Infrared Spectroscopic Study of the Adsorption of CO, CO₂ and NO on Fluorinated Alumina and Supported Molybdenum–Nickel Catalysts

By Jose Luis G. Fierro, Antonio Lopez Agudo and Luis G. Tejuca

Instituto de Catalisis y Petroleoquimica, Consejo Superior de Investigaciones Cientificas, Serrano 119, Madrid-6, Spain

and Colin H. Rochester*

Department of Chemistry, The University, Dundee DD1 4HN

Adsorption of CO, CO_2, NO and O_2 probe molecules has been used to study the surface of fluorinated alumina and of supported Mo–Ni catalysts. Addition of F to alumina drastically inhibited formation of carbonates from CO (at 673 K) and CO_2 (at room temperature) adsorption and also inhibited the formation of nitrates from NO adsorption at room temperature. Reduction with H_2 (773 K) followed by O_2 and NO adsorption at low temperatures suggest that the active-phase Mo–Ni is more highly dispersed in the catalyst with higher F content. These data are in agreement with spectroscopic results for NO adsorption. This effect of F on the degree of metallic dispersion is probably associated with the anchoring of the polymeric ion $Mo_7O_{24}^{6-}$ to the support, which is highly unfavoured by the partial substitution of hydroxyl groups by F^-.

In recent years there has been renewed interest in Mo–Co and Mo–Ni catalysts for the hydrocracking of heavy petroleum fractions and the upgrading of synthetic fuels derived from fossil fuels and coal. The advantages of such catalysts include their ability to remove sulphur, nitrogen and oxygen from complex hydrocarbons. In alumina-supported Mo–Ni catalysts the acidity required for hydrocracking functionality is usually enhanced by the addition of halides (normally the fluoride or chloride) to the support. The changes which occur upon fluorination of γ-alumina, particularly the characterization of the resulting acid centres, have received considerable attention in the literature.[1-8]

The addition of fluoride prior to the impregnation of Ni and Mo onto γ-alumina may affect the formation and distribution of the various Ni and Mo phases on the catalyst; also, the addition of both Mo and Ni may alter the acidity of the alumina surface. Such aspects have been scarcely dealt with.[8-11] Boorman *et al.*[9] reported the effect of adding fluoride to Mo–Co/Al₂O₃ catalysts on the activity for the hydrodesulphurization and hydrocracking of Athabasca bitumen. Murali Dahar *et al.*[10] also studied the effect of additives, including NH₄HF₂ and NH₄Cl, to Mo–Co/Al₂O₃ catalysts on their catalytic functionality for various model test reactions. In previous work[8] we showed the presence of different Brønsted- and Lewis-acid centres on fluorinated γ-alumina and on Mo–Ni/fluorinated γ-alumina samples. An increase in fluorination in the range 0–4 wt% F resulted in an increase in the Brønsted acidity, particularly of the type ascribed to isolated hydroxyl groups. This acidity was enhanced by the addition of Mo–Ni to the fluorinated alumina. It was also shown that fewer Brønsted centres of strong acidity were present on the reduced samples than

40-2

on the oxidized ones. The strongest acid sites were then associated with higher oxidation states of Mo and Ni. On the other hand, Segawa and Hall[11] suggested that the acidic centres in Mo/Al$_2$O$_3$ catalysts might be located on the partially hydrolysed molybdena clusters. They showed recently[12] that pyridine is adsorbed unselectively on both alumina and molybdena surfaces.

In this paper we report a further characterization, by infrared spectroscopy, of the catalysts studied in a previous paper[8] using probe molecules such as CO, CO$_2$ and NO. In addition, some gravimetric results for O$_2$ and NO chemisorption are also presented.

EXPERIMENTAL

SAMPLE PREPARATION

Fluorinated alumina samples were prepared by the incipient impregnation method of γ-Al$_2$O$_3$ (Girdler T-126, surface area 188 m^2 g^{-1}, pore volume 0.39 cm^3 g^{-1}, ground and sieved to sizes between 0.84 and 1.19 mm) with aqueous NH$_4$F (Riedel-de-Haen) solutions. The liquid was allowed to be in contact with the solid particles for 15 h at room temperature (r.t.). After this the excess of water was removed by heating at 383 K. The alumina was then heated in air at 648 K for 2 h and calcined at 823 K for 4.5 h. MoO$_3 \cdot$ NiO/Al$_2$O$_3$ catalysts with constant MoO$_3$ and NiO contents (8.0 and 3.5 g per 100 g of γ-alumina, respectively) were prepared by a two-step wet impregnation method of fluorinated alumina with (NH$_4$)$_6$Mo$_7$O$_{24} \cdot$ 4H$_2$O (Panreac) (first step) and Ni(NO$_3$)$_2 \cdot$ 6H$_2$O (Riedel-de-Haen) (second step) solutions. Removal of water, heating (648 K, 2 h) and calcination (823 K, 4.5 h) of the samples were effected as for alumina. Further procedural details have been given elsewhere.[8] The alumina and supported Mo–Ni samples used in this work were of the same batch as those studied previously.[8] They will be referred to as AlxF and MoNiAlxF (x being the nominal fluorine content in g per 100 g of γ-Al$_2$O$_3$).

