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Dissociation of dihydrogen and hydrogen sulfide over a sulfided NiMo–alumina catalyst as evidenced by D_2S–H_2 isotopic exchange

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To investigate the possible role of surface sulfur in the activation of dihydrogen, the reaction of D_2S with H_2 was carried out at 423 K on a presulfided NiMo–Al_2O_3 catalyst. The incorporation of D atoms in H_2 shows that the catalyst is capable of dissociating H_2S and H_2 into species which by recombination make the exchange of hydrogen atoms possible between these molecules. This can be considered as evidence of the involvement of surface sulfur in the activation of dihydrogen.

Keywords: D_2S; H_2; dissociation; isotopic exchange; NiMo–alumina catalyst

1. Introduction

Hydrodesulfurization and hydrodenitrogenation are industrially very important reactions which take place generally on sulfided CoMo– and NiMo–Al_2O_3 catalysts in the presence of dihydrogen and hydrogen sulfide. They involve various steps which include hydrogenation steps and carbon–heteroatom bond cleavages. To identify the mechanism of these reactions, it is essential to understand the processes of adsorption (and of activation) of dihydrogen and of hydrogen sulfide. Two aspects of the question can be considered: first the dissociation (and / or activation) of dihydrogen, second the existence and the role of sulfhydryl groups on CoMo– or NiMo–Al_2O_3 catalysts.

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According to Delmon [1] hydrogen atoms resulting from the activation of dihydrogen on specific centres of CoMo–Al_2O_3 catalysts (Co_9S_8 phase) would spill over to hydrogenation centres located on the MoS_2 phase. Another suggestion concerning the possible source of H_2 was made by Hanlon [2] to explain the effect of the molar ratio hydrogen sulfide to hydrogen on the activity in pyridine hydrogenolysis. This author proposed an equilibrium reaction between H_2S, H_2 and the catalyst surface:

$$H_2S + \square \rightleftharpoons \square{-}S + H_2 \qquad (1)$$

However, it is well known [3–5] that the isotopic exchange between H_2 and D_2 is possible over sulfided Mo/alumina catalysts, as well as between H_2S and D_2 which indicates that dihydrogen and hydrogen sulfide do dissociate, but it has not yet been demonstrated that H_2S could be able to provide some hydrogen which could be involved in hydrogenation reactions.

Very important roles are commonly attributed to SH groups in the catalytic activity of sulfided CoMo– or NiMo–Al_2O_3. They can actually be the source of the protonic acidity needed in the C–heteroatom bond cleavages or act as nucleophiles in the same reactions [6–9]. As suggested recently by Topsøe and Topsøe [10] "they may also be the source of hydrogen during a catalytic cycle". That is why the existence and origin of sulfhydryl groups on the surface of CoMo– or NiMo–Al_2O_3 catalysts has been the subject of numerous studies and speculations (ref. [10] and references therein).

Satterfield and coworkers [11–13] proposed that the adsorption and dissociation of a H_2S molecule can convert a sulfur vacancy (site I) into a Brønsted acid site (site II) containing a SH group. However, although sites I were considered as hydrogenation sites, nothing was said about to how they could be able to activate or dissociate dihydrogen. Actually, the first piece of evidence of the existence of SH groups was brought by Maternova [14] by using silver ion titration and confirmed by Raman spectroscopy [15]. The connection between the presence of these groups and Brønsted acidity was established only very recently by Topsøe and Topsøe [10]. This accounted for the fact that reactions involving a protonic mechanism could occur on sulfided catalysts [16–18]. According to these authors, SH groups could result from the dissociation of H_2S on vacancy sites. However, SH groups could also be generated by reduction of molybdenum by H_2 to form H^+ interacting with a sulfide ion. Another proposal was the formation of SH groups by reaction between H_2 and S_2^{2-} [19].

