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The Local Environment of Co(II), Cu(II), and Cr(III) Supported on Silica Gel

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INTRODUCTION

During the past 10 yr there have been several spectroscopic studies of transition metal ions supported on solid surfaces. The goal of these studies has been to determine the sites which these ions occupy on the surface. Information has been sought about the influence of adsorbed molecules and ions, methods of introduction of the ions, and heat treatment on the identity and symmetry of the surface complexes formed. A wide range of behavior has been observed. These observations can be divided into two broad classes: Those in which the pores or cages of the solid support act like minibeakers for normal homogeneous complex chemistry, and those in which surface ions interact with the supported ions, participating in the complexes formed. The first class contains primarily systems where the ions are introduced into the support by impregnation and no ion exchange takes place [e.g., Ni(II)/SiO_2 (*1*) or Cu(II) on Y Zeolite (*2*) when water is present in the pores]. The second includes ions exchanged into the support and samples thermally treated after introduction of the ions by impregnation or ion exchange [e.g., Zeolites ion exchanged with Ni(II) (*3*) and Cu(II) (*2*) after drying].

In this study, the effects of calcination and adsorption of water or ammonia were observed for Co(II), Cu(II) and Cr(III) introduced into silica gel by impregnation and ion exchange. The results of the present work are compared with the work of others. Some general characteristics of the behavior of supported ions are discussed.

EXPERIMENTAL PROCEDURES

The experimental approach was to combine near infrared spectroscopy with visible spectroscopy to observe changes in the environment of the ions. By recording both near infrared (2.5–0.8 μm) and visible spectra (0.8–0.5 μm) it is possible to observe the vibrational spectra of adsorbed molecules and the electronic spectra of the ions.

Both diffuse reflectance and transmission spectra were obtained with a Cary Model 14 spectrophotometer. The special cells for transmission spectra which were used to control the atmosphere around the sample are described elsewhere (*1*). One cell was equipped with a small heater to permit heating of the sample to 300°C in the spectrometer.

Diffuse reflectance spectra were obtained with attachments for the spectrometer available from the manufacturer. A special sample holder was constructed which permitted purging of the sample with dry nitrogen gas and introduction of ammonia or water for adsorption studies. Molecular water content of the samples was estimated from the intensity of the 1.9 μm (5300 cm^{-1}) band in the near infrared (*4*). Samples described below as "dry" or "dehydrated" did not exhibit this band and hence did not contain significant amounts of molecular water.

Sample preparation has been described in detail elsewhere (*1*). All samples were supported on Davison Grade 03 silica gel. Transmission samples were in the form of parallelipipeds 1 × 3 × 10 mm. Diffuse reflectance samples were ground to pass a 60 mesh screen. Calcined samples were heated to 500°C in laboratory air before transferring them to the spectrophotometer.

Dry nitrogen gas was obtained from boiloff of liquid nitrogen. All other gases and salts used were of reagent grade.

RESULTS

Cobalt

In Fig. 1, the visible portion of the spectrum of a sample freshly impregnated with $CoCl_2$ is shown (solid line). This spectrum is identical with the impregnating solution. Both spectra are characteristic of $[Co(H_2O)_6]$ (*5*).

Dehydration of impregnated samples by flushing with dry nitrogen produces major changes in the spectrum. The intensity is greatly increased and the band broadens and shifts to lower wavelengths. The band shape after drying resembles the spectrum of tetrahedral Co(II) complexes in solution (*5*) (see Fig. 1). It also resembles the spectrum of Co(II) supported on A zeolite reported by Klier (*6*). However, because the fine structure in the band resembles chloride complexes of Co(II) more closely and because the 6-ring oxygen structure of zeolites which form a part of Klier's complex are not present in silica gel, it is likely that a chloride-containing tetrahedral complex has been formed.

After rehydration, the spectrum reverts to that of the hexaquo complex.

$Co(NO_3)_2$ impregnated samples behave differently. Immediately after impregnation the spectrum is the same as that of $[Co(H_2O)_6]$. However, dehydration produces only a slight increase in band intensity and a small shift toward lower frequency. The band shape remains generally the same suggesting an octahedral complex (see Fig. 1).

The difference in spectra of chloride and nitrate impregnated samples after dehydration suggests that the anions participate in the complex present when water is removed. Similar conclusions were drawn from Ni(II) impregnated silica (*1*).

