JOURNAL OF CATALYSIS 86, 84–94 (1984)

Infrared Studies of Ni Held at Low Concentrations on Alumina Supports[1]

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Received August 2, 1983; revised October 3, 1983

Infrared studies, using adsorbed CO and NO as molecular probes, were made of Ni held at ≤1% by weight on alumina supports. Reduced Ni on pure aluminas typically showed strong support interactions. Adsorbed CO gave bands in the region 2090–2115 cm^{-1} arising from CO held strongly, by acidic nickel ($Ni^{\delta+}$) sites. Adsorption of CO on ionic and on fully reduced Ni^0 sites was also evident. Other adsorbed CO, giving bands in the region 2060–2090 cm^{-1}, was held less strongly than that held on $Ni^{\delta+}$ sites. Particularly if sulfate was initially present in the alumina, reduced Ni tended to hold CO weakly, giving a band in the region 2070–2090 cm^{-1}. Such behavior apparently conflicts with prevalent opinion relating strong binding with lower frequencies for adsorbed CO. Oxide, sulfide, or carbide partial overlayers on Ni may explain weak binding. Related effects were seen for adsorbed NO. Bands from adsorbed CO and NO varied markedly depending on the Ni salt (chloride or nitrate) and the alumina used in preparation, as well as on predrying and reduction procedures. Alumina readily stabilizes ionic Ni species, but after suitable reduction exposed Ni^0 and $Ni^{\delta+}$ atoms could be studied with computerized infrared techniques at total Ni concentrations of 250 ppm or less.

INTRODUCTION

Infrared studies of adsorbed molecular probes have long provided important information on oxide-supported metals (*1–13*). The variety of infrared bands observed for CO or NO on oxide-supported Ni shows that Ni atoms can be exposed on the surface in various ways (*4, 8–11*). An influence of the support was recognized very early (*1, 7*). Even silica, usually regarded as a fairly inert support, can interact strongly with Ni under some conditions (*8, 10*). Most previous work on supported Ni has been on samples containing at least 5 wt% Ni, however, and pretreated under conditions which minimize support effects.

At low metal concentrations, and on more-reactive supports, support effects become obvious. Alumina, which can strongly stabilize Ni ions in its surface (*14, 15*) and through spinel formation even within its bulk crystal structure (*16*), might not be considered an ideal support for studies of supported Ni. Support interactions can greatly modify catalytic properties of many metals however. The nature of these interactions is thus of both practical and theoretical interest. Previous infrared studies of Ni on alumina (*5–7, 13, 22*) have mostly used one special form of high-area alumina, Alon C, which is not really typical of commercial alumina supports.

The availability in recent years of commercial computerized dispersive and Fourier-transform infrared (FTIR) spectrometers has markedly improved the sensitivity of infrared studies of catalyst surfaces (*12*). The ease with which spectra can now be closely compared (*17, 18*) has revealed features which might easily have been overlooked before. Additional study of alumina-supported Ni was, therefore, made to clarify the nature of support interactions and the effects of different alumina

[1] Presented at the 185th ACS National Meeting, Seattle, Washington, March 23, 1983.

0021-9517/84 $3.00

TABLE 1

Alumina Properties

Alumina	Surface area (m^2/g)	Pore vol (cm^3/g)	Pore diam (Å)	Na_2O (wt%)	SO_4^{2-} (wt%)
Filtrol 90	282	0 39	60	0 02	3 5
KSA	290	1 5	200	0 008	Low
PHF (Aero 1000)	244	0 5	88	0 02	Low
Aero 100	238	0 82	138	0 30	0 50
Catapal SB	250	0 53	~80	0 004	0 01
Baymal	274	0 53	77	0 07	1 8

supports, preparation, or pretreatment procedures

EXPERIMENTAL

A Beckman IR-9 spectrometer was used in early work A computerized Beckman 4260–Wang 2200 VP system (*18*) was used later

A conventional glass high-vacuum system giving $<10^{-5}$ Torr pressure was used for most of the work, but in studies of Ni at very low concentrations this was supplemented with a Perkin–Elmer TNBX vacuum system This gave about 10^{-8} Torr pressure in the infrared cell prior to adsorption of probe molecules

The techniques used have mostly been described (*8, 18*) Infrared study was made of thin self-supporting disks, made by pressing 0 20 (or in early work 0 30) g of powdered Ni/Al_2O_3 in a stainless-steel die, 32 mm in diameter A quartz infrared cell with CaF_2 windows permitted pretreatment at temperatures to 800°C Spectra were obtained after cooling the sample Attenuation of the reference beam with screens was routine Spectra were normally recorded with 5–9 Torr of CO or NO and again after 5 min evacuation at ~50°C In some instances, study was made of progressive desorption by evacuation at higher temperatures