SPECTROSCOPIC MEASUREMENTS

Pretreatment of the samples was carried out in a greaseless infrared cell connected to a high-vacuum gas-handling system which allowed a dynamic vacuum of 10^{-6} mmHg (1 mmHg $\approx$ 133.3 N m^{-2}). Self-supporting wafers were made by pressing the finely divided powder to a pressure of 10^8 N m^{-2}, the disc thickness being 12 mg cm^{-2}.

The sample was outgassed at 773 K for 16 h and then contacted with 50 mmHg CO or CO$_2$ at r.t. for 1 h; after this the spectrum was recorded. Spectra were also recorded after allowing the sample to be in contact with the adsorbing gas for 1 h at the indicated temperature. For NO experiments the sample was outgassed at 773 K as above and contacted with 30 mmHg NO at r.t. for 1 h. The NO gas was then condensed at 77 K (1 min) before recording the spectra. For successive adsorption of CO$_2$ + NO, CO$_2$ was first adsorbed (50 mmHg, r.t., 1 h), then pumped (r.t., 1 h) and NO adsorbed as above. Some experiments were carried out on reduced samples [AlxF (red) or MoNiAlxF (red)]. For these, after the initial outgassing at 773 K the disc was contacted with 300 mmHg H$_2$ at 773 K for 1 h and subsequently outgassed for 2 h at the reduction temperature. The spectra were recorded with a Perkin-Elmer 682 grating spectrophotometer with a wedge attenuator in the reference beam.

GRAVIMETRIC MEASUREMENTS

NO and O$_2$ uptakes were measured gravimetrically with a Cahn RG microbalance connected to the high-vacuum system referred to above. The Mo–Ni catalysts were quantitatively reduced to a reduction degree (α) of 1 (Mo^{6+} to Mo^{4+} and Ni^{2+} to Ni^0) in 300 mmHg H$_2$ at 773 K, outgassed for 2 h at the same temperature and cooled to r.t. The sample was then contacted with 300 mmHg NO (at r.t.) or O$_2$ (at 195 K) for 1 h and the physically adsorbed part removed by pumping at 10^{-3} mmHg at the adsorption temperature until a constant weight was achieved. Further details have been given previously.[13]

GASES

CO$_2$ (99.98% volume), CO (99.97% volume), O$_2$ (99.99% volume) and NO (99.0% volume) were supplied by Sociedad Espanola del Oxigeno. Before storage these gases passed through a charcoal 4A molecular-sieve purification train, then condensed at 77 K and distilled, taking only the middle fraction.

RESULTS

ADSORPTION OF CO

I.r. spectra in the 2300–1900 cm^{-1} region obtained after CO adsorption on Al4F and on MoNiAlxF samples are given in fig. 1. CO adsorbed on Al4F at r.t. yielded a band at 2220 cm^{-1} [fig. 1(a)] (bands at 2175 and 2125 cm^{-1} in this and following spectra are due to CO gas). This spectrum did not change on heating the sample in the presence of the gaseous phase up to 873 K. Adsorption of CO on MoNiAl0.5F at r.t. [fig. 1(b)] produced a band at 2200 cm^{-1}. After heating at 473 K a broad band at 2150–2050 cm^{-1} appeared [fig. 1(c)] which became two well defined bands at 2140 and 2090 cm^{-1} after heat treatment at 673 K [fig. 1(d)]. On heating at 873 K these bands become less intense because of the lower transmittance of the reduced sample. The spectra observed after CO adsorption on MoNiAl4F at r.t. 473, 673 and 873 K [fig. 1(b')–(e')] showed bands at equal or lower wavenumbers than those given for CO/MoNiAl0.5F. In addition, a new band at 2060 cm^{-1} [fig. 1(d')] and a broad band centred at 1940 cm^{-1} [fig. 1(c')], which was replaced by two bands at 1960 and 1935 cm^{-1} after treatment at 673 K [fig. 1(d')], were also detected.

