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Aromatics saturation by sulfided Nickel–Molybdenum hydrotreating catalysts

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Abstract

The effect of H_2S on the rates of toluene hydrogenation of sulfided Mo, Ni, Ni–Mo and Ni–Mo–P/alumina catalysts has been determined at 6 MPa, 350°C over a large range of H_2S partial pressure. In those conditions, Ni/alumina is nearly inactive. For the three other catalysts, similar trends are found with in particular no effect of H_2S at high partial pressure. In the presence of NH_3, the effect of H_2S remains globally the same.

Keywords: Mo catalysts; Ni catalysts; Mo–Ni catalysts; Hydrogenation

1. Introduction

Hydrotreating catalysts contain usually molybdenum or tungsten disulfide promoted by nickel or cobalt and supported on alumina [1–4]. Industrially, they can be used in very different conditions and especially at very different H_2S and NH_3 partial pressures depending on the feedstocks composition. Vacuum gas-oil hydrodesulfurization, for example, generates high H_2S and NH_3 partial pressures whereas aromatics saturation of a desulfurized gas-oil generates low H_2S and NH_3 partial pressures for the hydrogenation catalyst [5].

Many studies have been reported in the literature on the influence of H_2S on the activity of hydrotreating catalysts for reactions such as hydrodesulfurization, hydrodenitrogenation or aromatic compounds hydrogenation. However, these studies have often been made for a short range of H_2S partial pressure. Nevertheless, these studies have shown that the effect of H_2S is complex with a report of promotional effect, inhibition effect or no effect depending on the reaction, the reactant and the experimental conditions considered [6–12].

In the case of the aromatics hydrogenation, the inhibiting effect of H_2S and NH_3 is well known indicating that it is better to work at low H_2S and NH_3 partial pressures to reach high activities. Therefore, it is of interest to study the influence of H_2S and NH_3 over a large range of partial pressures, separately and together, on the performances of hydrotreating catalysts. In this work, we report preliminary results on the influence of H_2S and/or NH_3 on the toluene hydrogenation activity of Ni, Mo, Ni–Mo and Ni–Mo–P catalysts.

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2. Experimental

All of the catalysts tested in this work were prepared by pore filling impregnation of γ-alumina (Rhône–Poulenc, 240 m^2/g, 0.57 cm^3/g, 1.2 mm cylindrical extrudates) with aqueous solutions of ammonium heptamolybdate, nickel nitrate and/or phosphoric acid. The wet samples were dried at 120°C overnight and calcined at 500°C for 4 h. The composition of the catalysts was measured by X-ray fluorescence and is reported in Table 1.

Toluene hydrogenation tests were performed in a high pressure fixed bed continuous flow 'Catatest' unit from Vinci Technologies at 6 MPa, 350°C, LHSV (liquid hourly space velocity) between 0.25 and 6 h^{-1}, $H_2/HC = 450$ Nl/l and 40 cm^3 of catalyst [13]. The liquid feed was composed of toluene (20 wt.-%), thiophene (between 0 and 13 wt.-%), n-butylamine (between 0 and 1 wt.-%) and cyclohexane (balance). Thiophene and n-butylamine were used as H_2S and NH_3 generators respectively. The tests were performed by decreasing successively the amount of thiophene or n-butylamine in the feed. Toluene conversion, ranging between 5 and 60%, was determined in a steady state reached generally after 4 h on stream.

Table 1
Composition of catalysts tested

Catalyst	Mo (wt.-%)	Ni (wt.-%)	P (wt.-%)
Mo/Al_2O_3	10.2	–	–
Ni/Al_2O_3	–	2.4	–
$Ni–Mo/Al_2O_3$	9.3	2.6	–
$Ni–Mo–P/Al_2O_3$	11.4	2.4	2.4

Prior to catalytic tests, the samples were sulfided in situ by passing a feed containing 2 wt.-% dimethyldisulfide in cyclohexane over the catalyst at 6 MPa and 350°C during 4 h.