Ammonia adsorption on impregnated samples which are either wet or dry produces the spectrum shown in Fig. 2. This spectrum strongly resembles other Co(II) tetrahedral complexes in solids, (*7*) particularly Co(II) impurities in quartz (*8*). It is also similar to those attributed to tetrahedral Co(II) on the surface of γ-Al_2O_3 (*9*).

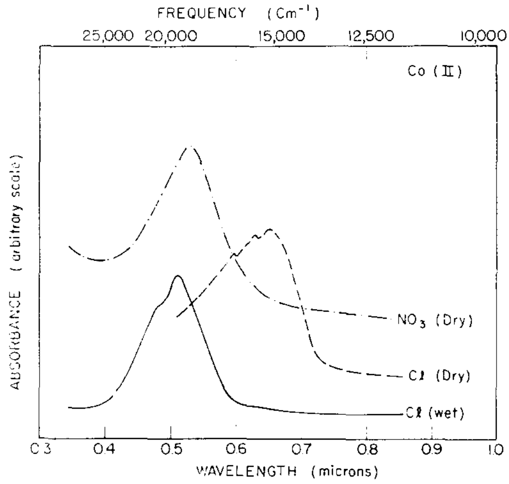

FIG. 1. Spectra of silica gel impregnated with Co(II) salts: (——) $CoCl_2$ impregnated, wet; (- - -) $CoCl_2$ impregnated, dried overnight in flowing N_2; (–·–) $Co(NO_3)_2$ impregnated, dried overnight in flowing N_2.

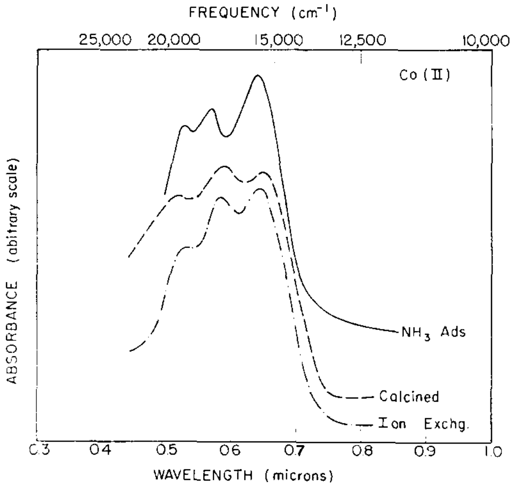

FIG. 2. Spectra of silica gel containing Co(II) ions: (——) $CoCl_2$ impregnated sample after ammonia adsorption; (- - -) $CoCl_2$ impregnated sample after calcining in air at 500°C for 1 hr; (–·–) Co(II) ion exchanged.

At the same time, a band is observed in the near infrared at 4980 cm^{-1}. A similar band found in Ni/SiO_2 (*1*) has been assigned to adsorbed ammonia participating in the coordination sphere of Ni(II). The simultaneous appearance of this band and changes in the visible spectrum of Co(II) upon ammonia adsorption show that Co(II) is accessible for ammonia adsorption and strongly suggests that ammonia enters the coordination sphere of Co(II). Thus the visible spectrum observed after ammonia adsorption is assigned to an ammonia-containing tetrahedral complex.

Ammonia is easily removed from impregnated samples by heating to 125°C or by flushing with dry nitrogen overnight. The spectrum then returns to the one appropriate for the dry impregnated sample. Rehydration then regenerates $[Co(H_2O)_6]$.

Calcining either $Co(NO_3)_2$ or $CoCl_2$ impregnated samples results in a spectrum (Fig. 2) like Co(II) impurities in quartz (*8*) or tetrahedral Co(II) on γ-Al_2O_3 (*9*). This spectrum, although somewhat broader than observed after ammonia adsorption on impregnated samples, is assigned to a tetrahedral complex. Ammonia adsorption produces slight shifts in the visible spectrum toward higher frequencies and the 4980 cm^{-1} band for ammonia bound to surface cobalt appears. Hence, the complex formed must be on the surface and accessible for ammonia adsorption.

Ion exchange of cobalt onto silica by the NaOH method described elsewhere (*1*) leads to a species which has a spectrum nearly identical with calcined samples and is also assigned to a tetrahedral species (Fig. 2).

Adsorption of H_2O and NH_3 produces slight shifts in the visible spectrum indicating that ion exchanged Co(II) is accessible for adsorption. This is confirmed by the appearance of the 4980 cm^{-1} band for NH_3 adsorbed on an ionic site. The small magnitude of the shifts in the visible spectrum suggest that NH_3 does not replace all of the ligands in the coordination sphere of Co(II). NH_3 can be removed by heating to 125°C or flushing with dry nitrogen as with impregnated samples.

