Nitric Oxide Chemisorption and Temperature-Programmed Desorption Study of Cobalt and Molybdenum Catalysts Supported on Activated Carbon and Alumina

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ABSTRACT

Molybdenum and cobalt catalysts supported on activated carbon or alumina were investigated for their activities in thiophene hydrodesulphurization (HDS) and ethylene hydrogenation (HYD) by using nitric oxide chemisorption and temperature-programmed desorption (TPD). The carbon supported catalysts showed higher HDS and HYD activities than the alumina supported catalysts, especially when the metal loading was small. Sequential adsorption of nitric oxide and oxygen showed that nitric oxide adsorption sites included the oxygen adsorption sites while the oxygen adsorption sites corresponded to a fraction of the nitric oxide adsorption sites. The TPD study indicated that a more active metal phase existed on the carbon support.

INTRODUCTION

As a result of the increasing interest in more effective hydrotreating catalysts, some recent studies were reported in which it was found that molybdenum based catalysts supported on carbon carriers showed high hydrodesulphurization (HDS) activity [1–3] and high coking resistance [4,5]. Carbon itself is generally known to have a large surface area and to be one of the least interactive support materials with metal phases. Thus it was desirable to compare the nature of active metal phases on a carbon support with that on a conventional alumina support.

Bachelier et al. [6,7] and Vissers et al. [8] correlated activities of thiophene HDS with dynamic oxygen chemisorption (DOC) for Mo/Al₂O₃, Ni/Al₂O₃ and Mo/C catalysts. In the present work, however, dynamic nitric oxide chemisorption was used. Nitric oxide (NO) has been widely used as an effective probe molecule to characterize the nature of active sites in CoMo/Al₂O₃ systems. Its chemisorption has been used to measure the degree of dispersion and
to titrate active sites of the molybdenum phase supported on alumina [9–11]. It was used in a selective poisoning test of the propylene metathesis reaction [12]. Also it appeared that NO chemisorption could be effectively used to di-
gnose the active sites, if combined with the NO temperature-programmed desorption (TPD), IR and electron paramagnetic resonance (EPR) tech-
niques [13]. The IR data showed that NO adsorbed on CoMo/Al₂O₃ catalysts in a dinitrosyl or dimer form which was characteristic for cobalt and molyb-
denum adsorption sites [14–16]. Recently Daly et al. [17] reported from a NO TPD study over a sulphided Mo/Al₂O₃ catalyst that NO desorbed only as NO itself and nitrous oxide (N₂O) and that the ratio N₂O/NO varied with the molybdenum loadings.

The present work was aimed mainly at investigating the nature of molyb-
denum and cobalt catalysts supported on carbon or alumina by using NO as a probe molecule. The active sites were characterized by thiophene HDS and ethylene HYD reactions, NO chemisorption and TPD, and sequential adsorp-
tion of NO and oxygen.

EXPERIMENTAL

Preparation of catalysts

A series of molybdenum and cobalt containing catalysts supported either on a γ-alumina or on an activated carbon were prepared by the incipient wetness technique. The pore volume and the surface area of the γ-alumina (Strem Chem. 13-2500) were 0.25 cm³/g and 220 m²/g (BET, N₂), respectively and those of the activated carbon (Darco G-60) were 0.82 cm³/g and 581 m²/g, respectively. Impregnation was carried out with aqueous solutions of ammonium hepta-
molybdate (Kanto Chem. GR grade) or cobalt nitrate (Kanto Chem. GR grade) of appropriate concentration. The molybdenum content of the Mo/C and Mo/
Al₂O₃ catalysts was between 1.0 and 14.8 wt.-% and the cobalt content of the Co/C and Co/Al₂O₃ catalysts was between 0.3 and 9.6 wt.-%. After impreg-
nation, each catalyst was dried in an air-circulating oven at 110°C for 24 h, and then kept in a desiccator. Calcination was carried out in the reactor in-
situ under a nitrogen atmosphere before each reaction or chemisorption experiment.

