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Influence of water and ammonia on hydrotreating catalysts and activity for tetralin hydrogenation

D. Chadwick *, A. Oen, C. Siewe

Department of Chemical Engineering and Chemical Technology, Imperial College of Science Technology and Medicine, London, SW7 2BY, UK

Abstract

The effects of H_2O and NH_3 on the kinetics of the liquid phase hydrogenation of tetralin to decalin at 6.9 MPa and 330°C over commercial P–Ni–Mo/alumina catalysts in the presence of H_2S have been investigated. H_2O functioned as a mild kinetic inhibitor to an extent sensitive to the H_2S level. Quasi in situ XPS was used to investigate the catalyst structure after exposure to H_2O/H_2S.

Keywords: Liquid phase hydrogenation; P–Ni–Mo catalysts

1. Introduction

The current and planned restrictions on the aromatic content of transportation fuels as a result of environmental concerns, has stimulated renewed interest in the kinetics of aromatics hydrosaturation reactions occurring during catalytic hydrotreating and in dedicated downstream processes [1]. In hydrotreating, the catalyst performance is influenced by the presence of H_2S, NH_3 and nitrogen compounds which are known to be inhibitors of hydrogenation activity in particular [2–6]. As a consequence, there have been many studies in recent years of the magnitude of these competitive effects [3]. Aromatics hydrosaturation reactions are also important in the hydroprocessing of middle distillates derived from direct coal liquefaction processes. Solvent extraction of coal followed by hydrocracking of the clean extract liquids produces high yields of middle distillates which have a high content of 2-ring and 3-ring aromatics. These liquids need further hydroprocessing to yield acceptable transportation fuels. The hydrogenation of tetralin is one of the most difficult reactions in this context. It is necessary to carry out the hydrogenation at moderate temperatures to avoid thermodynamic limitation of the conversion. At these conditions, competitive interactions from the other feed components, and the products from hydrotreating reactions will become particularly important. While the influence of H_2S and nitrogen compounds have been fairly extensively investigated [3], the effects of oxygen compounds and H_2O (the product of HDO), which are relevant to the hydroprocessing of coal-derived liquids, have received relatively little attention [3,6–9].

The present preliminary study has investigated the effects of water and ammonia in the

* Corresponding author.

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presence of H_2S on the kinetics of the hydrogenation of tetralin to decalin over commercial P–Ni–Mo/alumina catalysts in the liquid phase. Generally, competitive effects in catalytic hydrotreating have been interpreted in terms of Langmuir–Hinshelwood–Hougen–Watson models [3,10]. These models assume the absence of structural modification of the active phase. We have attempted to evaluate possible effects on the structure of the catalyst by use of quasi in situ XPS.

2. Experimental

Kinetic studies were carried out in a Berty reactor (Autoclave Engineers) with integrated facilities for catalyst presulphiding and periodic sampling. Commercial P–Ni–Mo/alumina catalysts were used as 1/16 in. extrudates and presulphided with a continuous flow of 10% H_2S/H_2 mixture (500 cm^3/min) at 0.48 MPa. The temperature of the reactor was raised slowly at 4°C/min to 400°C and kept at that temperature for two h. After presulphidation, the reactant mixtures were added under nitrogen and consisted of n-hexadecane as the solvent, tetralin at a concentration of 2.5 wt.-%, *t*-butyl sulphide to keep the catalyst in a constant state of sulphidation, or to vary the sulphur level, and n-decane as an internal standard for GC analysis. Cyclohexanol was added for in situ generation of water; ammonia was introduced via a 5% NH_3/H_2 mixture. The operating conditions used for the kinetic work were 6.9 MPa constant hydrogen pressure, 330°C, impeller speed 1500 rpm, 4 g of catalyst, and the reactor was loaded with 170 ml of liquid feed. Rate constants are quoted in g oil/g cat. min.

The XPS study was carried out using a gas-cell-type reactor constructed in the preparation vessel of a V.G. ESCA-3 instrument. Cyclic treatments and surface analysis were performed on the same catalyst sample without air contacting the sample between treatment and analysis. Details of the reactor construction and performance will be the subject of another publication [11]. XPS spectra were taken using Al Kα radiation and binding energies were referenced to Al 2p = 74.5 eV.