Samples of Ni/Al_2O_3 were made by impregnation of alumina powders with aqueous nickel nitrate or chloride, using an "incipient wetness" technique Typical properties of the aluminas studied are given in Table 1 Unless otherwise specified, Cyanamid Aero 1000 (or equivalent PHF alumina) was used This will be designated alumina A The CO used was Airco or Linde Assayed reagent Nitric oxide supplied by Linde, was purified by bulb to bulb distillation in the vacuum system Hydrogen was purified by diffusion through palladium silver alloy

Reduction was typically carried out by heating in 50 Torr of H_2 for 1 h after predrying by evacuation for 1 h at the same temperature The cell was then evacuated for 15 min before cooling the sample and recording spectra In some instances this procedure was modified as will be discussed

RESULTS AND DISCUSSION

Effects of Preparation and Pretreatment Variables

Figure 1 shows spectra obtained in early studies of CO adsorbed on a 1% Ni/Al_2O_3 (A) sample prepared with aqueous $NiCl_2$ The sample was reduced, as indicated, at 400, 500, and 600°C after evacuation at the same temperature Spectra were recorded

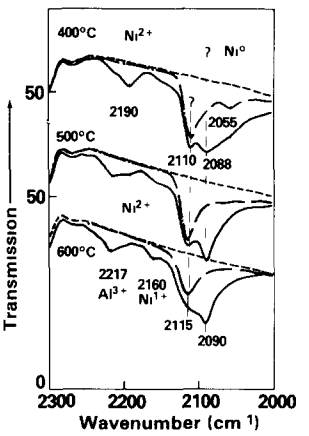

FIG 1 Spectra of CO adsorbed on 1% Ni (ex-$NiCl_2$) on alumina (A) prereduced at the indicated temperatures (°C) Dashed curves represent background spectra obtained after reduction of the catalyst, solid curves were after addition of 8–10 Torr of CO, dot-dash curves, after 5 min evacuation

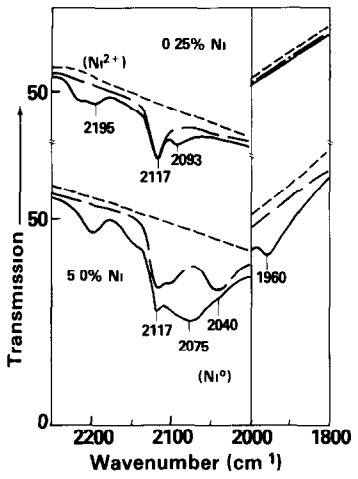

FIG 2 Spectra of CO adsorbed on Ni/Al_2O_3 (A) containing 0 25 and 5 0% Ni ($NiCl_2$ prep prereduced at 500°C) Spectra are keyed as in Fig 1

before and after CO addition The CO was then desorbed by evacuation at 300°C and spectra of adsorbed NO were obtained The sample was again reduced after evacuation at the next higher temperature The adsorption sites responsible for some of the bands are probably, as indicated in Fig 1, exposed Al^{3+} ions, exposed Ni^{2+} and Ni^{1+} ions stabilized in the alumina surface, and Ni^0 atoms in the surface of small Ni crystallites The band at 2110–2115 cm^{-1}, from strongly held CO, and that near 2090 cm^{-1}, from weakly held CO, will be discussed below

Figure 2 shows similar CO spectra obtained on 0 25 and 5 0% Ni/Al_2O_3 (A) again prepared by impregnation with $NiCl_2$ solution and reduced in H_2 after prior evacuation at 500°C At the lower Ni concentration the band at 2117 cm^{-1} is the most prominent Little evidence is seen for CO on Ni^0 (band 2020–2060 cm^{-1}) A band is also seen near 2117 cm^{-1} on the 5% Ni sample, but another band now appears near 2040 cm^{-1}, after evacuation, representing CO linearly adsorbed on Ni^0, and another is seen near 1960 cm^{-1}, evidently showing bridged adsorption of (weakly held) CO

No difficulty was found in reproducing spectra in early work Later, using a different vacuum system and spectrometer, it was initially not possible to obtain CO bands nearly as intense as those seen before, particularly for samples prepared with $NiCl_2$ The discrepancy was eventually traced to a difference in the extent of predrying and to readsorption of HCl In the early work, because of cooling when H_2 was admitted and possible overheating during evacuation, the effective reduction temperature was apparently 50°C, or more, below the drying temperature After deliberately predrying 50–100°C above the reduction temperature, similar CO bands were once again obtained Later work has confirmed that poor vacuum conditions during predrying will prevent subsequent observation of CO bands

Figure 3 illustrates variations in CO bands resulting from differences in predrying and reduction procedures The 1% Ni/Al_2O_3 (A) samples on which these spectra were obtained were precalcined in oxygen and dried by evacuation at the indicated temperature before reduction in H_2 at this, or a lower, temperature The CO band near 2110 cm^{-1} increased dramatically when the sample was predried above 400°C No evidence was seen for bridged adsorption of