The compositions of these oxide catalysts were checked by atomic absorp-
tion spectroscopy. The surface area of each catalyst was measured using a con-
ventional BET apparatus and a special in-situ quartz cell after the standard presulphiding step described below.
Activity measurements

Presulphiding

The activities of catalysts were measured in a stainless steel flow microreactor operating at atmospheric pressure. Before starting the reactions, each catalyst sample (about 100 mg) was presulphided in-situ as follows. The catalyst bed was heated up to 400°C over 0.5 h in a flow of nitrogen (60 cm³/min, Dong Jin 99.999%) and kept at 400°C for 0.5 h. The nitrogen flow was then replaced by a pre-mixed flow (60 cm³/min) of 10% hydrogen sulphide (Matheson CP grade) and 90% hydrogen (Matheson UHP grade) and the reactor kept at 400°C for 2 h. The sample was then flushed with nitrogen for 1 h at 400°C. All gases used except hydrogen sulphide were prepurified through 5A molecular sieve and copper–platinum traps.

Hydrodesulphurization (HDS) reaction

HDS of thiophene (Aldrich 99% +) was performed at 300, 325 and 350°C with a flow-rate of thiophene between 0.81·10⁻⁴ and 2.65·10⁻⁴ mol/min. The mole ratio of hydrogen to thiophene flow-rate was kept constant at 16. A standard reaction was carried out at 350°C with a thiophene flow-rate of 0.81·10⁻⁴ mol/min. Steady state was achieved after about 3 h. Reaction products were analyzed using a gas chromatograph with flame ionization detection (FID) and columns packed with OV-101 and n-octane on Porasil C.

Ethylene hydrogenation (HYD) reaction

Ethylene (Matheson CP grade) hydrogenation was adopted as a model reaction to characterize the active sites for alkene hydrogenation [18,19]. The reaction was carried out separately after the above standard presulphiding procedure. The standard reaction conditions were as follows: ethylene flow-rate of 5.1·10⁻⁴ mol/min, molar ratio of hydrogen to ethylene of 9, and a reaction temperature of 350°C. The reaction products were analyzed by gas chromatography using a column of Chromosorb 102.

Catalyst activities were compared as pseudo-first order rate constants (k_HDS or k_HYD) in both reactions assuming first order dependence on thiophene and ethylene, respectively [1]. The rate constant was expressed as mol/g_cat min which was obtained by multiplying the conventional first order rate constant by the initial concentration. This approximation was well justified under the reaction conditions with excess hydrogen partial pressure \((P_{H_2}/P_{TH} = 16, P_{H_2}/P_{C_2} = 9)\) and small conversions \((X_{TH} < 0.2, X_{C_2} < 0.3)\). The apparent activation energy of HDS reaction for each catalyst was obtained from Arrhenius plots for rate constants obtained at the three reaction temperatures, 300, 325 and 350°C.
NO Adsorption and TPD measurements

NO and oxygen chemisorption experiments and NO TPD experiments were performed by a dynamic method in a once-through flow apparatus equipped with a thermal conductivity detector (TCD). Helium (Matheson UHP grade), which had been further purified through a copper–platinum trap and a liquid nitrogen trap, was used as the carrier gas.

Prior to these experiments, each catalyst (0.3 g for the carbon supported catalyst, 0.6 g for the alumina supported catalyst) was presulphided in-situ. The presulphided sample was then purged with helium (60 cm³/min) for 2 h at 400°C and cooled to room temperature (30°C). The helium flow-rate was reduced to 12 cm³/min at this time.

A pulse of NO gas (Takachio UHP grade) was introduced at 30°C from a 6-port valve with a sample volume of 0.13 cm³. The interval between pulses was 5 to 6 min, and the unadsorbed portion was determined by TCD. When the peaks had a nearly constant area, saturation of the catalyst was assumed and the total uptake was calculated.

The temperature-programmed desorption was carried out by monitoring NO desorption from the aforementioned catalyst saturated with NO. The heating rate was 10°C/min over 30°C to 400°C. Before entering the TCD cell, at this time, the desorbed stream was passed through a N₂O trap packed with 5A molecular sieve to remove N₂O.

Sequential adsorption of NO and oxygen was carried out by the same procedure.

RESULTS AND DISCUSSION

Activity measurements

The HDS and HYD activity patterns of each series of catalysts are shown in Fig. 1 and Fig. 2. Fig. 1 shows the variation in activity with the metal loading and these values are re-expressed in Fig. 2 on the basis of the specific activity per metal atom as a function of the average surface loading.

