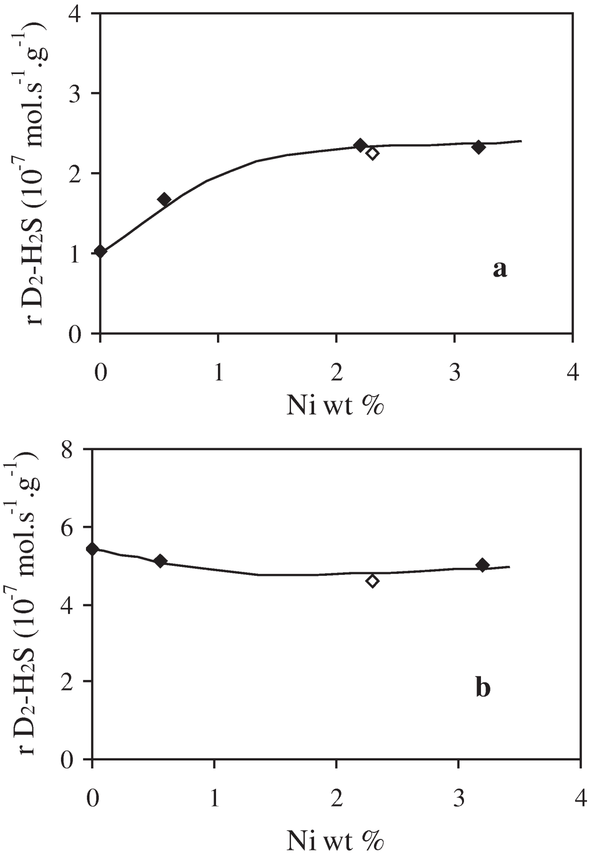

Figure 2. Influence of Ni loadings on the initial rates of the exchange reaction between D_2 and H_2S (80 °C; recycling reactor): (a) after pretreatment **1**, (b) after pretreatment **2**. ((◇) Commercial catalyst.)

After pretreatments **1** or **2**, the reactants (H_2 and D_2, or D_2 and H_2S; 0.5 bar of each) were introduced into the reactor (a 72 cm^3 recycling reactor). The H_2/HD/D_2 reaction mixture was analyzed by gas chromatography, using a column of alumina impregnated with $MnCl_2$ and maintained at −196 °C. The details concerning the apparatus and the procedure, as well as the calculations, have been published elsewhere [4].

The synergetic effect of nickel in DBT hydrodesulfurization was checked for this series [6]. The ratio of activities between the best NiMo catalyst ($Ni/(Ni + Mo) = 0.3$) and the non-promoted catalyst was 22 [6], which is in accordance with previous studies [1]. The initial rates of the exchange reactions between H_2 and D_2 and between H_2S and D_2 were measured after both pretreatments **1** and **2**. The effect of nickel loadings on the initial reaction rates is shown in figures 1 and 2. The amount of exchangeable hydrogen present on the catalysts was calculated from the isotope distribution [4] (see figure 3).

3. Influence of catalyst pretreatment

The results show that, for all the catalysts, the rate of formation of HD by H_2–D_2 exchange is greater by a factor of 10, after pretreatment **2** than after pretreatment **1**. The H_2S–D_2 exchange is less sensitive: the rate is only about twice greater. Moreover, after pretreatment **2**, the amounts of exchangeable hydrogen ($n\mathrm{H}_{\mathrm{ads}}$) are 3 or 4 times smaller than after pretreatment **1**. As shown in a previous study [5], the exchangeable hydrogen adsorbed over the catalysts after pretreatment **1** is due to a large extent to H_2S adsorption. The pretreatment under helium at 350 °C allows to desorb a large quantity of H_2S, and consequently the rate of the H_2–D_2 exchange increases significantly. This interpretation seems consistent with previous observations [4], although we cannot ignore the possibility of some modification of the surface by treatment at 350 °C in the absence of hydrogen [7]. Actually, it has been shown in a previous study [4] that H_2S inhibits the exchange reaction between H_2 and D_2. Since the isotopic exchange reactions with H_2S are less sensitive, it is supposed that H_2S, used as a reactant, allows restoration of surface conditions close to those obtained after pretreatment **1**.