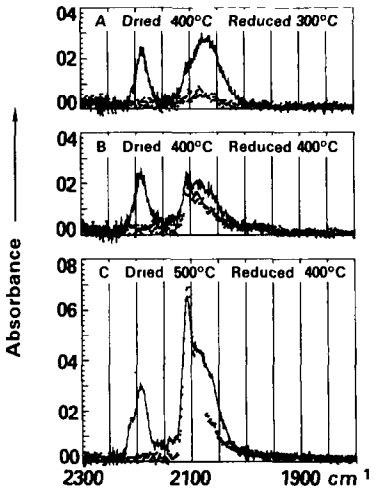

FIG 3 Spectra of CO adsorbed on 1% Ni (ex $NiCl_2$)/Al_2O_3 (A) Samples were predried at 400°C (A, B) and 500°C (C) and reduced at 300°C (*A*) or 400°C (*B, C*) as indicated Solid spectra are after CO addition, dotted spectra, after 5 min evacuation

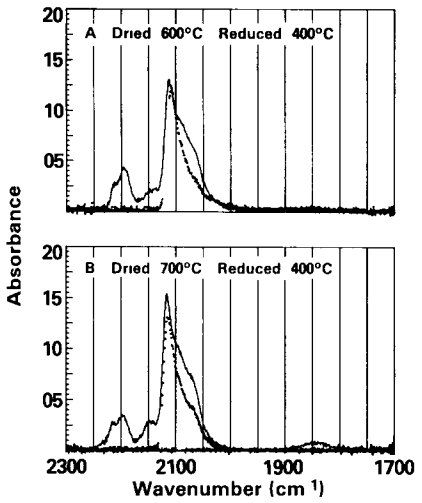

FIG 4 Spectra of CO adsorbed on 1% Ni (ex-Ni Cl_2)Al_2O_3 (A) Samples were predried at 600°C (*A*) and 700°C (*B*) before reduction at 400°C Solid spectra, after CO addition, dotted spectra, after 5 min evacuation

CO (band below 2000 cm^{-1}) As indicated by the CO bands near 2200 cm^{-1}, exposed Ni^{2+} ion sites (~2190 cm^{-1}) were present on samples predried at 400°C, but exposed Al^{3+} sites (~2210 cm^{-1}) appeared only after predrying at 500°C or higher

As shown in Fig 4, predrying at higher temperatures further increased the 2110-cm^{-1} CO band and the relative intensity of the CO/Al^{3+} band compared to the CO/Ni^{2+} band A band near 2150 cm^{-1}, probably reflecting CO/Ni^{1+}, also became more evident After predrying at 700°C adsorption of CO on the 400°C-reduced sample also produced a small band near 1840 cm^{-1} In all these spectra, a band or bands representing weakly held CO can be seen in the region 2050–2100 cm^{-1}, varying in intensity depending on pretreatment

Figure 5A shows spectra obtained when CO was adsorbed on 1% Ni/Al_2O_3 (A) prepared with $Ni(NO_3)_2$ instead of $NiCl_2$ This sample was predried and reduced at 500° Differences from the spectra of Figures 1 to 4 are evident The strongest CO band, again corresponding to strongly-held CO, near 2090 cm^{-1}, over 20 cm^{-1} lower than on the samples prepared with $NiCl_2$ Additional bands and shoulders are also evident The bands corresponding to weakly held CO in the region 2190–2230 cm^{-1} and below 2100 cm^{-1} are generally similar to those on the samples prepared from $NiCl_2$, but several appear to have shifted to slightly lower frequencies After weakly held CO is removed by 5-min evacuation a fairly sharp band appears near 1970 cm^{-1}, evidently corresponding to CO strongly held in a "bridged" configuration between two Ni atoms This band was not removed by 15 min additional evacuation at 150°C and, instead, increased somewhat in intensity as the remaining "linear" CO bands between 2060 and 2090 cm^{-1} decreased

The spectra of Fig 5B show that after removal of CO by evacuation at 300°C, the original CO bands were restored almost identically by readdition of CO These spectra again showed the changes observed previously as the CO was desorbed, indicating a fairly stable surface character

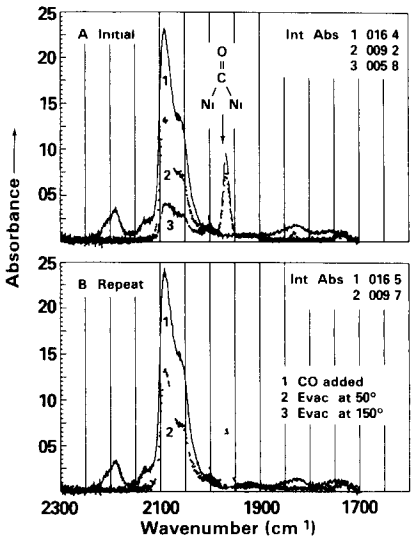

FIG 5 Spectra of CO adsorbed on 1% Ni (ex-Ni nitrate)/Al_2O_3 (A) Samples were dried and reduced at 500°C (*A*) After initial reduction spectra were obtained as indicated after CO addition, after 5 min evacuation at 50°C and after 15 min evacuation at 150°C (*B*) Following rereduction of the same sample at 500°C Spectra as indicated above Total integrated absorption for each spectrum is also as indicated above