Copper

Silica freshly impregnated with $CuCl_2$ exhibits a single broad band at about 0.72 μm (see Fig. 3). Unlike the spectra of freshly impregnated Ni (*1*) and Co samples or Cu(II) in Y zeolite (*2*), the spectrum is not identical to the spectrum of the impregnating solution which exhibits a band due to $[Cu(H_2O)_6]$ at 0.8 μm. The higher frequency of the band in the catalyst could result from disruption of the octahedral symmetry of the ions in solution by the surface.

Upon drying, the spectrum shifts to about 0.85 μm (Fig. 3). The observed shift is not large enough to indicate the formation of a tetrahedral complex (*10*, *11*). Therefore, it is probably the result of replacement of water by chloride ions in the coordination sphere of Cu and/or formation of a square planar complex.

Samples freshly impregnated with $Cu(NO_3)_2$ exhibit the same spectrum as samples freshly impregnated with $CuCl_2$. Upon drying, however, almost no spectral shift occurs. This could result either from entry of NO_3 into the coordination sphere of Cu(II) or from clustering of the copper ions. The former suggestion is consistent

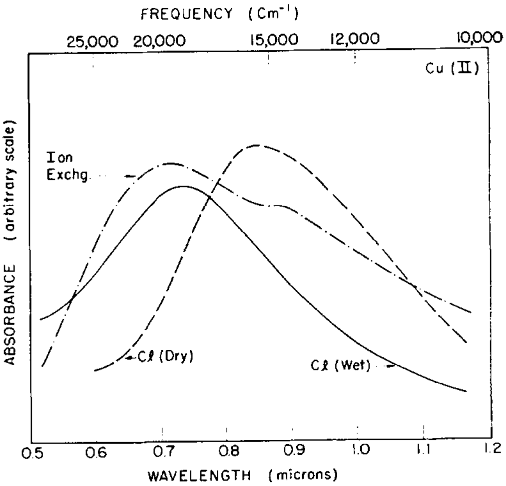

FIG. 3. Spectra of silica gel containing Cu(II): (——) impregnated with $CuCl_2$, wet; (- - -) impregnated with $CuCl_2$, dried in flowing N_2 overnight; (-·-) Cu(II) ion exchanged.

with the suggestion made above for cobalt ions and elsewhere (*1*) for nickel ions.

When ammonia is adsorbed on samples impregnated with either chloride or nitrate solutions, the band at 4980 cm^{-1} for ammonia adsorbed in the coordination sphere of an ion is observed. At the same time the 0.7 μm band of Cu(II) shifts to shorter wavelengths. The magnitude of the shift depends upon the ammonia concentration. As ammonia is added, the band shifts progressively to shorter wavelengths until it reaches about 0.62 μm. Then, further addition of ammonia causes the band to shift back toward longer wavelengths. This behavior is also observed in aqueous solution as ammonia replaces water in $[Cu(H_2O)_6]^{2+}$ (*5*). When $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is reached, the shortest wavelength (0.57 μm) for the absorption band is observed. Formation of $[Cu(NH_3)_5H_2O]^{2+}$ causes distortion of the octahedral complex toward square planar and produces a smaller band shift than the octahedral complex. Thus, the behavior of Cu(II) species on impregnated samples is similar to aqueous systems.

Ammonia may be removed by flushing with dry nitrogen or heating to 125°C. This is similar to the observations for Co(II) and Ni(II) (*1*).

Samples ion exchanged with Cu(II) using the NaOH method (*1*) exhibit a band at about 0.7 μm. The band has a double maximum (Fig. 3) indicating a species different from the impregnated samples.

Small spectral shifts occur with water and ammonia adsorption indicating that only some of the ligands in the coordinating sphere are replaced by adsorbed gases. Appearance of the 4980 cm^{-1} band for ammonia confirms that ammonia does indeed adsorb on Cu(II) sites.

It is difficult to deduce the structure of these complexes in detail from the spectra alone. However, the appearance of only a broad band in the 0.7 μm region indicates octahedral or distorted octahedral complexes (*13*). Only if this band is not a *d–d* adsorption but a charge transfer band is it possible that tetrahedral species as reported by Kazanskii (*12*) are present. Since tetrahedral Cu(II) complexes are rare and charge transfer bands do not appear at shorter wavelengths as in some tetrahedral complexes studies (*13*), it seems most likely that tetrahedral species are not present.