The liquid products of the reaction were analyzed by gas chromatography using a 50 m PONA column at 60°C and a flame ionization detector.

From the conversion of toluene, the first order rate of hydrogenation in mmol/(g h) has been computed and corrected from the variation of hydrogen and toluene partial pressures induced by the thiophene and/or n-butylamine decomposition reactions assuming first orders of reaction relatively to H_2 and to toluene. Then, all rates of hydrogenation reported in this work are referred to 4 MPa H_2 and to 0.37 MPa toluene partial pressure, respectively.

3. Results

The rate of toluene hydrogenation has been measured for the Mo, Ni, Ni–Mo and Ni–Mo–P

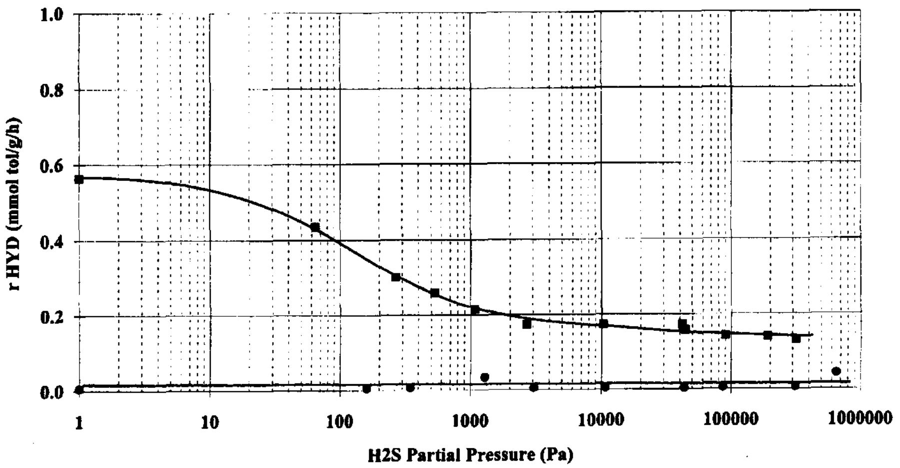

Fig. 1. Effect of H_2S on the rate of toluene hydrogenation at 6 MPa and 350°C for (■) Mo and (●) Ni catalysts.

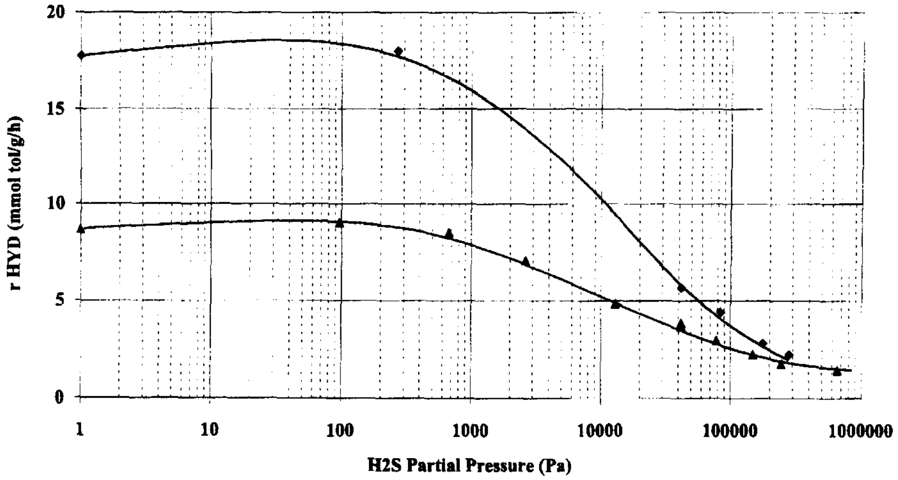

Fig. 2. Effect of H_2S on the rate of toluene hydrogenation at 6 MPa and 350°C for (▲) Ni–Mo and (◆) Ni–Mo–P catalysts.

catalysts in a large range of H_2S partial pressure (from 700 kPa to 0 Pa) and in absence of NH_3. The results obtained with Mo and Ni catalysts are reported in Fig. 1.

