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A Study of Water and Ammonia Adsorption on Silica Supported Ni(II) Using Visible and Near Infrared Spectroscopy

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Near infrared and visible spectroscopy have been used to observe the overtone and combination vibrational spectra of adsorbed water and ammonia and the electronic spectra of silica-supported Ni(II). The local environment of Ni(II) has been found to depend upon the means of introduction of Ni(II) into the gel, sample heat treatment and the presence of adsorbed molecules. In general, Ni(II) occupies octahedral or distorted octahedral sites on the gel surface in which the coordinating ligands can be surface functional groups, adsorbed anions or adsorbed molecules. No evidence for tetrahedrally coordinated Ni(II) was found.

INTRODUCTION

The activity of supported metal catalysts can depend strongly on the method of production of the catalyst. In particular, catalyst properties may be very sensitive to the means by which the metal is introduced into the support material. This is probably because metal ions introduced into supports by different ion exchange or impregnation procedures are present in different environments. Investigation of this possibility is difficult because little is known about the sites for adsorption of ions by supports or the coordination of adsorbed ions on the support surface. The purpose of this paper is to provide information about the local environment of Ni(II) adsorbed on silica gel.

The approach used in this study has been to combine near infrared spectroscopy with visible spectroscopy. By recording the near infrared (2.5 to 0.8 μ) and visible spectra (0.8 to 0.3 μ) of transparent silica gel plates containing Ni(II), it is possible to observe the vibrational spectra of adsorbed molecules and the electronic spectra of adsorbed transition metal ions on the same sample. This permits determination of the effects of the SiO_2 surface, adsorbed gases, and anions on coordination of the Ni(II) ions.

For the experiments reported in this paper, Ni(II) was introduced into silica gel by ion exchange and by impregnation with Ni(II) salt solutions. In general, the behavior of impregnated ions is similar to their behavior in aqueous solutions. Major changes in the environment of the ions are caused by changing the anions and the concentration of adsorbed gases. Bonding to the silica surface is weak. On the other hand, Ni(II) introduced by ion exchange interacts strongly with the surface. Its environment is also modified by the presence of adsorbed gases.

EXPERIMENTAL METHOD

All samples were prepared using Davison Grade 03 silica gel. The manufacturer (*1*) reports that this gel has a surface area of 700-800 m^2/g and a pore volume of 0.48 cc/g. Large pieces of gel were selected by hand and shaped into parallelipipeds 1 × 3 × 10 mm by sanding. The surfaces were finished with 100-mesh abrasive paper.

Impregnation of the samples with metal salts was done as follows: After shaping, the sample was placed in a closed container at about 100% relative humidity overnight.

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This treatment prevented cracking of the sample when it was immersed in a salt solution for impregnation. The solution strengths were varied to have metal concentrations in the sample which gave spectra of intensity convenient for measurement. Concentrations between 0.1 and 5% by weight metal were used. After remaining in the impregnating solution overnight the samples were removed and dried on filter paper to remove excess solution from their surfaces. Samples were again stored at 100% humidity for a minimum of 3 hr before use to minimize cracking.

Ni(II) could easily be removed from these samples by washing in water for a few seconds.

Two ion exchange methods described by Burwell, *et al.* (*2*) were used. For both techniques, samples were shaped and stored at 100% relative humidity overnight. Samples used in the first method (NaOH method) were then immersed in NaOH solution at pH 9 for a minimum of 30 min. They were then washed with water a few minutes and transferred to a nickel salt solution for exchange. After 30 min of exchange, the samples were washed in distilled water for 30 min and stored at 100% relative humidity a minimum of 3 hr before use.

Ion exchange by the second method (ammonia method) was performed by immersing the samples in a solution of nickel salt in dilute NH_4OH. (A typical solution contained 5 g $Ni(NO_3)_2 \cdot 6H_2O$, 50 cc H_2O and 10 cc NH_4OH solution [approx 58% NH_4OH].) After about ½ hr in the solution, samples were removed and placed directly in the infrared cell. (Some samples were heated to 100° in the nickel solution in a sealed autoclave for 1 hr.)