Chromium

$CrCl_3$ impregnated silica exhibits the same spectrum as the impregnating solution. Samples impregnated with freshly prepared $CrCl_3$ solution are green and have absorption bands at 0.44 and 0.62 μm. These bands are attributed to octahedral $[CrCl_2(H_2O)_4]^+$ ions (*5*). Upon standing for several weeks both the gel samples and the solution exhibit bands at 0.41 and 0.58 μm (Fig. 4). These changes are due to replacement of chloride ions by water to form octahedral $[Cr(H_2O)_6]^{3+}$. Hence, as for silica impregnated with other ions, the freshly impregnated sample has the same behavior as the impregnating solution.

On drying, the bands of either $[Cr(H_2O)_6]^{3+}$ or $[CrCl_2(H_2O)_4]^+$ shift continuously to 0.45 and 0.63 μm indicating a weakened crystal field retaining octahedral symmetry. Readsorption of water regenerates the spectrum of $[CrCl_2(H_2O)_4]^+$.

Adsorption of ammonia causes shifts of the bands to 0.40 and 0.56 μm (Fig. 5).

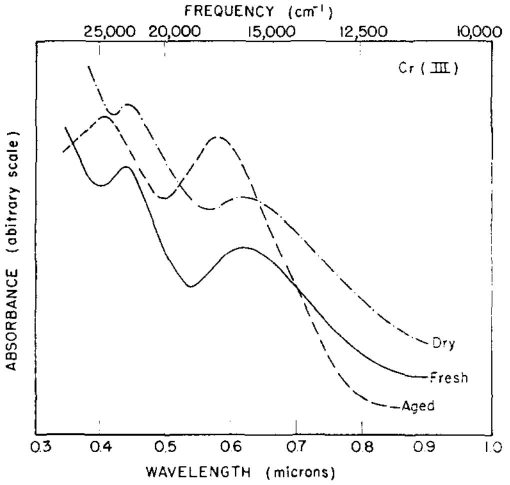

FIG. 4. Spectra of silica gel impregnated with $CrCl_3$: (——) freshly impregnated; (- - -) aged several weeks at room temperature in air; (–·–) dried overnight in flowing N_2.

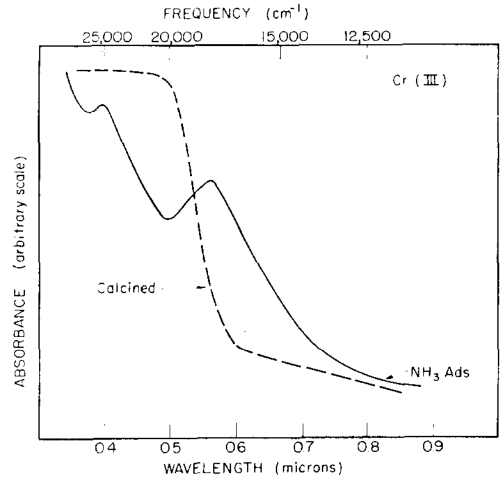

FIG. 5. Spectra of silica containing Cr ions: (——) impregnated with $CrCl_2$ after ammonia adsorption; (- - -) calcined in air at 500°C for 1 hr.

These shifts are not as great as expected for $[Cr(NH_3)_6]^{3+}$ formation, hence only part of the coordinating ligands on the dry sample are replaced by NH_3. The 4980 cm^{-1} band for ammonia on ionic sites also appears indicating again that the ions are accessible for adsorption of ammonia. Flushing with dry nitrogen overnight at room temperature removes the ammonia.

Calcination of Cr(III) impregnated samples at 500°C in air produces a brillant yellow or orange sample. Spectra show that this color is the result of a strong absorption band which extends through the blue region of the spectrum (Fig. 5). This color is characteristic of Cr(VI) compounds (*5*), and a similar spectrum is found for both silica and alumina impregnated with chromic acid (*13*). Therefore, it is likely that Cr(III) is oxidized to Cr(VI) during calcination. Adsorbed ammonia exhibits the 4980 cm^{-1} band indicating that the Cr(VI) ions are on the surface and can act as adsorption sites for ammonia.