In our experimental conditions, the Ni catalyst is almost inactive whatever the H_2S partial pressure. The Mo catalyst is much more active and Fig. 1 shows that the H_2S partial pressure has a complex effect on the rate of hydrogenation. At low H_2S partial pressure ($<$ 10 Pa), the rate of hydrogenation is nearly constant and maximum. Between 10 and 2000 Pa H_2S, the rate of hydrogenation decreases when the H_2S partial pressure increases to reach a minimum but constant value at high H_2S partial pressure.

Fig. 2 shows that the Ni–Mo and the Ni–Mo–P catalysts exhibit the same behaviour as the Mo catalyst. Whatever the H_2S partial pressure, the Ni–Mo and Ni–Mo–P catalysts are clearly more active than the Mo or Ni catalysts, showing the well known promoting effect of nickel on molybdenum. In addition, the Ni–Mo–P formula is more active than the Ni–Mo formula due to the presence of phosphorus.

The influence of H_2S on the rate of hydrogenation of the Ni–Mo–P catalyst was also

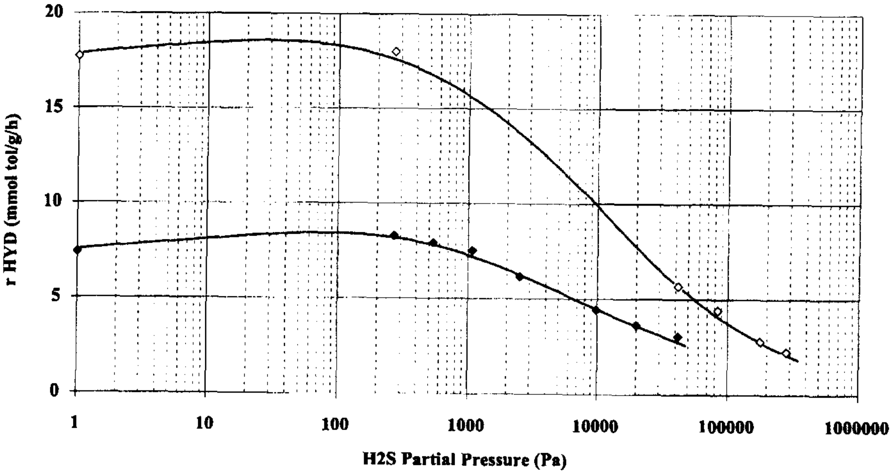

Fig. 3. Effect of H_2S on the rate of toluene hydrogenation at 6 MPa and 350°C for Ni–Mo–P catalyst (◆) at 12300 Pa NH_3, (◇) at 0 Pa NH_3.

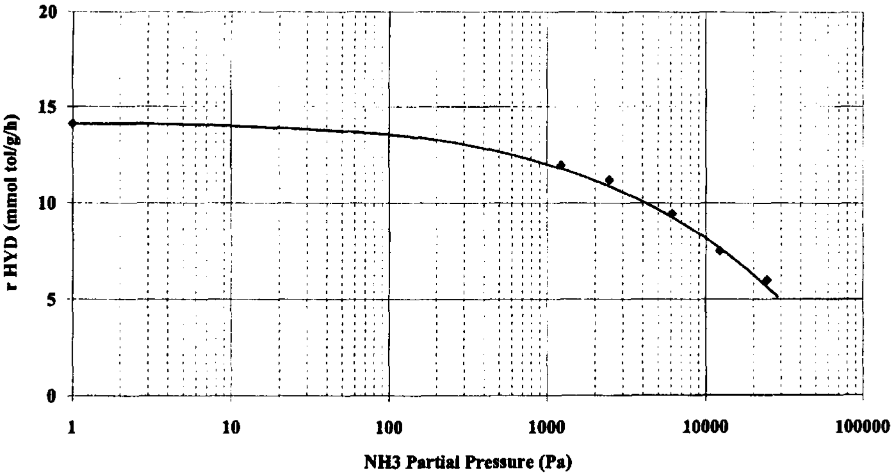

Fig. 4. Effect of NH_3 on the rate of toluene hydrogenation at 6 MPa, 1075 Pa H_2S and 350°C for the Ni–Mo–P catalyst.