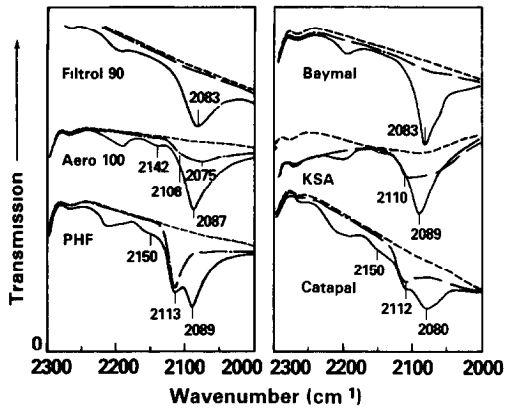

FIG 6 Spectra of CO/1% Ni (ex-$NiCl_2$) on various aluminas Spectra are keyed as in Fig 1

Effects of Differences in Alumina Supports on CO Spectra

Figure 6 shows spectra of CO adsorbed on 1% Ni/Al_2O_3 samples made by $NiCl_2$ impregnation of six, similarly precalcined, commercial aluminas Most samples were prereduced at 500°C The KSA and Catapal-supported samples were prereduced at 600°C Catapal resembles PHF alumina as a support, Ni/Catapal giving a band from strongly held CO at 2112 cm^{-1} and one from weakly held CO at 2080 cm^{-1} The higher frequency CO band was weaker on Ni/KSA and Ni/Aero 100 alumina and was not seen at all on Ni/Filtrol 90 and Ni/Baymal aluminas All samples weakly held some CO producing a band in the region 2080–2090 cm^{-1} A band arising from weakly held CO or CO_2 was sometimes seen around 1840–1845 cm^{-1} On Filtrol 90 1% Ni prepared with nitrate instead of chloride showed CO spectra after reduction at 400, 500, and 600°C almost identical to those seen on the sample made with $NiCl_2$ After adsorption and desorption of NO, which oxidized the Ni, CO adsorption after rereduction gave the same bands seen originally

Spectra of Adsorbed NO—Effects of Differences in the Support

Figure 7 shows spectra of NO adsorbed on 1% Ni/Al_2O_3 (A) prepared from $NiCl_2$ after prereduction at 400, 500, and 600°C The intensity of the 1870-cm^{-1} band decreased with increasing prereduction temperature while a band at 1910–1915 cm^{-1} initially increased and then possibly decreased slightly in intensity A third band, representing weakly held NO, apparently exists near 1900 cm^{-1} These bands probably arise mainly from NO held on Ni ions, possibly created in part, by initial reaction of NO with reduced Ni sites Desorption of NO at 200°C left a surface, presumably oxidized, which no longer adsorbed CO Reduction in H_2 restored the surface to its original condition, however Spectra, not shown, of NO on 1% Ni/Al_2O_3 (A) made from $Ni(NO_3)_2$ after similar pretreatment and reduction resembled those of Fig 7, except that no evidence was seen for the small band above 1900 cm^{-1}

Figure 8 shows spectra obtained for NO on 1% Ni/Filtrol 90, similarly prereduced in H_2 at 400, 500, and 600°C The frequency of the single NO band shifted from 1875 cm^{-1} after 400°C reduction to 1850 cm^{-1} after prereduction at 600°C At the same time, a band at 1380 cm^{-1} (not shown) caused by surface "sulfate" groups also decreased The use of $Ni(NO_3)_2$ rather than $NiCl_2$ in preparation made little difference in the NO bands obtained with Ni/Filtrol 90

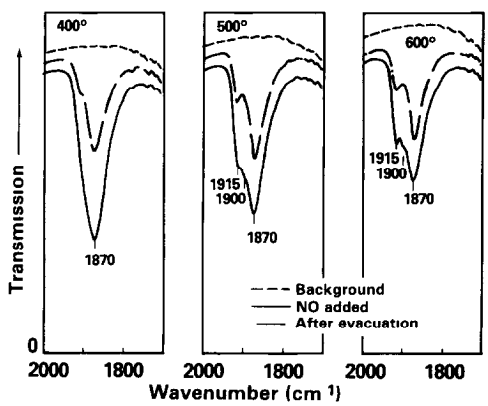

FIG 7 Spectra of NO adsorbed on 1% Ni (ex-$NiCl_2$) reduced at indicated temperatures Dashed spectra, background, solid spectra, after NO addition, dot-dash spectra, after 5 min evacuation