Peri[2] found a band at 2240 cm^{-1} for CO on fluorinated alumina. Thus the band at 2220 cm^{-1} [fig. 1(a)] can be assigned to adsorbed CO on Al^{3+}. Bands *ca.* 2200 cm^{-1} have been observed after CO adsorption on supported nickel oxide,[14] cobalt oxide,[15] cobalt oxide–molybdenum oxide[15] and molybdenum oxide[16] catalysts. Peri[17] assigns bands above 2130 cm^{-1} to CO adsorbed on metallic ions and bands below this wavenumber to linear (2130–2000 cm^{-1}) and bridged (2000–1880 cm^{-1}) CO on metallic sites. Bands at 2205, 2200 and 2140 cm^{-1} (fig. 1) are therefore attributed to CO on non-reduced or partially reduced metal ions (Mo^{4+}, Mo^{3+}, Ni^{2+}). These bands may be compared with bands for Co–Mo catalysts at 2200 (or 2190) and 2160 (2130) cm^{-1} which were assigned[15] to CO adsorbed on Co^{2+} sites by analogy with corresponding bands at 2204 and 2170 cm^{-1} in the spectra of CO ligands on the Co^{2+} cations in a cation-exchanged X-zeolite.[18] Carbon monoxide ligands on Ni^{2+} ions in an X-zeolite gave an infrared band at 2211 cm^{-1}; it therefore appears probable that the present maxima at 2200 and 2205 cm^{-1} may be ascribed to CO adsorbed on exposed Ni^{2+} surface sites. The assignment of the band at 2140 cm^{-1} is less certain. The bands at 2100 and 2090 cm^{-1} may be compared with maxima at 2070–2090 cm^{-1} for CO on metallic nickel which have been attributed to CO ligands attached linearly to isolated nickel atoms in an oxidic environment.[19] Similarly, the band at 1960 cm^{-1} falls within the range 1950–1975 cm^{-1}, which for CO on nickel contains bands ascribed to bridged CO species on a slightly oxidised nickel surface. The bands at 2060 and 1935 cm^{-1} are assigned to CO linearly adsorbed and bridge bonded, respectively, on nickel atoms in a more reduced environment.

Spectra in the 1900–1200 cm^{-1} region recorded after CO adsorption at 673 K (at lower temperatures no bands were observed in this region) on Al0F, Al0.5F and Al1.5F are given in fig. 2. The system CO/Al0F [fig. 2(a)] yielded bands at 1830 and 1785 cm^{-1} due to organic and bidentate carbonates,[20, 21] respectively. Other bands at 1590, 1395 and 1235 cm^{-1} can be assigned to monodentate carbonate and bicarbonate (1235 cm^{-1}) structures.[21, 22] The band intensities decreased with increasing fluorine content (because of the substitution of hydroxyls by fluoride groups). The decrease was more marked for the bands of bridged carbonates which disappeared from the spectrum for Al1.5F [fig. 2(c)]. Only very weak bands were observed for Al4F.

Formation of carbonates was greatly reduced on MoNiAlxF samples (for example on MoNiAl0F after adsorption at 673 K only a band at 1595 cm^{-1} was observed) as hydroxyl groups are eliminated in the process of anchoring molybdate species to the support.
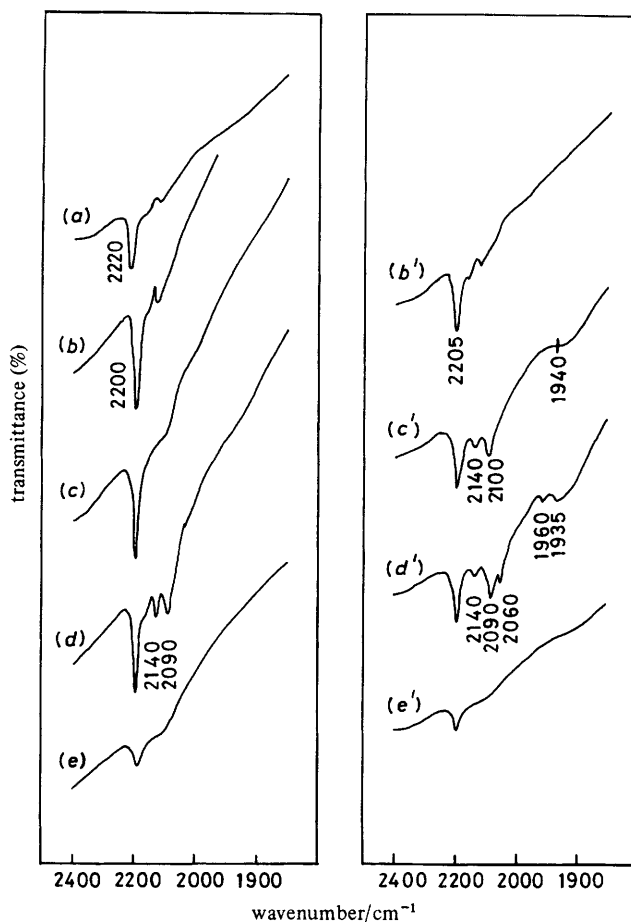
Fig. 1. Spectra after adsorption of CO: (a) on Al4F at r.t., on MoNiAl0.5F at (b) r.t., (c) 473, (d) 673 and (e) 873 K and on MoNiAl4F at (b') r.t., (c') 473, (d') 673 and (e') 873 K.

ADSORPTION OF CO_2

Spectra obtained after CO_2 adsorption on alumina and on supported Mo–Ni samples at r.t. are given in fig. 3. The bands produced by the system CO_2/Al0F [fig. 3(a)] at 1860, 1820 and 1190 cm^{-1} were removed by pumping at r.t. and can be assigned to organic carbonates. Other bands are attributed to bidentate carbonates (1790 cm^{-1}) and bicarbonates (1645, 1485, 1460 and 1235 cm^{-1}).[23–25] The high splitting of the v_3 bands is caused by the high polarization power of the Al^{3+} ion.[21] All the bands decreased in intensity or disappeared on increasing F content [fig. 3(b) and (c)].