studied in presence of 12300 Pa NH_3 (Fig. 3) and no major differences are found except that the rate of hydrogenation is lower. In absence of NH_3, a reaction order relative to H_2S (between 40 and 300 kPa) equal to -0.5 is found. In presence of NH_3, the order of reaction (between 1 and 40 kPa) is found equal to -0.3 suggesting no major perturbation of NH_3 on the inhibiting effect of H_2S.

The effect of NH_3 partial pressure on the rate of hydrogenation of the Ni–Mo–P catalyst in presence of 1075 Pa H_2S has been determined and is reported in Fig. 4. The inhibiting effect of NH_3 on the rate of hydrogenation seems to increase when the NH_3 partial pressure increases. Between 1 and 30 kPa NH_3, a reaction order relative to NH_3 partial pressure equal to -0.3 can be found, i.e., a value similar to the order relative to H_2S partial pressure.

4. Discussion

It is usually assumed that H_2S has an inhibiting effect on the hydrogenation activity of hydrotreating catalysts [6]. The results reported in this work indicate that this is the case in a certain range of H_2S partial pressure whatever the Mo, Ni–Mo or Ni–Mo–P catalyst. However at high H_2S partial pressure, H_2S has no more effect on the rate of hydrogenation of both the Mo and Ni–Mo catalyst.

This confirms a previous work on a Mo catalyst following a different testing procedure. The three domains of H_2S partial pressure were observed at almost the same H_2S partial pressure values and were interpreted by kinetic rate laws deduced from heterolytic reaction mechanisms [11]. The similarity between the curves rate of hydrogenation versus the H_2S partial pressure for the three catalysts studied suggests that the same kind of reaction mechanism prevails for the Ni–Mo and Ni–Mo–P catalysts.

The curves rate of hydrogenation versus H_2S partial pressure for the Ni–Mo and Ni–Mo–P catalysts are shifted compared to the one for the Mo catalyst. This can be assigned to different heat of adsorption of H_2S on these catalysts. The shift of the activity curve of the Ni–Mo catalyst towards higher H_2S partial pressure compared to the Mo catalyst suggests that H_2S is less strongly adsorbed on Ni–Mo sulfide than on the Mo sulfide catalyst. Similarly, the shift towards even higher H_2S partial pressure for the Ni–Mo–P catalyst suggests that H_2S is less strongly adsorbed on the P doped Ni–Mo sulfide phase than on the undoped Ni–Mo sulfide phase. Then the following ranking of the catalysts according to the strength of H_2S adsorption can be proposed:

Ni–Mo–P < Ni–Mo < Mo

Ammonia is known to be a strong inhibitor of aromatics hydrogenation. However for the low NH_3 partial pressures employed in this work it is found that the inhibiting effect of ammonia is of the same magnitude as the effect of H_2S. One needs, however, to explore even higher NH_3 partial pressure to determine if the inhibiting effect of NH_3 continues to increase or stabilises as observed for H_2S.

5. Conclusion

This work has shown that the effects of H_2S and NH_3 on the rate of toluene hydrogenation over Ni, Mo, Ni–Mo and Ni–Mo–P sulfided catalysts are complex. Depending on H_2S or NH_3 partial pressure, it is observed either a negative effect of H_2S or NH_3 on the rate of hydrogenation or almost no effect in the case of low H_2S or NH_3 partial pressure. At very high H_2S partial pressure, no variation of the rate of hydrogenation is found. In the range of partial pressure investigated, the inhibiting effect of ammonia is equivalent to the inhibiting effect of H_2S.

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