Ni(II) could not be removed from ion exchanged samples by washing in water for up to ½ hr.

Some impregnated samples were calcined by heating in laboratory air in a tube furnace to 500°C for 1 hr. They were then cooled in air before transfer to the spectrophotometer cells.

Spectra were obtained with a Cary Model 14 spectrophotometer. The special cells which were used to control the atmosphere around the sample were described elsewhere (*3*). One cell was equipped with a small heater to permit heating of the sample to 300°C in the spectrometer.

The nitrogen gas used was boiled-off from liquid nitrogen of 99.99% purity. Ammonia gas was obtained from Matheson at 99.9% purity and used without further purification.

RESULTS AND DISCUSSION

Impregnated Samples, Water Adsorption

In Fig. 1 the visible portion of the spectrum of a sample freshly impregnated with $NiCl_2$ solution is compared with the spectrum of $[Ni(II)(H_2O)_6]^{2+}$ ion which is present in the impregnating solution. The aqueous ion has octahedral symmetry, and its absorption spectrum consists of three bands at 9,000, 14,000 and 25,000 cm⁻¹. These three bands have been assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively (*4*). The absorption spectrum of a tetrahedral complex, $[Ni(II)(Ph_3AsO)_2Br_2]$ is shown for comparison. The band at 15,000 cm⁻¹ is attributed to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition and the band at 7,500 is assigned to the $^3T_1(F) \rightarrow {}^3A_2$ transition. The spectrum of tetrahedral complexes is about 40 times more intense than the octahedral complexes. The similarity of the peak posi-

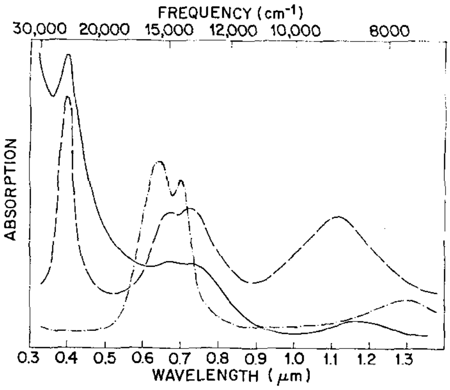

FIG. 1. Visible spectrum of the $NiCl_2$ impregnating solution, (———); a gel sample freshly impregnated with $NiCl_2$ (- - -); and a solution of $Ni(Ph_3AsO)_2Br_2$, (- · -) (see text).

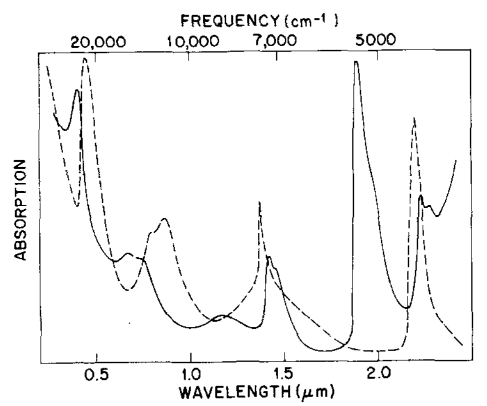

FIG. 2. Near infrared and visible spectra of silica gel impregnated with $NiCl_2$; wet (———), dry (- - -).

tions and intensities spectra of the solution and the impregnated gel suggests that Ni(II) is present in the gel as octahedral $[Ni(II)(H_2O)_6]^{2+}$.

The near infrared portion of Fig. 2 shows bands at about 4,400, 5,200 and 7,100 cm^{-1}. The band at 4,400 cm^{-1} has been assigned to a combination stretching plus out-of-plane deformation of surface Si–OH groups bound to adsorbed water molecules (*5*). The bands at 5,200 and 7,100 cm^{-1} are bending plus stretching combination and the first overtone of the OH stretching modes of adsorbed water molecules (*5*). The near infrared bands shown in Fig. 2 are identical with the bands seen in hydrated silica gel in the absence of Ni(II). Thus, there is no spectroscopic evidence of any interaction between Ni(II) and the gel surface in a freshly impregnated sample. $[Ni(H_2O)]_6^{2+}$ ions from the impregnating solution enter the gel pores unchanged.