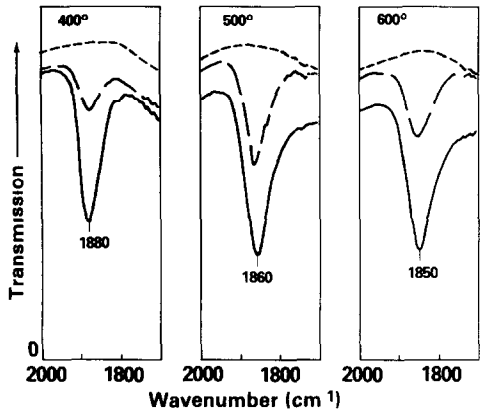

FIG 8 Spectra of NO on 1% Ni/Filtrol 90 alumina ($NiCl_2$ prep) reduced at indicated temperatures Spectra are as in Fig 7

The most important variable in the alumina supports of Figs 6 to 8 was apparently sulfate content As shown in Table 1, this was highest for Filtrol 90, but Baymal also held a substantial amount of sulfate Deliberate addition of H_2SO_4 or reaction of alumina (A) with $SO_2 + O_2$ at 200°C or higher changed the support properties to resemble those of Filtrol 90 Physical mixtures of sulfated alumina with samples holding metals on pure alumina supports also gave surface properties for the metal, after subsequent reduction in H_2, which closely resembled those seen on sulfated alumina Sulfate on the alumina results in mild treatment of the supported metal with $H_2S + S$ during reduction in H_2 at 400–600°C Other factors can also be important, but sulfate can be of major importance in determining the surface properties of supported nickel

Ni at Very Low Concentrations

Using spectral averaging to improve signal to noise ratios, and improved vacuum conditions, good spectra could be obtained of adsorbed CO at Ni concentrations of 250 ppm or less, as illustrated in Fig 9 The 0 025% Ni sample was prepared by impregnation with very dilute $Ni(NO_3)_2$ solution and reduced at 600°C after calcination in O_2 and evacuation (to 10^{-8} Torr) at the same temperature In collecting background and other spectra, 25 scans were averaged, and 2 extra decimal places were retained in averaged spectra To obtain spectrum (a) The gas phase CO contribution was subtracted In addition to bands in the region 2210–2235 cm^{-1} reflecting adsorption of CO on Ni^{2+} or Al^{3+} sites on the dry alumina, a band corresponding to strongly held CO can be seen at about 2080 cm^{-1}, roughly as observed on the 1% Ni (ex-nitrate) samples except about 2% as intense

Interpretation of Spectra

The CO and NO spectra present some major problems in interpretation Assignments, summarized in Tables 2 and 3, should be considered tentative Despite extensive past infrared study of supported Ni, much confusion remains regarding interpretation, experimental conditions, and observations Reasonable interpretations have been offered for most previous observations (*4, 10, 11*) Attention to detail is important in comparing results of different studies, however, particularly regarding the binding of the CO causing various bands Little attention has been given to this in the past Often only band frequencies are re-

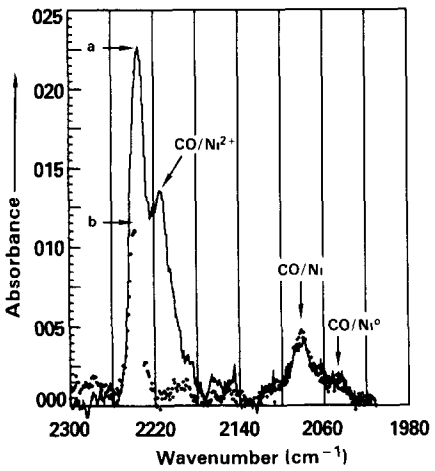

FIG 9 CO adsorbed on 250 ppm Ni (ex-Ni nitrate)/Al_2O_3 (A) after prereduction at 600°C Solid spectra, after adding 10 Torr of CO, dotted spectrum after 5 min evacuation

TABLE 2

Assignments of Bands from CO on Ni/Al_2O_3

Wavenumber range (cm^{-1})	Binding of CO	Adsorption site
2200–2240	Weak-linear	Al^{3+} or $Al^{3+}O^{2-}$ (*27, 28*)
2190–2200	Weak-linear	Ni^{2+} (*4, 8*)
2130–2160	Weak-linear	Ni^{1+} (*4*)
2110–2120	Strong-linear	$Ni^{\delta+}$ (ex Cl^-)
2080–2100	Strong-linear	$Ni^{\delta+}$ (ex-NO_3^-)
2050–2090	Weak-linear	$Ni^{\delta+}$ or Ni^0 associated with O^{2-}, S^{2-}, or C^{2-} partial overlayer
2020–2065	Strong-linear	Ni^0 (clean crystals) (*4*)
1960–1980	Strong-bridged	$Ni^{\delta+}$ (ex-NO_3^-)

ported Frequency alone does not prove that the same type of CO adsorption has been observed in different experiments