After adsorption of CO_2 on the reduced form Al0F (red) the spectra obtained were practically the same as on the oxidized supports, although the bands were slightly less intense. This shows that the sites in the alumina surface involved in carbonate formation were only altered slightly by reduction with H_2 at 773 K. The addition of F markedly inhibited the formation of carbonates. However, the presence of residual structures of this type after adsorption of CO or CO_2 on Al4F shows that the substitution of OH$^-$ by F$^-$ was not complete.
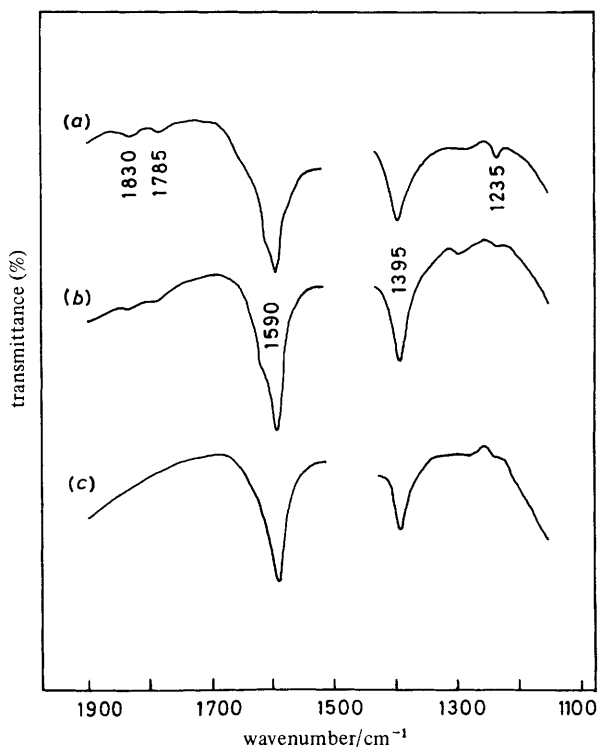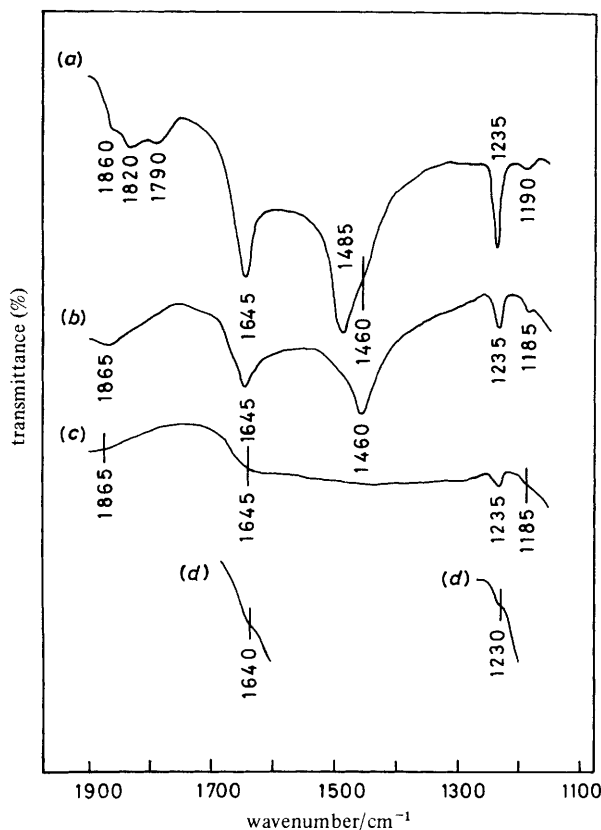
Fig. 2. Spectra after adsorption of CO at 673 K on (*a*) Al0F, (*b*) Al0.5F and (*c*) Al1.5F.

The adsorption of CO_2 on MoNiAl0F yielded bands of low intensity at 1640 and 1230 cm^{-1} [fig. 3(*d*)] assigned to bicarbonate species, showing that the active-phase Mo–Ni is in a highly disperse state on the support, covering most of its surface. The fact that no significant differences were found between spectra of CO_2 adsorbed on MoNiAl0F and MoNiAl4F catalysts suggests that the inhibiting effect for carbonate formation due to the presence of the active phase is larger and masks the effect of fluorine in these catalysts. As with samples of the support, only small differences in band intensities were observed between reduced and oxidised catalysts.