4. Influence of nickel loadings

After pretreatment **1**, the nickel-promoted catalysts have slightly greater activities for both reactions than the non-promoted catalyst. Whatever the nickel loadings, the rate is about twice the activity of the non-promoted catalyst. However, the promoting effect of nickel is much less significant than for dibenzothiophene HDS. Moreover, after

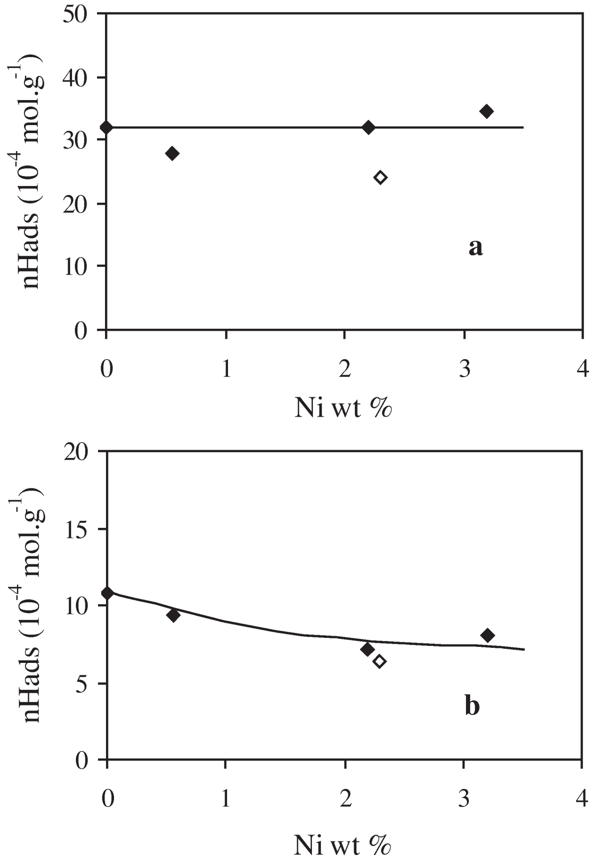

Figure 3. Influence of Ni loadings on the amount of exchangeable hydrogen: (a) after pretreatment **1**, (b) after pretreatment **2**. ((◇) Commercial catalyst.)

pretreatment **2**, the promoted catalysts have the same or even a more reduced activity than the non-promoted catalyst. Neither does the amount of exchangeable hydrogen on the catalyst depend on the nickel loadings. In addition, it is worth noting that H atoms of sulfided $NiMo/Al_2O_3$ catalysts, including those present on the support can exchange quite readily with gaseous D_2 at a temperature as low as 80 °C [5], i.e., at a temperature much lower than under the industrial conditions. Therefore, it seems difficult to interpret the promoting effect of Ni on the basis of the activation of H_2. However, one could object that the conditions under which the isotopic exchange was studied (in particular the hydrogen pressure) were quite different from the ones used in the HDS of dibenzothiophene, which could explain the difference in magnitude of the promoting effect. This could be the case, for instance, if the promoting effect observed in the HDS of dibenzothiophene under high hydrogen pressure (30 bar, as with our series of catalysts [6]) were much greater than under milder conditions like those for H–D exchange. However, it has been reported in several studies that a promoting effect of approximately the same magnitude as for dibenzothiophene was obtained in the HDS of thiophene at atmospheric pressure [8,9]. This indicates that there is apparently no significant influence of the hydrogen pressure on the magnitude of the promoting effect in HDS. How can we then explain the promoting effect, especially the one evidenced in experiments carried out with physical mixtures of the promoter and of the main sulfide phase (molybdenum sulfide, for instance) deposited on distinct carriers [2,3], if it cannot be ascribed to activated and spillover hydrogen? One explanation could be that we are dealing with classical bifunctional catalysis as Weisz demonstrated long ago for hydrocracking [10]. We would simply have to assume that an intermediate of the HDS process would be formed very readily on one of the components of the mixed catalyst and transform itself on the other one.

5. Conclusion

It is clear that the activation and the dissociation of hydrogen on hydrotreating catalysts is an easy process which is not (or is very slightly) sensitive to the presence of the nickel promoter. This seems difficult to reconcile with any attempt to explain the promoting effect on the basis of the activation of hydrogen or of the amount of hydrogen available on the catalyst surface. Consequently one may have to reconsider the contact synergy model in terms of classical bifunctional catalysis. Although the experimental conditions, under which we carried out the isotopic exchange experiments, were far from practical hydrotreating conditions (which means that our conclusions may be questioned), we think our results corroborate the idea that the promoting effect of nickel observed in hydrotreating reactions is related to the activation of the organic molecule on centers involving the promoter in one way or the other [11].

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