Previous studies of $CO/Ni/Al_2O_3$ generally show bands in the region 2030–2060 cm^{-1}, corresponding to CO adsorbed strongly or moderately strongly in a linear form, and bands in the region 1910–1970 cm^{-1} from strongly adsorbed bridged CO In addition, linear CO held more-weakly appears to give a band in the region 2070–2090 cm^{-1} Samples were generally prepared by $Ni(NO_3)_2$ impregnation of Alon C, and Ni concentrations were typically near 10 wt%, although one 1 5% sample was studied Previous workers apparently did not see the bands in the region 2080–2120 cm^{-1} caused by strongly held CO seen in the present study The A_H bands observed by Primet *et al* (*10*) on Ni/SiO_2 at 2070–2080 cm^{-1} corresponding to "irreversibly held" linear CO are similar to those seen near 2080 cm^{-1} on Ni/Al_2O_3 prepared from $Ni(NO_3)_2$ A second linearly bound CO species on Ni/SiO_2 gave a band (A_L) near 2040 cm^{-1} The A_H band was tentatively attributed to CO on Ni atoms interacting with an oxide phase (unreduced Ni or silica) while the A_L band was thought to show CO on unperturbed Ni atoms

Bands near 2200 cm^{-1} generally show weak adsorption of CO on exposed Ni^{2+} ions (*4, 8*) and bands near 2140–2150 cm^{-1} are evidently caused by CO on Ni^{1+} ions (*4*) Variations in band frequencies may result from differences in the coordination of the ions in the surface (*8*) Bands slightly above 2200 cm^{-1} are produced by CO held on Al^{3+} ions or $Al^{3+}O^{2-}$ sites on the alumina support (*27, 28*) Bands in the region 2020–2065 cm^{-1} arising from CO held strongly, or moderately strongly, are thought to show CO held linearly by Ni^0 in small crystals ("unperturbed" Ni^0) (*4*) Exact frequencies of these bands apparently depend on crystal face exposure, size, surface coverage, and possible inductive effects of the support

Present theory relates CO band frequency to the strength of binding Strongly held CO which gives bands above 2090 cm^{-1}, and weakly held CO which gives bands in the region 2060–2090 cm^{-1} thus appear inconsistent Bands in the region 2060–2090 cm^{-1} from weakly held CO have usually been attributed to CO held by isolated Ni^0 atoms or noncrystalline Ni, e g , Ni next to oxygen atoms or oxide support (*4, 9*) Weakly held CO giving bands near 2060 cm^{-1} has also been reported on NiO and attributed to CO held by Ni^{2+} ions (*19*), but this assignment has generally been dismissed on the basis that the NiO was probably partially reduced by CO Such bands might also arise from weakly adsorbed $Ni(CO)_4$ or unstable surface carbonyls holding more than one CO molecule (*11*) Similar bands on sulfur-poisoned Ni and Ni/SiO_2 have been attributed to $Ni(CO)_4$ which

TABLE 3

Assignments of Bands from NO on Ni/Al_2O_3

Wavenumber range (cm^{-1})	Binding of NO	Adsorption site
1910–1920	Strong-linear	$Ni^{\delta+}$ (ex-Cl^-)
1870–1880	Strong-linear	Ni^{2+} (O^{2-} neighbors)
1850–1860	Moderately strong-linear	Ni^{2+} (S^{2-} neighbors)

forms more readily in the presence of sulfur Adsorbed $Ni(CO)_4$ may sometimes produce bands in this region, but repeated desorption of $Ni(CO)_4$ and readsorption of CO would probably markedly change the concentration and nature of Ni on low-concentration Ni/Al_2O_3 catalysts This was not evident in the present study The bands seen here are also produced quickly when CO is added rather than slowly as might be expected if $Ni(CO)_4$ formation were responsible Formation of $Ni(CO)_4$ probably does not occur readily in low-concentration Ni/Al_2O_3 samples On high-index planes of Ni, or where contamination with C, O, etc might most easily occur, formation of $Ni(CO)_4$ is less likely than, for example, on a 111 plane (*25, 26*) Weakly held CO also produces bands in the region 2020–2080 cm^{-1} on Mo/Al_2O_3 (*18*) where $Ni(CO)_4$ formation cannot be the explanation

Weak adsorption of CO giving bands in the region 2060–2090 cm^{-1} can be explained by other factors Current opinion holds that CO initially weakly donates lone pair electrons from the carbon atom to a reduced metal atom which then back-donates electrons to antibonding orbitals of the CO, weakening the C—O bond but strengthening the M—C bond The C—O vibrational frequency is thereby lowered (from ~2143 cm^{-1}) and a strong M—C bond established When CO is adsorbed by metal ions, which cannot easily back-donate electrons, bonding to the surface is weak, and the CO frequency is usually not lowered but instead increased One explanation of weak adsorption combined with lowering of the gas phase CO frequency might be that electrons are donated to antibonding orbitals of CO not from the adsorbing metal atom but from adjoining anions, such as oxide