ADSORPTION OF NO ON FLUORINATED ALUMINA

I.r. spectra obtained after NO adsorption on fluorinated alumina with different F contents at r.t. and at 573 K are given in fig. 4(A) and (B) [(*a*), (*b*) and (*c*) refer to Al0F, Al1.5F and Al4F, respectively]. The system NO/Al0F yielded intense bands at 1620, 1590, 1565–1560, 1305–1295 and 1255–1240 cm^{-1}. The intensity of these bands decreased markedly with increasing F content, the spectrum obtained on Al4F being similar to the ground spectrum (after evacuation at 773 K for 15 h). The band at 1255–1240 cm^{-1} shifted towards lower wavenumbers for Al1.5F and Al4F. The adsorption of NO on the reduced samples [fig. 4(C)] yielded only two bands of low intensity at 1595 and 1235 cm^{-1}. In this case the inhibiting effect of F was not as marked as in the unreduced samples.
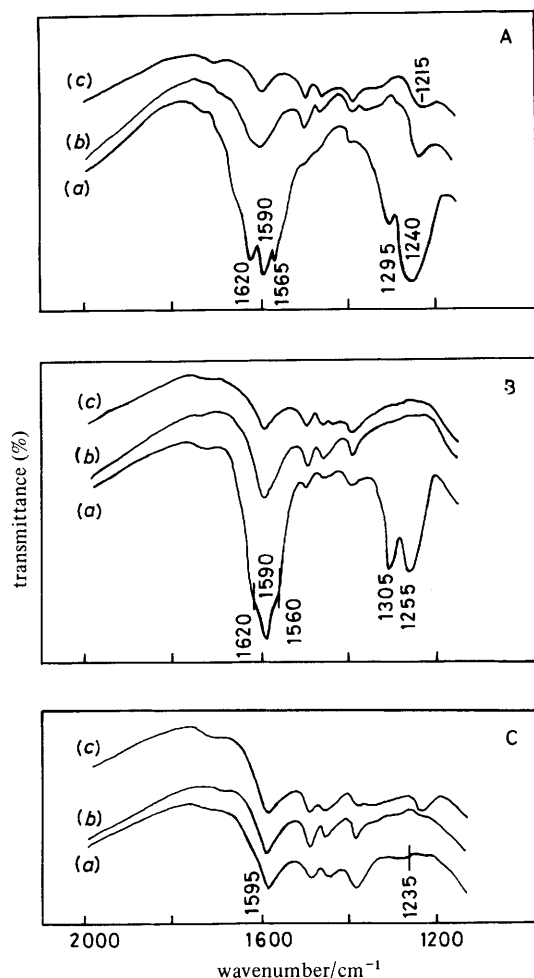
The bands resulting from the adsorption of NO can be assigned to bidentate (1620, 1595–1590 and 1255–1235 cm^{-1}) and monodentate (1565–1560 and 1305–1295 cm^{-1})

Fig. 3. Spectra after adsorption of CO_2 at r.t. on (a) Al0F, (b) Al1.5F, (c) Al4F and (d) MoNiAl0F.

nitrates[26] formed by associative adsorption of NO on surface O^{2-} ions. Bidentate nitrates predominate for unreduced samples as the most intense bands shown in fig. 4(A) and (B) are at 1620, 1590 and 1256–1240 cm^{-1}. However, formation of monodentate nitrates was enhanced after the 573 K treatment as shown by the intensity increase of the band at 1305 cm^{-1} [fig. 4(B)(a)] compared with the intensity of the band at 1295 cm^{-1} in fig. 4(A)(a). The results suggest that some conversion of bidentate into monodentate species was caused by increasing the temperature of NO adsorption from r.t. to 573 K. Activated adsorption would occur in this temperature range. Both nitrate species were strongly bound to the alumina surface as their removal needed evacuation at 773 K.

It has been reported that NO chemisorbs to some extent on Cr_2O_3 and Fe_2O_3.[27] However, no evidence for the adsorption of NO on V_2O_5 was found.[28] In this last oxide and because of the low energy of the V—O bond, the outgassing of the surface at a high temperature should give way to a high concentration of anion vacancies which would prevent the formation of nitrates. Fluorinated and/or reduced alumina presents a similar behaviour. In any case, an O^{2-}-deficient surface would be generated and therefore the formation of nitrates would be inhibited.

Fig. 4. Spectra after adsorption of NO: (A) on (a) Al0F, (b) All.5F and (c) Al4F at r.t., (B) on (a) Al0F, (b) All.5F and (c) Al4F at 573 K and (C) on (a) Al0F (red), (b) All.5F (red) and (c) Al4F (red) at r.t.