As these samples are dehydrated by flushing with dry nitrogen gas, changes occur in the adsorbed water, the Si–OH, and the Ni(II) spectra. (See Fig. 2.) In the near infrared, the water combination and overtone bands decrease in intensity as do the intensities of the combination band for Si–OH groups bound to water molecules. New bands appear at about 7,300 and 4,550 cm^{-1}. These bands are the first overtone and combination band of Si–OH groups not bound to water molecules. These changes are the same as those normally observed during dehydration of silica gel (*5*).

The 5,200 cm^{-1} combination band for water molecules can be used to estimate the amount of water adsorbed (*3*). As water is removed all of the Ni(II) lines shift continuously to lower frequency. When the water content drops below about a monolayer (8 μmole/m^2), the Ni(II) lines have shifted to a position similar to those of solid $NiCl_2 \cdot 6H_2O$ and its solution in HCl. In both solid $NiCl_2 \cdot 6H_2O$ and HCl solutions of NiCl, Ni(II) is present as *trans*-$[Ni(II)\,Cl_2(H_2O)_4]$. This suggests that as part of the water is removed from the SiO_2 surface, water is also removed from the nickel complexes in the gel and that two H_2O molecules in the Ni(II) coordination spheres are replaced by Cl^- ions. Figure 3 shows that in these samples the 5,200 cm^{-1} water combination band is much broader on Ni(II) containing gels than on pure silica gel. Thus, most of the water molecules remaining are interacting with Ni(II); probably as coordinating ligands.

During further dehydration the Ni(II) spectral lines continue to shift to lower frequencies and no new lines appear. Thus,

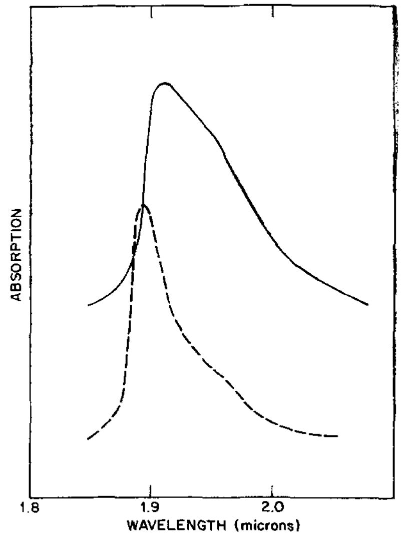

FIG. 3. The 1.9 μ combination band of water adsorbed on silica gel (- - -) and $NiCl_2$ impregnated silica gel (———).

the nickel appears to remain octahedrally coordinated on the dried gel. This conclusion is supported by measurements of the magnetic susceptibility of dry gel containing 5% Ni by weight.* The susceptibility was found to be 4.0×10^{-6} emu/gram. Using the Langevin formula (*6*), the magnetic moment of Ni(II) is calculated to be 3.4 μ_B. This is the range expected for octahedral Ni(II) (2.8–3.4 μ_B) and below the range for tetrahedral Ni(II) (*7*) (3.5–4.2 μ_B).

Similar experiments were carried out with gels impregnated with $Ni(NO_3)_2$ solutions. The results were generally the same except that little shifting of the Ni(II) adsorption spectrum took place during drying of the gel. This is to be expected if Cl^- and NO_3^- replace water in the coordination sphere of Ni(II) on partially dehydrated samples because NO_3^- is closer to H_2O in the spectrochemical series than Cl^-.

Readsorption of water causes the spectrum to return to the $[Ni(II)(H_2O)_6]^{2+}$ spectrum for both $NiCl_2$ and $Ni(NO_3)_2$ impregnated gels.

These experiments show that Ni(II) introduced by impregnation is always octahedrally coordinated. When sufficient adsorbed water is present, the coordination sphere of Ni(II) consists of water molecules. At lower adsorbed gas concentrations some of the water molecules may be replaced by Cl^- or NO_3^-. This behavior is similar to the behavior of Ni(II) in solutions where the identity of the coordinating ligands depends upon their concentration in the solution.