Partial overlayers of anions, such as oxide, sulfide, or carbide, with associated underlying Ni ions probably, however, affect both the binding and frequency of adsorbed CO through local electrical field effects Linear attachment of CO to a Ni^0 atom would normally give a fairly strong M—C bond and a frequency in the range 2020–2065 cm^{-1} The presence of an adjacent ion pair containing oxide or sulfide ion could both weaken the C—Ni attachment and somewhat increase the C—O frequency by abstracting electrons otherwise available for back donation from the Ni^0 atom, and increase the C—O bond frequency (above 2060 cm^{-1}) through a local electrical field effect

Some NiO can be strongly stabilized by the surface of alumina (*14, 15*) On sulfate-containing aluminas, or after pretreatment of with H_2S, residual NiO (or $NiCl_2$) should be converted, at least partially, to NiS Sulfide or oxide anions can also be held in a partially filled overlayer on a Ni crystal surface without preventing adsorption of CO on exposed Ni atoms The exposed Ni atoms could, however, be rendered slightly positive ($\delta+$) by the presence of adjacent Ni^{2+} ions

Weak binding of CO giving bands in the region 2060–2090 cm^{-1} seems, as concluded by others (*4, 10*), to reflect adsorption on Ni atoms associated with anions The alumina surface either holds $NiCl_2$, NiO, or NiS in sites which affect Ni^0 atoms, or traces of O_2, HCl, H_2O, or H_2S partially reoxidize reduced Ni Because spectra are reproducible for a given Ni/Al_2O_3, and different for different preparations, accidental reoxidation does not appear to be of principal importance

Strongly held CO giving bands in the region 2080–2120 cm^{-1} is probably held by Ni atoms which *do* back-donate electrons to the CO, strengthening the M—C bond The high frequencies require explanation, however A shift to higher frequencies ("blue shift") is observed for CO held by metal cations, including Ni^{2+} (*4, 8*) This has been ascribed to changes in the CO bond resulting from electron withdrawal by the metal cation, which contribute to a CO bonding pattern closer to that of a pure triple bond, $\bar{C}\equiv\overset{+}{O}$ (*4*) The σ electrons in carbon occupy a MO that is slightly antibonding, and donation of these electrons should alone

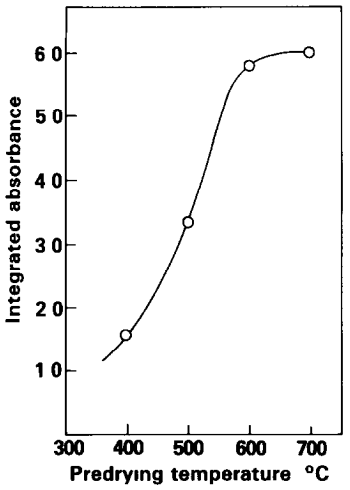

FIG 10 Dependence of $Ni^{\delta+}$ sites (intensity of CO band at 2110 cm^{-1}) on predrying temperature for 1% Ni (ex-$NiCl_2$)/Al_2O_3 (A)

somewhat increase C—O bond strength and frequency Increase in the frequency of adsorbed CO with increasing positive charge on the adsorbing metal atom has long been recognized On this basis, attachment of CO to a slightly electropositive Ni atom, symbolized by $Ni^{\delta+}$, might explain both higher frequency and strong binding The $\delta+$ charge (and possible local electrical field effects) could shift the frequency higher than expected for CO on Ni^0, but back-donation of electrons from the $Ni^{\delta+}$ atom could still lower the frequency (from 2143 cm^{-1}) and strengthen the M—C bond

The $Ni^{\delta+}$ designation represents slight partial and variable electron deficiency Such $Ni^{\delta+}$ atoms may exist wherever a reduced Ni atom adjoins a positive ion This could result from partial oxidation of reduced nickel crystallites, through interaction of Ni^0 with Ni^{2+} ions stabilized on the support surface (e g , replacing H in preexisting OH groups), or from interaction with Al^{3+} ions exposed on the alumina support

The $Ni^{\delta+}$ sites evidently increase in number as the predrying temperature is increased In Fig 10 relative integrated absorbances of the CO bands of Figs 3 and 4, primarily of the band near 2110 cm^{-1}, left after evacuation are plotted against predrying temperature The increase roughly parallels the expected appearance of Lewis acid–base sites on alumina dried above 400°C (*20*) A model for the γ-alumina surface (*21*), suggests that reduced Ni atoms might occupy some of the acidic defects created in an outermost oxide layer by drying Such Ni atoms would cover Al^{3+} ions otherwise exposed and thus acquire a slightly positive ($\delta+$) charge Reduced Ni atoms might subsequently aggregate around these atoms The $Ni^{\delta+}$ sites could also be formed by association of Ni^0 with exposed tetrahedral Ni^{2+} ions The relative number of Ni^{2+} atoms in tetrahedral, as against octahedral, sites reportedly increases on Ni/Al_2O_3 samples heated above 500°C (*14, 15*)