ADSORPTION OF NO ON Mo–Ni CATALYSTS

Spectra obtained after adsorption of NO on Mo–Ni catalysts in their oxidised (MoNiAl0F, MoNiAl4F) and reduced [MoNiAl0F(red), MoNiAl4F(red)] forms are given in fig. 5. Formation of nitrates on these samples was severely inhibited (even on MoNiAl0F) because of the presence of the Mo–Ni phase on the support surface. This indicates, in agreement with the results for CO_2 adsorption, that the active phase is highly dispersed on the alumina. The spectrum of NO/MoNiAl0F [fig. 5(a)] exhibits a band at 1880 cm^{-1} characteristic of linear NO adsorbed on Ni^{2+} ions. This band increased in intensity and shifted to 1885 cm^{-1} for the system NO/MoNiAl4F [fig. 5(b)]. The shift can be accounted for in terms of the higher surface acidity of this catalyst with respect to MoNiAl0F. This increased acidity will lower the back-donation of d electrons of the nickel to the antibonding orbital of the NO molecule. Therefore
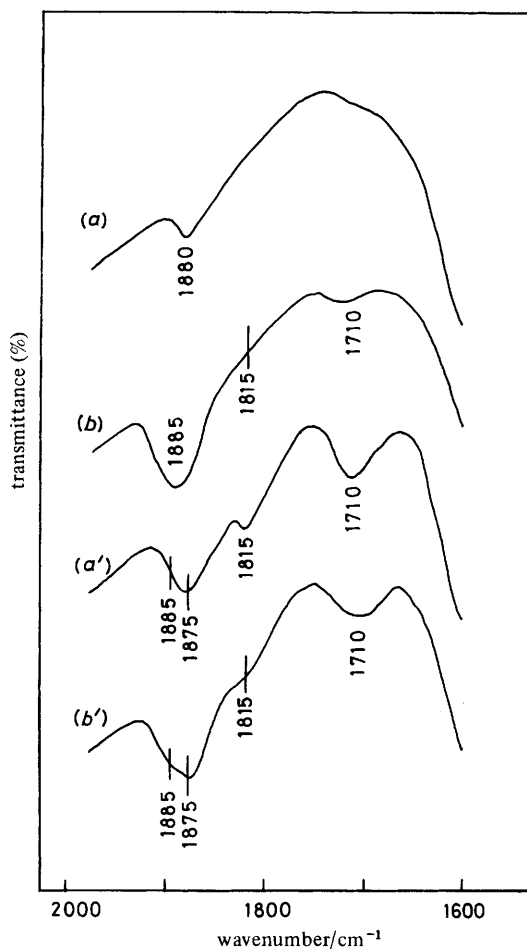
Fig. 5. Spectra after adsorption of NO at r.t. on (a) MoNiAl0F, (b) MoNiAl4F,
(a') MoNiAl0F (red) and (b') MoNiAl4F (red).

the Ni—No bond will be weakened and the stretching frequency of the NO bond will increase. Nitric oxide on metallic nickel gives an infrared band at slightly lower wavenumbers.[29] The present band is ascribed to NO on nickel-ion sites not only because of the band position but also because the spectra of CO adsorbed on a similar catalyst [fig. 1(b')] showed no evidence for the presence of exposed nickel atoms resembling metallic nickel. The shoulder at $1815 \, cm^{-1}$ and the band at $1710 \, cm^{-1}$ [fig. 5(b)] are both attributed to NO absorbed on reduced molybdenum species[30] generated in the process of outgassing the sample. The bands at 1815 and $1710 \, cm^{-1}$ were more intense for reduced catalysts, suggesting that reduction increased the surface concentration of the reduced molybdenum ions. Peri[17] achieved a greater extent of reduction of molybdenum ions than that found in our catalysts after the dynamic reduction of an Mo/Al_2O_3 samples at 773 K.

In the spectra of the reduced catalysts [fig. 5(a') and (b')], in addition to the band at $1885 \, cm^{-1}$ a band appeared at $1875 \, cm^{-1}$. In comparison Topsøe and Topsøe[31] reported that NO is adsorbed on Co–Mo/SiO$_2$ and Co/SiO$_2$ catalysts to give infrared
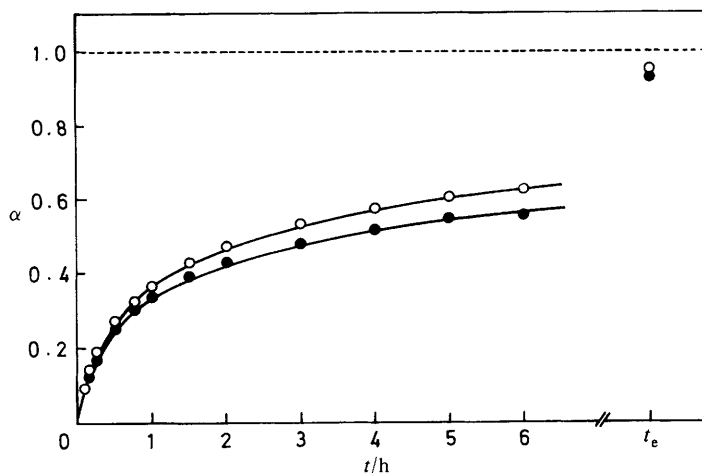
Fig. 6. Kinetic curves of reduction (300 mmHg H_2) at 773 K of $\bigcirc$, MoNiAl0F and $\bullet$, MoNiAl4F.

bands at 1885 and 1860 cm^{-1}, respectively. The bands were at 1885 cm^{-1} for Co–Mo/Al$_2$O$_3$ and at 1885 shifting to 1850 cm^{-1} with increasing cobalt loading for Co/Al$_2$O$_3$.[30] In accordance with the interpretations of the data for supported Co–Mo catalysts,[27, 31] the present result shows that reduction of Ni–Mo/Al$_2$O$_3$ catalysts generated a nickel-containing phase which differed from the predominant phase in unreduced samples. The possibility that some exposed nickel atoms were generated is suggested by the spectra of adsorbed CO, which showed that partial reduction of catalyst led to infrared bands characteristic of CO adsorbed on metal sites.