Mo/Al₂O₃ versus Mo/C

The Mo/C series of catalysts revealed higher HDS and HYD activities than the Mo/Al₂O₃ series as shown in Fig. 1 and Fig. 2. Fig. 1 shows that this aspect was more pronounced at a lower molybdenum loading. For surface loadings below about 1 atom/nm², the specific activity of the Mo/Al₂O₃ catalyst increased with loading while that of the Mo/C catalyst decreased. This trend was previously reported for the Mo/Al₂O₃ series and interpreted by the strong metal–support interaction for development of an active metal phase at a low loading, due to the heterogeneity of the alumina surface [6,20]. The present
Fig. 1. Variation of activity with metal loading in HDS (A) and HYD (B); an apparent activation energy, kcal/mol, between parentheses; (●-●) Co/C, (▲-▲) Mo/C, (○-○) Co/Al_2O_3, (△-△) Mo/Al_2O_3.
study showed that this was not confined to the HDS reaction. The HYD reaction exhibited similar behaviour. It appears, therefore, that molybdenum was used more effectively on the carbon support. The activation energies for the HDS reaction, indicated in parentheses adjacent to the points of Fig. 1a, varied with metal loading less for the Mo/C series than the Mo/Al$_2$O$_3$ series, suggesting a greater uniformity of active sites on the carbon support.
Co/Al₂O₃ versus Co/C

For the cobalt catalysts, the effect of the support on the activity was large, especially for the HDS reaction. HDS and HYD activities of the Co/C series increased very sharply with metal loading but levelled off quickly, whereas the Co/Al₂O₃ series showed low activities over the whole range of metal loading. The lower activities of the Co/Al₂O₃ series are the result of a strong interaction between the cobalt and the alumina which inhibits the effective use of cobalt. This suggests that the cobalt was used more effectively on the carbon rather than the alumina support.

Mo/C versus Co/C

Compared to the Mo/C series, the Co/C series showed higher HDS activities but lower HYD activities.

Sequential adsorption of NO and oxygen

Sequential adsorption experiments using NO and oxygen were performed in order to investigate adsorption sites for the NO probe molecule relative to those for the oxygen probe molecule. The results are shown in Fig. 3.

Fig. 3a shows the results when the surface of each model catalyst was partially precovered with oxygen at room temperature (30°C) prior to NO adsorption at 30°C. The total NO uptake decreased linearly as the preadsorbed oxygen increased. However, even after the surface was saturated with oxygen at 30°C, considerable amounts of NO adsorption still occurred (points p, q, r and s of Fig. 3a). This result reveals that oxygen adsorption sites comprised only a fraction of the total NO adsorption sites. The remaining NO adsorption sites were not detected by the oxygen probe at 30°C.

Fig. 3b shows the results of sequential adsorption when the surface of the catalyst was partially precovered with NO prior to the oxygen adsorption. The fall off in the oxygen uptake with coverage by NO was much steeper than that for the reverse adsorption order in Fig. 3a, indicating more preferential adsorption of NO on oxygen adsorption sites. For a surface saturated with NO at 30°C, oxygen uptake was very small in all cases (points p', q', r' and s' of Fig. 3b).

In order to increase the total oxygen uptake the catalyst surface was presaturated with oxygen at higher temperatures since it was believed that surface oxidation, which might have been incomplete for a certain site (for example, some single anion vacancy sites) at 30°C, proceeded further with the increase of the DOC temperature, probably accompanying the bulk oxidation [6,7]. The results for 60°C (points p', q', r' and s') and 120°C (points p'', q'', r'' and s'') exposure are shown in Fig. 3a. As the temperature increased, much more oxygen adsorption occurred and the subsequent NO uptake at 30°C decreased proportionally but by a lesser amount than the increase in oxygen
Fig. 3. (Continued on p. 315)
uptake. Some NO adsorption sites existed even after the surface was saturated with oxygen at 120°C. Conversely, when presaturation by NO was made at 120°C, total NO uptake values were less than the values at 30°C and subsequent oxygen adsorption at 30°C occurred in small amounts (points p_q', q_o', r_o' and s_o' of Fig. 3b).

This alternative adsorption sequence can be easily delineated as shown in Fig. 3c. If oxygen and NO compete for the same adsorption site and the adsorption stoichiometry does not change with surface coverage, the reference equilibrium will be represented by the dotted straight line p_0p_1. However, the actual adsorption deviates from this ideal behaviour. When the surface is pre-covered with oxygen by the amount p_o, the subsequent total NO uptake is more by p_5p_8 than the reference p_5p_2. On the other hand, with NO preadsorbed at o_p, the resultant oxygen uptake is less by p_6p_2 than the reference p_4p_2. The four kinds of catalysts studied showed a similar trend.