When sufficient adsorbed water, Cl^-, or NO_3^- ions are available to complete the octahedral coordination of Ni(II), no interaction between the Ni(II) and the surface takes place. However, at low concentrations of adsorbed water on $NiCl_2$ impregnated gels, too few ligands are present to complete octahedral coordination of Ni(II) ions. The spectral and magnetic data show that the coordination of Ni(II) is still octahedral. Therefore, either 1) clustering of Ni(II) and Cl^- occurs and anhydrous $NiCl_2$ crystallites form in the pores or 2) surface ligands participate in the coordination. One way the latter may occur has been proposed by J. B. Peri (*8*) and is shown in Fig. 4. In this picture, Ni(II) sits above the center of a triangle of surface Si–OH groups. Two Cl^- ions fill two of the three remaining positions in the octrahedron; the third remains open. This open site can be occupied by H_2O when small amounts of water are adsorbed. Unfortunately, it is not possible to distinguish from the spectra between this picture and formation of anhydrous nickel chloride crystals in the gel pores.

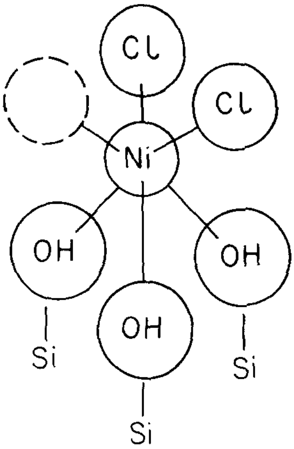

FIG. 4. A possible environment for Ni(II) in $NiCl_2$ impregnated silica gel after drying.

Ammonia Adsorption

When a dried sample of gel not containing Ni(II) is exposed to ammonia, adsorption occurs very rapidly by hydrogen bonding to surface Si–OH groups. After adsorption, near infrared absorption bands occur at 6,580, 5,020, and 4,520 cm^{-1} (see Fig. 5). These bands may be assigned as follows: The 4,520 band is a combination of the symmetric N–H deformation mode of ammonia (*9*) at 1,050 cm^{-1} with the asymmetric NH stretching mode at 3,400 cm^{-1}. This band overlaps the Si–OH combination band at 4,500 cm^{-1}. The 5,020 cm^{-1} band is a combination of the asymmetric N–H deformation mode of ammonia at 1,620 cm^{-1} with the N–H stretching mode

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* This measurement was performed by S. Akhtar of Stanford University using a standard Faraday balance.

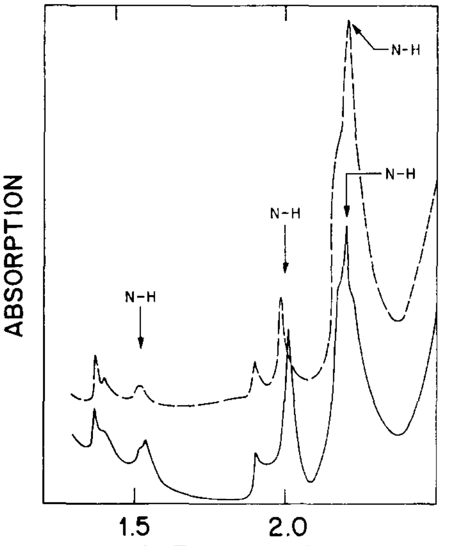

FIG. 5. Spectra after NH_3 adsorption: (---) silica gel, (———) silica gel impregnated with $NiCl_2$.

at 3,400 cm^{-1}. The 6,580 cm^{-1} band is the first overtone of the N–H stretching bands.