3. Results and discussion

3.1. Kinetic studies of the effects of H_2O and NH_3 on hydrogenation

For the study of the hydrogenation of tetralin in the presence of water, concentration vs time

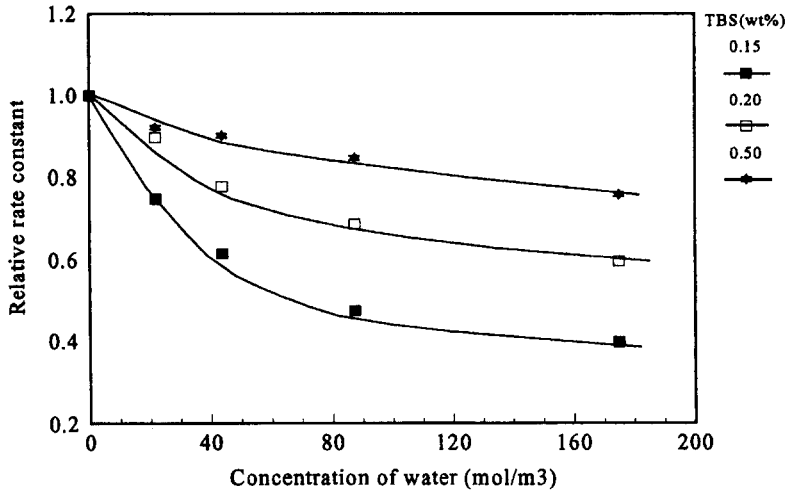

Fig. 1. Effect of water on the hydrogenation of tetralin (a) 0.15, (b) 0.20 and (c) 0.50 wt.-% *t*-butyl sulphide.

curves have been obtained over a P–Ni–Mo catalyst (18.6% Mo, 3.8% Ni, 6.7% P as oxides) for initial concentrations of 0.5, 1.0, 2.0, 4.0 wt.-% cyclohexanol. Preliminary studies demonstrated that at the experimental conditions used, cyclohexanol converted very rapidly to cyclohexane and water. The experimental rate constants for hydrogenation of tetralin were determined from the concentration-time curves obtained after the complete conversion of cyclohexanol, based on the assumption of pseudo first order kinetics. Data was obtained for three H_2S levels generated by using *t*-butyl sulphide concentrations of 0.15, 0.20 and 0.50 wt.-% corresponding to nominal H_2S/H_2 ratios of 0.0075, 0.010 and 0.025, respectively. For each series of experiments, an initial run was performed with only the desired concentration of *t*-butyl sulphide added to the tetralin reaction mixture to provide the baseline hydrogenation activities in the absence of cyclohexanol. The initial hydrogenation rate constants showed the expected decline in hydrogenation activity with increasing H_2S level.

The effect of H_2O on tetralin hydrogenation is shown in Fig. 1 for the three H_2S levels investigated. The hydrogenation activity declined with increasing H_2O concentration. The inhibition effects were mild, reaching only 60% at the highest H_2O level studied which corresponded to a nominal H_2O/H_2 ratio of 0.29. The extent of inhibition by water was found to be sensitive to the H_2S level, lower inhibition by H_2O being observed at the higher H_2S level. The inhibition following exposure to the highest water concentration was not completely reversible; for the lowest H_2S level only about 50% of the inhibiting effect was reversed. Not surprisingly, the degree of reversibility was greater at the highest H_2S level, where the activity recovered almost to the original value. It is not certain that this lack of reversibility was entirely due to the presence of water. In fact, at each H_2S level the data was a reasonable fit to a LHHW model in which H_2O, H_2S and tetralin compete for the same site.

Table 1
Effect of NH_3 on the hydrogenation of tetralin over a P–Ni–Mo catalyst

Run No.	%NH_3 in H_2	Rate constant (min^{-1})	Inhibition (%)
1	0	0.071	–
2	5	0.015	80
3	0	0.070	1

In the case of ammonia, composition vs time curves have been obtained for the hydrogenation of tetralin over a similar commercial P–Ni–Mo/alumina catalyst in the presence of 0.20 wt.-% *t*-butyl sulphide and for 5% NH_3 in H_2, corresponding to an NH_3 pressure of 3.45 MPa, at the same H_2S level. The results are given in Table 1. The presence of NH_3 caused a 80% reduction in the rate constant for tetralin hydrogenation. Despite the strong influence, the effect of NH_3 was found to be reversible at the conditions used, Table 1.