Oxygen adsorption sites seemed to correspond to a fraction of the total NO adsorption sites and had a more site-specific property. If it is assumed that the oxygen adsorption sites at room temperature are the double anion vacancy sites which can easily accept dissociative adsorption of oxygen [6], NO adsorption sites may include both single and double vacancy sites. It should be noted that the oxygen sensitive sites were developed more easily on the Mo/C catalyst than on the Mo/Al_2O_3 catalyst for comparable total NO uptake (points q_1 and r_1 of Fig. 3b).
Fig. 4. Variation of NO uptake (A) and adsorption stoichiometry (B) with metal loading. Symbols as in Fig. 1.
Correlation of NO uptake and catalytic activities with metal loading

Fig. 4a shows the variation of total NO uptake at 30°C with metal loading for each series of catalysts. In Fig. 4b, NO/Mo or NO/Co (molecule per metal atom) are plotted against the metal loading. This provides the adsorption stoichiometry or the effective number of active sites per metal atom. Total NO uptake values are correlated with the HDS and HYD activities (Fig. 1) in Fig. 5. The specific activity per adsorption site ($k_{\text{HDS}}/\text{NO}$ or $k_{\text{HYD}}/\text{NO}$) can be obtained from the slope of each point on Fig. 5. The adsorption stoichiometry and the specific activity of each series are summarized in Table 1.

**Mo/Al_2O_3 versus Mo/C**

The correlation between HDS activity and NO uptake for the Mo/Al_2O_3 series (Fig. 5a) was very similar to previous findings using oxygen as the probe molecule [6,8]. Fig. 5a can be divided into two regions. A linear correlation exists in region I, but an increase in activity per adsorption site is apparent in region II, possibly due to the change of the nature of the sites [8]. The behaviour for HYD showed a similar trend but with a steeper slope in region II'.

The HDS correlation of the Mo/C series revealed a linear shape representing a rather uniform nature of the HDS sites over the whole region, whereas the HYD correlation showed region II with lower HYD activity per site (Fig. 5b). The apparent higher HDS and HYD activities of the Mo/C series compared to the Mo/Al_2O_3 series, especially at a small loading (Fig. 1), seem to be due to higher specific activity as well as higher adsorption stoichiometry as shown in Table 1.

**Co/Al_2O_3 versus Co/C**

The correlations shown in Fig. 5d for the Co/C series are very interesting. There is no region in which the correlation is linear (the regions were divided simply for convenience of comparison of the values in Table 1). The NO/Co, $k_{\text{HDS}}/\text{NO}$ and $k_{\text{HYD}}/\text{NO}$ values all decreased continuously with cobalt loading as shown in Table 1. At low loadings the cobalt phase was in a highly dispersed form (NO/Co = 0.75) and had the highest value of $k_{\text{HDS}}/\text{NO}$. Thus it revealed a structure sensitive character, since $k_{\text{HDS}}/\text{NO}$ and $k_{\text{HYD}}/\text{NO}$ decreased as the NO/Co value declined. It should also be noted that the HDS activation energy varied continuously with loading as shown in Fig. 1a. Total NO uptake for the Co/Al_2O_3 series did not increase much with cobalt loading (Fig. 4a). As shown in Table 1, NO/Co values decreased sharply with loading while both $k_{\text{HDS}}/\text{NO}$ and $k_{\text{HYD}}/\text{NO}$ values were comparable to those of the Co/C catalyst with the highest cobalt loading (9.6 wt.-%). The apparent lower activities of Co/Al_2O_3 series seem to be related as much to ineffective use of cobalt on alumina as to the low activity per site.

For similar loadings, Co/C catalysts had higher or comparable $k_{\text{HDS}}/\text{NO}$
values but lower $k_{HYD}/NO$ values than Mo/C catalysts. This is in accord with the known hydrogenation ability of the conventional CoMo/Al$_2$O$_3$ system which seems to be related mainly to the molybdenum phase [21].