On the samples with impregnated Ni(II) ions, two additional bands are seen at 6,530 and 4,980 cm^{-1} after ammonia adsorption. Because these bands are associated with the presence of Ni(II) (Fig. 5) and because their intensity correlates with the changes in the frequency of the electronic spectrum of Ni(II), these bands may be assigned to NH_3 bonded to Ni(II). This assignment is supported by the observation of similar bands in the fundamental region for ammonia adsorbed on boron and phosphorus impurities in porous glass (*9*) and by the appearance of N–H vibrational bands shifted to lower energy in ammonia salts of transition metal ions (*10*). The appearance of a sharp, resolved band (4,980 cm^{-1}) assigned to NH_3 bound to Ni(II) makes it possible to monitor the behavior of Ni(II) as a function of the amount of NH_3 adsorbed on Ni(II) ions.

When the 4,980 cm^{-1} band of ammonia bound to Ni(II) is present, changes occur in the Ni(II) electronic spectrum. This is to be expected since the electrochemical series predicts that replacement of NO_3^-, H_2O, or Cl^- by NH_3 in the first coordination sphere will increase the intensity of the crystal field and therefore cause shifts of the Ni(II) spectral lines to higher frequencies. (See Fig. 6.) Furthermore, these shifts proceed smoothly as NH_3 adsorption increases and no new lines appear in the spectrum. This suggests that the environment of Ni(II) remains octahedral. The visible spectrum of samples with high ammonia coverage is the same as that of aqueous solutions containing $[Ni(NH_3)_6]$ indicating that complete octahedral coordination of Ni(II) by NH_3 has taken place.

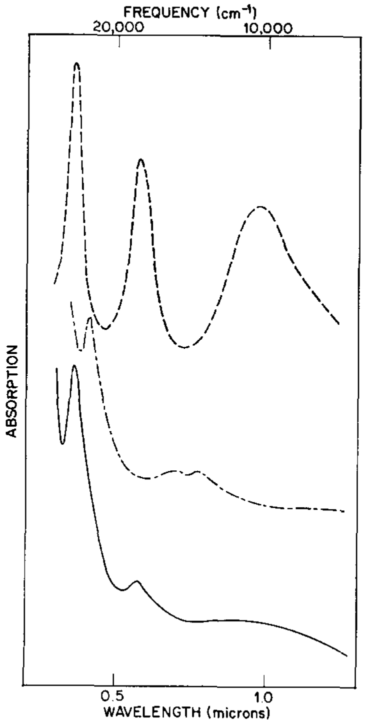

FIG. 6. Spectra of $[Ni(NH_3)_6]^{2+}$ (---), $NiCl_2$ impregnated silica (wet) (-·-·), and dried $NiCl_2$ impregnated silica after NH_3 adsorption (———).

Ammonia on both the Ni(II) sites and the Si–OH sites can be desorbed by heating to 125°C or by flushing the cell with N_2. However, the ammonia adsorbed in the Si–OH sites desorbs more rapidly. Almost total desorption from both sites can be accomplished by heating at 125° for 24 hr or by flushing with N_2 for several days. As ammonia is desorbed, the Ni absorption bands shift continuously to lower frequency. The Ni(II) spectrum of samples after ammonia desorption is the same as before adsorption.

Thus, adsorbed ammonia and water behave in a similar manner. When present they enter the octahedral coordinating positions of nickel or hydrogen bond to surface Si–OH groups. As they are removed, anions and surface groups replace them in the nickel coordination sphere.

Impregnated Samples—Calcined

Heating $NiCl_2$ impregnated samples to temperatures up to 500°C in air (calcined) produces changes in the Ni(II) spectrum and causes HCl to be evolved. After calcination, the Ni(II) spectral band in the 15,000 to 20,000 cm^{-1} region of the spectrum (solid curve in Fig. 7) splits into bands. Shifting and splitting indicates that the octahedral environment has been modified.