SH groups could indeed be a source of hydrogen if heterolytic dissociation of H_2S and H_2 were considered over dual sites constituted by a vacancy and a sulfur atom [20] as shown here:

$$H_2 + \bigstar{-}V + \bullet{-}S^{2-} \rightleftharpoons \bigstar{-}H^- + \bullet{-}SH^- \qquad (2)$$

$$H_2S + \bigstar\text{–}V + \bullet\text{–}S^{2-} \rightleftharpoons \bigstar\text{–}SH^- + \bullet\text{–}SH^- \tag{3}$$

If this were to be the case, it could be expected on the basis of microscopic reversibility that the exchange of H atoms between surface SH groups (hence between H_2S) and dihydrogen could be possible.

The aim of this work is to demonstrate the existence of such an exchange by reacting H_2 in the presence of D_2S-enriched H_2S on a NiMo–Al_2O_3 catalyst previously sulfided with a H_2S–H_2 mixture. We chose to use a D_2S–H_2 mixture instead of a H_2S–D_2 mixture [4,5] to avoid the interference of surface hydrogen which could possibly be generated during presulfidation of the catalyst by the H_2–H_2S mixture. By using D_2S and H_2 any incorporation of D atoms into dihydrogen constitutes a clear evidence of the existence of H–D exchange between D_2S (H_2S) (hence between SD groups (SH)) and H_2.

2. Results and discussion

A commercial NiMo–Al_2O_3 catalyst (250 mg; 3.0 wt% NiO, 14 wt% MoO_3 on γ-Al_2O_3, 200 m^2/g) was loaded into a small fixed-bed reactor (35 cm^3) and presulfided in situ in a flow of H_2S (10%) and H_2 (90%) at 673 K for 15 h under atmospheric pressure. The catalyst was then cooled down to 423 K and swept with H_2. The outlet of the reactor was closed and D_2S-enriched H_2S (15% D_2S) was introduced so as to reach a total pressure of 0.4 MPa. Gas samples were taken from the reactor as function of reaction time and analyzed by mass spectrometry (Balzers QMG412). The same experiments were carried out with alumina (the catalyst support) with the empty reactor and with the reactor filled with glass beads: no reaction was detected in either case.

We can see from table 1 that the H–D exchange with the NiMo–Al_2O_3 catalyst (7–8% HD) after a reaction time of 240 min was quite significant and that the results were reproducible. However, the exchange did not produce the amount expected from a total scrambling of the D and H atoms in the D_2S–H_2S–H_2 mixture

Table 1
Formation of HD [a] (mol%) on catalysts (NiMo–Al_2O_3 or Al_2O_3) at 423 K

Time (min)	Exp. 1 NiMo–Al_2O_3	Exp. 2 NiMo–Al_2O_3	Exp. 3 NiMo–Al_2O_3	Exp. 4 Al_2O_3
15	1.8	1.7	–	0.3
60	5.1	5.4	–	0.5
120	–	–	5.2	0.6
240	–	6.8	7.7	0.9

[a] No D_2 (or only traces of) was detected. According to the calculation 1.2 mol% only could be expected.

(20% HD). This could be an indication that deactivation, the origin of which is not yet understood, did occur. Another explanation could be that some hydrogen would be present on the surface of the catalyst (either on the support or on the active phase) and would take part in the exchange, which we did not take into account when we estimated the amount of expected HD at equilibrium. Noticeably alumina itself, though much less than NiMo–Al_2O_3, is active for H–D exchange between D_2S and H_2. Nevertheless, the incorporation of D atoms in H_2 shows that the catalyst is capable of dissociating H_2S (D_2S) and H_2 into species presumably SH (SD) groups which make the exchange of hydrogen atoms possible between the two molecules. This means that surface sulfur atoms are able to dissociate dihydrogen presumably through a heterolytic process (assuming that the dissociation of H_2S is heterolytic). Although this process is relatively fast (even at a temperature as low as 423 K), it does not signify that these sites are the only ones capable of hydrogenating unsaturated substrates under hydrotreatment conditions.

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