**Effect of the presulphiding temperature**

In order to investigate the thermal behaviour of carbon supported catalysts, HDS activities and NO uptake of some model catalysts were measured with variation of the presulphiding temperature. The results are presented in Fig. 6.
and Table 2. It is apparent that the effect of presulphiding temperature on HDS activity was more pronounced for the carbon supported catalysts, especially for the Co/C catalyst as shown in Fig. 6. The optimum presulphiding temperature was near 300°C in both Mo/C and Co/C catalysts. Although there is little information available, the decrease of HDS activities at the presulphiding temperature above 300°C seems to be related to sintering of the cobalt or molybdenum sulphide phase, considering the decrease of NO/Mo (or NO/Co) values with the temperature (Table 2) and the recent report of temperature-programmed sulphiding (TPS) on a Mo (8.0 wt.-% )/C catalyst by Vissers et al. [22]. Measurement of BET surface areas for the Mo/C and Co/C catalysts indicated little variation with presulphiding temperature within experi-
TABLE 1

Adsorption stoichiometries and intrinsic HDS and HYD activities for each series of catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fig. 5</th>
<th>Region</th>
<th>NO/metal atom</th>
<th>$k_{\text{HDS}}$/NO (min$^{-1}$)</th>
<th>$k_{\text{HYD}}$/NO (10$^{-1}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Al$_2$O$_3$</td>
<td>A</td>
<td>I</td>
<td>ca. 0.11</td>
<td>ca. 0.42</td>
<td>ca. 0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II'</td>
<td>−0.07*</td>
<td>−0.54</td>
<td>1.27</td>
</tr>
<tr>
<td>Mo/C</td>
<td>B</td>
<td>I</td>
<td>0.25 −0.12</td>
<td>ca. 0.69</td>
<td>ca. 1.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>−0.09</td>
<td>ca. 0.66</td>
<td>ca. 1.40</td>
</tr>
<tr>
<td>Co/C</td>
<td>D</td>
<td>I</td>
<td>ca. 0.75</td>
<td>ca. 1.06</td>
<td>ca. 0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>−0.52</td>
<td>−0.89</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>III</td>
<td>−0.22</td>
<td>−0.50</td>
<td>0.08</td>
</tr>
<tr>
<td>Co/Al$_2$O$_3$</td>
<td>C</td>
<td></td>
<td>0.32 −0.03</td>
<td>0.12 −0.32</td>
<td>0.04 −0.09</td>
</tr>
</tbody>
</table>

* −: Approaches the quoted value with increasing metal loading.

Fig. 6. Variation of HDS activities with the presulphiding temperature; Co (4.2 wt.-%)/C, Mo (6.8 wt.-%)/C, Mo (6.6 wt.-%)/Al$_2$O$_3$, and Co (4.1 wt.-%)/Al$_2$O$_3$. Symbols as in Fig. 1.

Temperature-programmed desorption profiles for the NO probe molecule

Figs. 7 and 8 show the TPD profiles of each series. All catalysts, if not otherwise specified, were presulphided at 400°C.

Mo/Al$_2$O$_3$ and Mo/C

Fig. 7 shows that at least two kinds of adsorption sites were present in each series. The shoulders in both figures around 110–120°C seem to be related to the site which developed more easily in the bulk molybdenum phase (refer to...
### TABLE 2

Adsorption stoichiometries and intrinsic HDS activities of model catalysts with the presulphiding temperature

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Presulphiding temperature (°C)</th>
<th>$k_{\text{HDS}}$ (×10^4 mol/gcat·min)</th>
<th>NO uptake (×10^4 mol/gcat)</th>
<th>NO/metal atom</th>
<th>$k_{\text{HDS}}$/NO (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(6.6 wt.-%)/Al₂O₃</td>
<td>300</td>
<td>3.43</td>
<td>8.78</td>
<td>0.12</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>3.57</td>
<td>8.47</td>
<td>0.12</td>
<td>0.42</td>
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<tr>
<td></td>
<td>500</td>
<td>4.05</td>
<td>7.64</td>
<td>0.11</td>
<td>0.53</td>
</tr>
<tr>
<td>Mo(6.8 wt. %)/C</td>
<td>300</td>
<td>9.28</td>
<td>11.89</td>
<td>0.17</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>6.48</td>
<td>9.01</td>
<td>0.13</td>
<td>0.72</td>
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<tr>
<td></td>
<td>500</td>
<td>5.41</td>
<td>8.11</td>
<td>0.11</td>
<td>0.67</td>
</tr>
<tr>
<td>Co(4.2 wt.-%)/C</td>
<td>300</td>
<td>44.30</td>
<td>38.20</td>
<td>0.53</td>
<td>1.16</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>18.61</td>
<td>24.17</td>
<td>0.34</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>10.22</td>
<td>16.75</td>
<td>0.23</td>
<td>0.61</td>
</tr>
<tr>
<td>Co(4.1 wt.-%)/Al₂O₃</td>
<td>300</td>
<td>1.04</td>
<td>3.48</td>
<td>0.05</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.10</td>
<td>3.67</td>
<td>0.05</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1.20</td>
<td>2.96</td>
<td>0.04</td>
<td>0.40</td>
</tr>
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</table>