The changes in the Ni(II) spectrum after calcination are not great, however. The small shifts observed and the evolution of the HCl suggest that Cl^- has been replaced by some other ligand or ligands higher in the spectrochemical series than Cl^-. In addition, the tighter binding of Ni(II) to the surface, indicated by the difficulty of removing the nickel by washing, suggests that Ni(II) is adsorbed on different type of surface sites after calcination than on freshly impregnated gels. One possible structure, which incorporates these changes, can be formed from Fig. 4 if Cl^- are replaced by OH and the Si–OH surface groups have been replaced by surface Si–O^- groups. Formation of Ni(II) ion in a site of this type can be accomplished by reaction of the chloride ions with water being formed by dehydroxylation of the silica surface. Dehydroxylation also transforms some or all of the Si–OH groups of Fig. 4 into Si–O^- groups. Stronger interaction of Ni(II) with Si–O^- than with Si–OH would account for the difficulty in removing Ni(II) from the surface by washing.

Adsorption of NH_3 on a calcined gel produces shifts of the Ni(II) bands to higher frequency, (dashed curve in Fig. 7) and the 4,980 cm^{-1} band of adsorbed ammonia appears. This indicates that Ni(II) is accessible for ammonia adsorption. However, the shifts in the Ni(II) band positions caused by NH_3 are smaller than on freshly impregnation samples indicating only partial coordination of Ni(II) by ammonia.

Ion Exchanged Samples—NaOH Method

The spectrum before drying of Ni(II) introduced by the NaOH ion exchange method is similar to the spectrum of freshly impregnated (wet) samples indicating the presence of $[Ni(H_2O)_6]^{2+}$ (Fig. 8). This is in agreement with the model proposed by Burwell, *et al.* (*2*) for ion exchange by base treated silica gel. They suggest that NaOH treatment produces

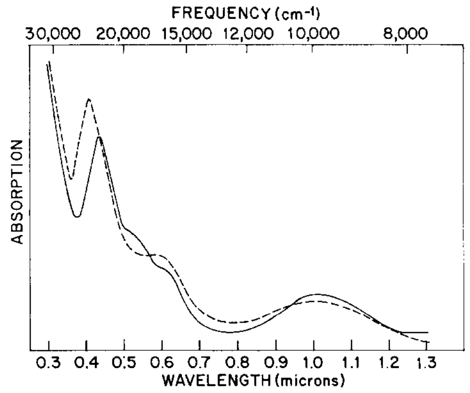

FIG. 7. Spectrum of $NiCl_2$ impregnated silica gel after calcination at 500°C for 1 hr in air (———); and of a calcined sample after NH_3 adsorption (- - -).

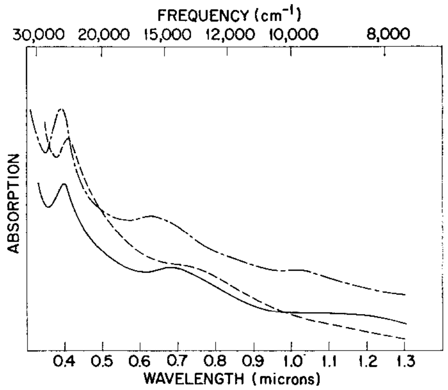

FIG. 8. Spectra of Ni(II) ion exchanged on silica gel by the NaOH method; (———) wet, as exchanged; (- - -) dried; (- · - -) dried with adsorbed NH_3.

negative sites (such as Si–O$^-$) on the surface by reaction of Si–OH groups with hydroxyl ions to split off water. Sodium ions from the solution adsorb on these sites and can exchange with [Ni(II) $(H_2O)_6]^{2+}$ ions from solution. They suggest further that the surface Si–O$^-$ groups can enter the coordination sphere of the nickel by displacing some of the water molecules. The spectrum of these surface complexes should be similar to the hexaquo-complex since replacement of water by Si–O$^-$ should not effect the crystal field greatly.

After drying in flowing N_2 or heating to 125° overnight, there are only slight shifts in peak positions to longer wavelengths indicating some weakening in the strength of the crystal field. This could be due to decomposition of the water molecules into hydroxide ions attached to the nickel and protons which migrate over the surface to other sites. Proton surface migration is known to take place on silica surfaces (*11*).