Different frequencies of CO bands in the region 2080–2120 cm^{-1}, depending on the salts used in preparation, evidently reflect the influence of different anion neighbors of the Ni sites holding CO Samples made with $Ni(NO_3)_2$ form NiO on heating, and this is partially stabilized in the surface Some may also react with CO to form carbonates of various types When $NiCl_2$ is used in preparation effects of residual Cl are seen Effects of chloride in increasing the frequency of CO on Pt/Al_2O_3 have previously been demonstrated (*24*) The character of $Ni^{\delta+}$ sites thus reflects a local environment which can be strongly influenced by the preparation and pretreatment of the sample

The 1% Ni/Al_2O_3 (A) prepared from $Ni(NO_3)_2$ showed another intriguing difference from the $NiCl_2$ preparation, namely the "bridged" CO band at 1970 cm^{-1} (Fig 5) Apparently a transition occurs from linear bonding, on an Ni surface filled with CO, to stronger bridged bonding to two Ni atoms when the surface is sparsely covered The absence of a similar band on 1% Ni/Al_2O_3 (A) prepared from $NiCl_2$ suggests that residual chloride is retained in such a way as to restrict such "bridged" adsorption of CO Possibly, however, different Ni

crystal faces are preferentially exposed on the two samples

Interpretation of the NO spectra presents additional problems, because NO reacts fairly easily with Ni^0 or $Ni^{\delta+}$ sites The spectra of NO on Ni/Al_2O_3 are distinguished from spectra of NO on Mo/Al_2O_3, Cr/Al_2O_3, and other catalysts in that they show only one major band, typically at 1870–1880 cm^{-1} Other smaller bands or shoulders are seen, but not a clear doublet suggesting a dinitrosyl or adsorbed NO dimer The NO may be held predominantly on Ni ions of one type, exposed in such a way that they do not readily bind more than one NO molecule The preference of Ni^{2+} ions for octahedral coordination (*23*), and the decrease in the CO/Ni^{2+} band near 2190 cm^{-1} (Figs 3 and 4) along with decrease in the 1870-cm^{-1} NO band (Fig 8) as reduction temperature is increased, suggests that the 1870-cm^{-1} band probably mainly represents NO mainly held on Ni^{2+} ions exposed in incomplete octahedral sites The concurrent increase in the intensity of the smaller NO band at 1900–1915 cm^{-1} seen in Fig 8 seems to correlate with the increase in intensity of the CO band at 2110–2120 cm^{-1} attributed to $CO/Ni^{\delta+}$ Disparity in the relative sizes of the CO and NO bands attributed to adsorption on the same types of sites should not be surprising When CO is weakly adsorbed the adsorption sites are very incompletely occupied at the low pressures used The NO is usually held much more strongly on ionic sites

On Ni/Filtrol 90 alumina, adsorbed NO (Fig 9), might be expected, like adsorbed CO (Fig 7), to reflect an influence of sulfide The ionic Ni sites that hold NO are apparently not greatly affected by sulfide after prereduction at 400°C, but after reduction at 500 or 600°C the major NO band shifts to lower frequencies (1850 cm^{-1} after 600°C reduction) No evidence is seen for the smaller NO band near 1915 cm^{-1} As shown by the CO spectra, $Ni^{\delta+}$ sites are eliminated by sulfiding That the salt used in preparing the $NiAl_2O_3$ makes little difference in the spectra of NO adsorbed on Filtrol 90 is easily understood if sulfide replaces Cl^- or O^{2-} ions near Ni Because bands similar to those seen in this study can, in some cases, be seen for CO or NO adsorbed on Ni held on SiO_2 They might simply reflect exposure of different crystal faces or of edge and corner atoms The evidence seems to be against this Through reaction with OH groups, for instance, Ni^{2+} ions can be stabilized on silica (4) where they probably inductively create $Ni^{\delta+}$ from any Ni^0 atoms they adjoin Such behavior probably explains the strongly adsorbed CO giving the bands at 2070–2080 cm^{-1} on Ni/SiO_2 observed by Primet *et al* (*10*) The nickel nitrate hexammine solutions used in sample preparation could have caused more incorporation of Ni^{2+} ions in the SiO_2 surface than would have occurred with use of aqueous nickel nitrate

CONCLUSIONS

The surface chemistry of nickel on alumina is complex, and much further work is needed before it can be fully understood and related to catalytic behavior Present infrared techniques provide evidence which should, when properly interpreted, yield a fairly detailed picture of Ni adsorption sites Exposed positively charged metal atoms ranging from those with fractional charge up to doubly charged ions can be strongly stabilized on alumina and other supports Sulfate impurities in alumina supports and changes in preparation or pretreatment variables can all markedly alter the nature of supported Ni

Correlation of surface chemistry with catalytic properties is the ultimate goal of this type of investigation Various factors can markedly affect the surface chemistry of supported metals, and measurements of activity and selectivity should be made on a catalyst sample which, at the least, has had pretreatment identical to that of the sample characterized by infrared or other techniques Infrared characterization under re-

action conditions may prove essential but such characterization is usually not simple

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