Fig. 7. TPD profiles of (A) Mo/Al₂O₃ series; A(Mo 2.0 wt.-%), B(Mo 6.6 wt.-%), C(Mo 14.5 wt.-%), H(as B, sulphided at 500°C), R(bulk MoS₂) and (B) Mo/C series; A(Mo 2.0 wt.-%), B(Mo 6.8 wt.-%), C(mo 14.8 wt.-%), H(as B, sulphided at 500°C).
Fig. 8. TPD profiles of (A) Co/Al₂O₃ series; A (Co 0.6 wt.-%), B (Co 4.1 wt.-%), C (Co 9.3 wt.-%), H (as B, sulphided at 500°C), R (A bulk Co₃S₈) and (B) Co/C series; A (Co 0.6 wt.-%), B (Co 2.2 wt.-%), C (Co 4.2 wt.-%), D (Co 9.6 wt.-%), H (as C, sulphided at 500°C), L (as C, sulphided at 300°C).

The profile R of the bulk MoS₂, considering they grew faster at the higher molybdenum loading and the higher presulphiding temperature. The main peak of the Mo/C series appeared at a higher temperature (190°C) than that of the Mo/Al₂O₃ series (165°C). Apparently the profiles of both series correspond to adsorption sites of different nature.

**Co/Al₂O₃ and Co/C**

Fig. 8a shows the TPD profiles of the Co/Al₂O₃ series. A broad peak developed around 200°C at a small cobalt loading (profile A). As the cobalt loading
increased and at a higher presulphiding temperature of 500°C, a shoulder around 240°C grew gradually (Profile B, C and H). These adsorption sites were different from those of either the Co/C series shown in Fig. 8b or the bulk cobalt sulphide phase (profile R for Co₉S₈).

The TPD profiles of the Co/C series were very informative (Fig. 8b). A broad peak extending from 220°C to 330°C grew at a small loading of about 0.6 wt.-% (Profile A). If the loading was increased to 2.2 wt.-%, where HDS and HYD activities for the Co/C series reached a maximum as shown in Fig. 1, a main peak developed at about 250°C and a shoulder around 310°C (profile B). This shoulder grew faster at a higher cobalt loading (profile C and D). However, the adsorption site of the cobalt phase, even at the highest loading of 9.6 wt.-% (profile D), was still different from that of the bulk cobalt sulphide phase (profile R of Fig. 8a). Meanwhile, development of the main peak around 250°C was conspicuous at the optimum presulphiding temperature of 300°C (profile L), for which the HDS activity was about twice that for presulphiding at 400°C. At the presulphiding temperature of 500°C (profile H), however, a strong shoulder at about 140°C appeared while the shoulder at 310°C disappeared. The shoulder at 140°C seems to be related to the bulk Co₉S₈ phase (refer to the profile R of Fig. 8a), suggesting its appearance at the higher presulphiding temperature. The main peak at 250°C could be assigned to another cobalt phase with a higher adsorption site density (thus a higher dispersion) and a higher intrinsic activity per site. Ledoux et al. [23] has also suggested from an NMR study that the cobalt sulphide phase on carbon, especially at a small loading, does not have the exact character of bulk Co₉S₈.

CONCLUSION

Four different series of catalysts, Mo/C, Mo/Al₂O₃, Co/C and Co/Al₂O₃, were prepared by the incipient wetness technique. Their catalytic activities for thiophene hydrodesulphurization and ethylene hydrogenation were correlated with NO chemisorption and TPD. The effect of the support on the activity was discussed. Also, sequential adsorptions of oxygen and NO were carried out to explain the nature of NO adsorption sites. The major conclusions found or confirmed by the present study are (i) NO adsorption sites included oxygen adsorption sites, (ii) more favourable molybdenum or cobalt phases with higher active site density and higher intrinsic activity per site were formed on the carbon support than on the conventional alumina support, and (iii) carbon supported catalysts were more sensitive to the presulphiding temperature and exhibited a lower optimum presulphiding temperature (around 300°C).
REFERENCES