The band at *ca.* 1880 cm^{-1} due to NO adsorbed on nickel-ion sites was of considerably greater intensity for MoNiAl4F [fig. 5(*b*)] than for MoNiAl0F [fig. 5(*a*)], showing that fluorination of the alumina before impregnation increased the resulting population of exposed nickel-ion surface sites in the supported Mo–Ni catalyst. A similar effect was apparent for the reduced catalyst [fig. 5(*a'*) and (*b'*)], although in this case the significant intensity increase was for the band at 1875 cm^{-1}. The results suggest that fluorination of alumina before impregnation with Mo–Ni improved the dispersion of the nickel in the supported catalyst in the sense that more nickel ions were available as adsorption sites.

Spectra of adsorbed NO obtained after preadsorption of CO$_2$ (with an intermediate outgassing at r.t. for 1 h) in the region 2000–1700 cm^{-1} were similar to those obtained after adsorption of NO on a clean surface (fig. 5), although the intensity of the bands (particularly those of NO on molybdenum ions in the reduced catalysts) was lower. This should be due to steric hindrance by CO$_2$ of the subsequent adsorption of NO.

REDUCTION AND ADSORPTION OF NO AND O$_2$

Kinetic curves of reduction (300 mmHg H_2, 773 K) of MoNiAl0F and MoNiAl4F, α against t (for $\alpha = 1$, Mo^{6+} and Ni^{2+} would be reduced to Mo^{4+} and Ni^0), are given in fig. 6. Reduction of MoNiAl4F was slower than that of MoNiAl0F, as indicated by the initial reduction rates (r_0) calculated by analytical differentiation of the integral data and extrapolation to zero time (table 1). Also, 54 and 36 h were needed in order to reach a reduction degree $\alpha = 0.95$ for the fluorinated and unfluorinated catalysts, respectively. These results point to a stronger interaction of Mo and Ni phases with

Table 1. Initial reduction rates and chemisorption data of NO and O$_2$

sample	r_0^a/mg g^{-1} min^{-1}	NO$_{irrev}^b$/mmol g^{-1}	O$_{2,\,irrev}^b$/mmol g^{-1}
MoNiAl0F	0.318	0.110	0.154
MoNiAl4F	0.232	0.160	0.223

^{a} r_0 is the initial reduction rate as measured by loss of sample weight. ^{b} NO$_{irrev}$ and O$_{2,\,irrev}$ are the amounts of NO and O$_2$ irreversibly adsorbed.

the support surface in the MoNiAl4F sample. This conclusion is strengthened by the results of the chemisorption experiments involving NO and O$_2$ (table 1) on the reduced catalysts, which indicate a higher adsorption and therefore a higher dispersion of Mo and Ni on the fluorinated catalyst. [For details of the use of NO and O$_2$ as probe molecules for the evaluation of metallic sites see, for example, ref. (12), (13) and (32).] These findings are consistent with the enhanced intensities for fluorinated samples of the infrared bands due to NO adsorbed on nickel sites.

DISCUSSION

CO$_2$ adsorbs at r.t. on O^{2-} centres in the alumina surface to form carbonates while NO adsorbs, as such, on metallic sites (unreduced or reduced) of supported Mo–Ni catalysts and also on O^{2-} of alumina-yielding nitrates. Therefore the successive adsorption of these molecules can be used to characterise the part of the surface occupied by the active Mo–Ni phase. Preadsorption of CO$_2$ will occupy the uncovered fraction of the support while the subsequent adsorption of NO will occur on Mo or Ni sites. Adsorption of CO can also be used to gain information about the metallic sites in these catalysts as CO adsorbs selectively on metallic centres at r.t. with no formation of carbonates on the uncovered alumina.

Reduction of alumina, at 773 K in H$_2$, inhibited the formation of nitrates from NO adsorption at r.t. more severely than the formation of carbonates either from the adsorption of CO at 673 K or from the adsorption of CO$_2$ at r.t. This finding points to important differences between the O^{2-} centres involved in both types of processes and to higher surface requirements from the former case. For CO$_2$ the difference could be explained by the fact that this molecule would require only one oxygen ion from the lattice to form carbonate structures, while for nitrate formation NO would need adsorption centres each composed of two neighbouring oxygen ions probably of differing natures.

The increase in dispersion of the active phase with increasing fluorine content in MoNiAlxF samples, as suggested by spectroscopic results for NO adsorption and also by reduction and by O$_2$ and NO adsorption data, may tentatively be explained by considering the isoelectric point of the aluminas and the presence of monomeric and polymeric Mo species, MoO$_4^{2-}$ and Mo$_7$O$_{24}^{6-}$, in equilibrium in the impregnating solution. The surface of fluorinated alumina (isoelectric point 5.6)[33] will be charged negatively in the ammonium heptamolybdate solution (pH 6.5). Under these conditions the adsorption of the highly charged polymeric Mo species will be less favoured than the adsorption of the monomeric MoO$_4^{2-}$ on this support. Conversely, on the surface of unmodified alumina (isoelectric point 7) the adsorption of the polymeric species will be most favoured. This would result in a higher Mo dispersion on Al4F than on Al0F. On the other hand, the anchoring of the bulky Mo$_7$O$_{24}^{6-}$ to the support will need a higher number of neighbouring OH$^-$ groups than the anchoring of MoO$_4^{2-}$. Thus

the adsorption of the polymeric species on Al4F will be highly impeded because of the substitution of hydroxyls by F^- effected on this support. An increase in Mo dispersion by the incorporation of fluorine into the starting alumina, similar to that found in this work, has also been observed by Boorman et al.[9] by means of X.p.s. analyses.