3.2. XPS investigation of the effects of H_2O on catalyst structure

Quasi in situ XPS was used to investigate the structure of the P–Ni–Mo catalyst used in the kinetic studies reported above, before and after sulphiding, and after exposure to H_2O/H_2S. The catalyst was sulphided in the gas reaction cell in the spectrometer using 10% H_2S/H_2 at 400°C for 2 h. The catalyst was then exposed to $H_2O/H_2S/H_2/N_2$ (ratio 7:7:60:27) and H_2O/N_2 mixtures in the reaction cell at atmospheric pressure and the reaction temperature of 330°C. The spectra are shown in Fig. 2 and the XPS data are given in Table 2.

The spectra showed that when the catalyst was exposed to water in the presence of $H_2S/H_2/N_2$ at the reaction temperature of 330°C, there was no significant difference in the binding energies (be) of Mo, Ni or S compared with the sulphided state. Furthermore, the S 2p/Mo 3d area ratio of the sulphided catalyst before and after exposure to $H_2O/H_2S/H_2/N_2$ were similar, implying no significant change in

Table 2
Influence of H_2O on P–Ni–Mo catalyst studied by in situ XPS

Binding Energies [a]					
Conditions	P 2p	O 1s	S 2p	Mo 3d	Ni 2p
Fresh, dried	133.7	531.0	–	232.6	855.5
10%H_2S/H_2 400°C	134.3	532.1	162.3	229.2	854.5
$H_2O/H_2S/N_2/H_2$ 330°C	134.1	532.1	162.5	229.3	854.3
H_2O/N_2 330°C	134.3	532.1	162.2	229.1	854.5
Area ratios					
Conditions	Mo 3d/Al 2p	P 2p/Al 2p	S 2p/Mo 3d		
Fresh, dried	1.7	0.21	–		
10%H_2S/H_2 400°C	1.3	0.19	0.43		
$H_2O/H_2S/N_2/H_2$ 330°C	1.2	0.21	0.44		
H_2O/N_2 330°C	1.2	0.20	0.40		

[a] Binding energies referenced to Al 2p = 74.5 eV.

the structure of the catalyst. These results are consistent with water functioning as an inhibitor mainly by competitive adsorption. The very high H_2O/H_2 ratios reached in some of the kinetic studies were simulated by exposure of the catalysts to H_2O/N_2 at 330°C. Surprisingly, even this did not result in any significant difference in Mo 3d, S 2p spectra or Ni 2p be, although there was evidence of a small sulphur loss.

Although the Mo 3d/Al 2p ratios decreased slightly after treatment with H_2O, this effect was barely significant. Unfortunately, the Ni 2p areas were difficult to determine accurately, but appeared to decrease slightly after treatment with water, particularly with H_2O/N_2. These results could imply that while the immediate effect of water may be to poison hydrogenation as a mild kinetic inhibitor, longer term deactivation processes associated with changes in dispersion may be induced. The irreversibility observed in the kinetic studies, which was greatest for the low H_2S–high H_2O situation, may be associated with this effect and/or with sulphur loss as noted above.

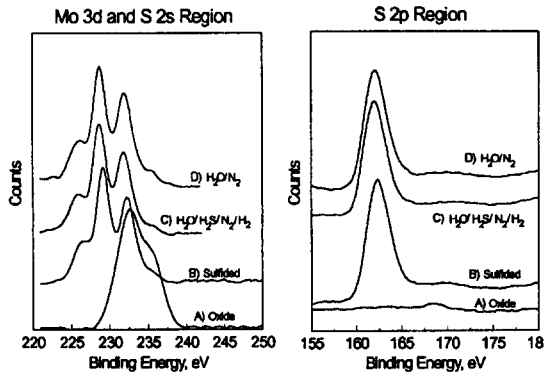

Fig. 2. XP spectra for P–Ni–Mo catalyst before and after treatment.

4. Conclusions

The inhibiting effects of H_2O and NH_3 on the hydrogenation of tetralin to decalin over Ni–Mo catalysts has been demonstrated. H_2O acted as a mild kinetic inhibitor and was sensitive to the H_2S level, while NH_3 produced a much stronger reduction in activity. The immediate stability of the sulphided catalyst to treatment with $H_2O/H_2S/H_2/N_2$ at the reaction temperature was confirmed by the XPS study. There was evidence of a small sulphur loss in H_2O/N_2 mixtures.

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