Both NH_3 and H_2O can adsorb on the Ni(II). This is indicated by shifts in the Ni(II) spectrum and the appearance of the broadened 5,200 cm^{-1} band for water and the 4,980 cm^{-1} band for ammonia. The spectral shift in the Ni(II) bands immediately after H_2O or NH_3 adsorption are smaller than the corresponding shifts in freshly impregnated gels. (Compare Figs. 2, 6 and 8.) As with the calcined samples, this indicates only partial coordination of the Ni(II) ions by H_2O or NH_3. However, after several days in ammonia at atmospheric pressure, the shifts increase slowly to a value characteristic of $[Ni(NH_3)_6]^{2+}$.

Removal of NH_3 and H_2O from the ion exchanged gels prepared by NaOH method is similar to that on impregnated gels. Heating to 125°C or flushing with dry N_2 for several days will reduce the water content below one water molecule per nickel ion.

Changes in the overtone region of the Si–OH spectrum indicate that the surface of silica gel can be modified by NaOH treatment. In fresh samples (Fig. 9) only one sharp SiOH overtone band is seen at 7,300 cm^{-1} with a tail to longer wavelengths. After the sample is soaked in NaOH at pH 9 for times of the order of 16 hr there are two Si–OH space bands at 7,300 and 7,220 cm^{-1} (see Fig. 9). The 7,220 cm^{-1} band is attributed to OH group in the interior of SiO_2 particles (*12*). This spectral change indicates that considerable rearrangement of the surface can take place in NaOH solution. Thus, although there is no spectroscopic evidence for it in ion exchanged samples, surface rearrangement during exchange could play a role in determining the environment of Ni(II).

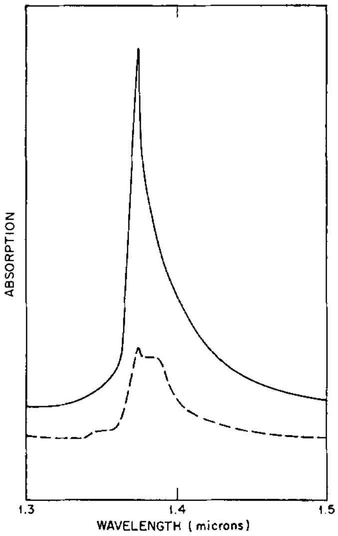

FIG. 9. Changes in the 1.37 μ OH stretching overtone produced by NaOH treatment; (———) fresh sample, (- - -) sample soaked in NaOH (pH9) overnight.

NH_4OH *Method*

When Ni(II) is introduced by the NH_4OH ion exchange method, Ni is present initially as $[Ni(NH_3)_6]^{2+}$ as indicated by the fact that the color of freshly exchanged gels (deep blue) is the same as the exchange solution. Slight drying which takes place before spectra can be taken causes the color to change to blue-green with a spectrum shown in Fig. 10. At this stage, Ni(II) is probably bound to the surface as a complex analogous to those present in samples exchanged by the NaOH method. That is, some of the ammonia molecules are replaced by surface Si–O$^-$ groups pro-

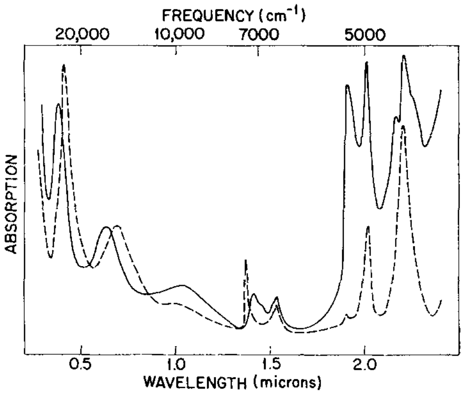

FIG. 10. Spectra of silica gel ion exchanged with Ni(II) by the NH_4OH method; (———) freshly exchanged (wet); (- - -) dried.

duced in the basic solution. The adsorbed species is probably

$$[Ni(II)(NH_3^+)_{6-x}(SiO^-)_x]$$

The appearance of the Ni(II) bands in Fig. 10 for the exchanged sample is similar to the appearance of the bands on ion-exchanged gels (NaOH method) or calcined samples when NH_3 has been adsorbed. (Compare Figs. 7, 8 and 10.) The frequencies of the bands are not as high as for $[Ni(NH_3)_6]^{2+}$ indicating that the octahedral coordination of NH_3 or NH_4^+ is not complete.