It is difficult to exchange much Cr(III) onto silica, hence, the spectra are weak. However, they show bands at 0.42 and 0.61 μm indicating the presence of octahedral Cr(III). Only a slight shift in the spectrum was noted when ammonia was adsorbed on the ionic sites as indicated by the presence of the 4980 cm^{-1} ammonia band.

Kazanskii (*14*) has observed Cr(III) spectra similar to those for impregnated samples in this study. His materials, however were made by reducing both alumina and silica impregnated with chromic acid. This suggests that chromium ions can be both oxidized and reduced while remaining on the support surface.

DISCUSSION AND CONCLUSIONS

As indicated above, the behavior of transition metal ions supported on silica surfaces can be divided into two classes: those in which the surface participates in the complexes formed and those in which there is no support–ion interaction. The latter case applies in freshly impregnated samples where sufficient adsorbed water is present to form aquo-complexes with the transition metal ions. Thus, freshly impregnated samples usually display the same spectrum as the impregnating solution as if the pores of the gel acted like mini-beakers to hold the solution.

As impregnated samples are dried, complete aqueous coordination of isolated ions becomes impossible. The observed coordination of partly dry and completely dry samples (as determined from the intensity of the 5300 cm^{-1} band for molecular water) can result either from clustering of the ions or from entry of anions and/or surface groups into the coordination sphere. It is not possible to distinguish between these possibilities from the spectra alone. However, the differences between the spectra of dehydrated chloride and nitrate impregnated samples suggests that anions enter the coordination sphere. Furthermore, studies of other supported ion systems (*2, 3, 6, 10, 12, 14*) suggest that the ions remain isolated. If this is so in the present case as well, then one may picture the ions as sitting above the center of the exposed face of an SiO_4 tetrahedron. Since the gel used in this work is fully hydroxylated, this means that the surface is probably contributing three OH groups to the coordination sphere of the ion. The remaining site above the tetrahedron for tetrahedral

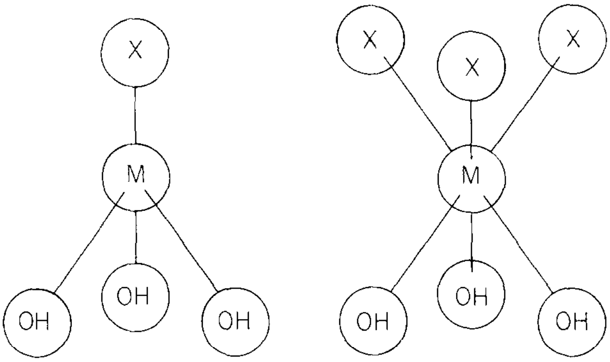

FIG. 6. Schematic picture of the environment of transition metal ions in impregnated samples. OH groups are surface SiOH groups. X represents sites which can be occupied by anions or adsorbed molecules.

coordination or the remaining three sites for octahedral coordination can be occupied by anions. Perhaps one site may remain vacant (see Fig. 6).

Readsorption of water removes the ions from the surface and regenerates the original aqueous complexes of the impregnating solution.

The behavior of calcined or ion exchanged samples is different. As in dried impregnated samples, the observed coordination number in dry samples requires that surface groups belong to the coordination sphere. Unlike impregnated samples, however, the surface groups are not displaced by adsorbed water or ammonia. Thus, the ions cannot be washed from the sample, nor can they be fully coordinated by ammonia. Since both heating and ion exchange dehydroxylate the surface (*4*, *15*), it is reasonable to picture the ions as in Fig. 6 except that some or all of the OH groups have been replaced by O^{2-} ions. The remainder of the coordination of the ion can be made up of adsorbed gases or perhaps OH groups.

Thus, one side of the ion is coordinated by a triangle of surface groups which appears to remain unchanged by adsorption etc. The remainder of the coordination sphere is composed of available molecules or ions arranged to complete tetrahedral, octahedral or more complicated surface complexes. As with aqueous complexes, stronger ligands like ammonia can displace weaker ones like chloride in the coordination sphere.

This picture is essentially the same as proposed for transition metal ions supported on zeolites (*2*, *3*, *6*), ion exchange resins (*10*), silica (*12*, *14*) or alumina (*12*, *14*). Thus, it appears that the *general features* of the complex chemistry of supported transition metal ions are not different in concept from support to support or from homogeneous systems. However, the *details* depend upon the identity of the ion, the support and the identity and concentration of anions or adsorbed gases present.

It would be of interest to explore whether or not the observed structural differences can be related to such things as variations in catalyst activity as a function of the support used or the preparation method.

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