[1] H. R. Gerberich, F. E. Lutinski and W. K. Hall, J. Catal., 1966, 6, 209.
[2] J. B. Peri, J. Phys. Chem., 1965, 69, 211; 1968, 72, 2917.
[3] T. R. Hughes, H. M. White and R. J. White, J. Catal., 1969, 13, 58.
[4] V. R. Choudhary, Ind. Eng. Chem., Prod. Res. Dev., 1977, 16, 12.
[5] P. O. Scokart, S. A. Selim, J. P. Damon and P. G. Rouxhet, J. Colloid Interface Sci., 1979, 70, 209.
[6] E. R. A. Matulewicz, F. P. J. M. Kerkhof, J. A. Moulijn and H. J. Reitsma, J. Colloid Interface Sci., 1980, 77, 110.
[7] F. P. J. M. Kerkhof, J. C. Oudeans, J. A. Moulijn and E. R. A. Matulewicz, J. Colloid Interface Sci., 1980, 77, 120.
[8] L. Gonzales Tejuca, C. H. Rochester, A. Lopez Agudo and J. L. G. Fierro, J. Chem. Soc., Faraday Trans. 1, 1983, 79, 2543.
[9] P. M. Boorman, J. F. Kriz, J. R. Brown and M. Ternan, Proc. Climax 4th Int. Conf. Chemistry and Uses of Molybdenum, ed. H. F. Barry and P. C. H. Mitchell (Climax Molybdenum Co., Ann Arbor, Michigan, 1982), p. 192.
[10] G. Murali Dahar, F. E. Massoth and J. Shabtai, J. Catal., 1984, 85, 44.
[11] K. Segawa and W. K. Hall, J. Catal., 1982, 76, 133.
[12] K. Segawa and W. K. Hall, J. Catal., 1982, 77, 221.
[13] J. L. G. Fierro, S. Mendioroz, J. A. Pajares and S. W. Weller, J. Catal., 1980, 65, 263; J. L. G. Fierro, A. Lopez Agudo, P. Grange and B. Delmon, Preprints 8th Int. Congr. Catal. (Springer Chemie, Berlin, 1984), vol. 2, p. 363.
[14] J. B. Peri, Discuss. Faraday Soc., 1966, 41, 121.
[15] P. Ratnasamy and H. Knozinger, J. Catal., 1978, 54, 155.
[16] W. S. Millman, M. Crespin, A. C. Cirillo Jr, S. Abdo and W. K. Hall, J. Catal., 1979, 60, 404.
[17] J. B. Peri, J. Phys. Chem., 1982, 86, 1615.
[18] C. L. Angell and P. L. Schaffer, J. Phys. Chem., 1966, 70, 1413.
[19] N. Sheppard and T. T. Nguyen, Adv. Infrared Raman Spectrosc., 1978, 5, 67.
[20] N. D. Parkyns, J. Chem. Soc. A, 1969, 410.
[21] G. Busca and V. Lorenzelli, Mater. Chem., 1982, 7, 89.
[22] N. D. Parkyns, J. Phys. Chem., 1971, 75, 526.
[23] E. Guglielminotti, L. Cerruti and E. Borello, Gazz. Chim. Ital., 1977, 107, 447.
[24] C. Morterra, A. Zecchina, S. Coluccia and A. Chiorino, J. Chem. Soc., Faraday Trans. 1, 1977, 73, 1544.
[25] E. Baumgarten and A. Zachos, Spectrochim. Acta, Part A, 1981, 37, 93.
[26] N. D. Parkyns, Proc. 5th Int. Congr. Catal. ed. J. W. Hightower (North-Holland, Amsterdam, 1973), vol. 1, p. 255.
[27] L. Cerruti, J. Chem. Soc., Faraday Trans. 1, 1974, 73, 29.
[28] M. Takagi, T. Kawai, M. Soma, T. Onishi and K. Tamaru, J. Catal., 1977, 50, 441.
[29] A. Terenin and L. Roev, Spectrochim. Acta, 1959, 11, 946.
[30] N-Y. Topsøe and H. Topsøe, J. Catal., 1982, 75, 354.
[31] N-Y. Topsøe and H. Topsøe, Bull. Chem. Soc. Belg., 1981, 90, 1311.
[32] J. Valyon, W. K. Hall, J. Catal., 1983, 84, 216.
[33] K. Jiratova, Appl. Catal., 1981, 1, 165.