Drying of the gel in flowing nitrogen at room temperature produces little change in the Ni(II) bands (see Fig. 10). However, shifts are observed which are not uniform. The bands at 22,000 and 14,000 cm^{-1} shift to lower frequencies while the 10,000 cm^{-1} band shifts to a higher frequency. This indicates that the environment of Ni(II) has become somewhat distorted.

In freshly exchanged gels, bands are seen in the near infrared at 5,200 cm^{-1} for water, at 5,020 and 4,980 cm^{-1} for ammonia and at 4,500 cm^{-1} for Si–OH groups. A new band at about 4,700 cm^{-1} also appears as a shoulder of the 4,500 cm^{-1} Si–OH combination band. (See Fig. 10.) This band can be assigned as a combination of the 1,400 cm^{-1} deformation band and 3,300 cm^{-1} stretching band for NH_4^+ (*8*). During drying this band disappears. The NH_3 bands remaining are similar to those on dry impregnated gels.

Complete removal of NH_3 is difficult. Some ammonia remains even after 1 hr at 400°C. One hour of treatment at 500° removes the remaining NH_3. After this treatment, the spectrum of Ni(II) is identical with the spectrum of Ni(II) on impregnated gels after calcination. NH_3 readsorbs on these gels giving NH_3 and Ni(II) spectra which are identical with the spectra of calcined gels with adsorbed NH_3.

CONCLUSIONS

This investigation has demonstrated that information about the local environment of silica-supported transition metal ions can be obtained from near-infrared and visible spectroscopy.

In particular, it was found that silica-supported Ni(II) is always present in octahedral or distorted octahedral coordination. No evidence for tetrahedral or triangular coordinated nickel as suggested by Peri (*8*) was found. This is not surprising because the site preference energy of Ni(II) favors octahedral or square planar complexes (*13*).

In all samples, nickel ions were accessible to water or ammonia. In dry impregnated samples, nickel was easily solvated by adsorbed water or ammonia to produce octahedral complexes in the gel pores similar to those in solution. Nickel ions in calcined and ion exchanged samples were only partially solvated by adsorbed H_2O and NH_3. This indicates that the complex of the Ni(II) with the surface formed in those materials is more stable than in impregnated samples. It was suggested that stronger interaction of nickel with the surface occurs with $Si–O^-$ sites on calcined and exchanged samples than with Si–OH groups on impregnated samples.

REFERENCES

1. Davison Chemical Division, W. R. Grace and Co.

2. BURWELL, R. L., JR., PEARSON, R. G., HALLER, G. L., TJOK, P. B., AND CHOCK, S. P., *Inorg. Chem.* 4, 1123 (1965).

3. ANDERSON, J. H., JR., Ph.D. dissertation, Stanford University, Stanford, Ca, 1965.

4. COTTON, F. A., AND WILKINSON, G. A., "Advanced Inorganic Chemistry," p. 577. Interscience, New York, 1962.

5. ANDERSON, J. H., JR., AND WICKERSHEIM, K. A., *Surf. Sci.* **2**, 252 (1964).

6. VANVLECK, J. H., "The Theory of Electric and Magnetic Susceptibilities," pp. 27–41. Oxford Press, London, 1932.

7. Ref. (*4*) p. 738.

8. PERI, J. B., *Discuss. Faraday Soc.* **41**, 121 (1966).

9. LITTLE, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.

10. SVANTOS, G. F., CURRAN, D., AND QUAGLICINO, J. V., *J. Amer. Chem. Soc.* **77**, 6159 (1965).

11. ANDERSON, J. H., AND PARKS, G. A., *J. Phys. Chem.* **72**, 3662 (1968).

12. Ref. (*9*) pp. 278–280.

13. ORGEL, L. E., "An Introduction to Transition Metal Chemistry: Ligand Field Theory," p. 77, Wiley, New York, 1960.