

Raman Spectra of Molybdenum Hexacarbonyl Adsorbed on Porous Silica and of Pyridine on Supported Nickel Oxide

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The Raman spectrum of $\text{Mo}(\text{CO})_6$ on porous Vycor is like that of a solution of the complex in a high dielectric constant solvent, except for the structure in the E_g band region which indicates interaction with the surface at a low-symmetry site. Adsorption of pyridine on Vycor-supported nickel oxide yields a band at 1012 cm^{-1} due to pyridine on nickel sites.

INTRODUCTION

Raman spectroscopy of surface-adsorbed species is an area of great potential interest and value holding out promises of complementarity, wider range, and greater ease of sampling than the established equivalent in experiment. However, it must be admitted that the field has so far failed to live up to its early promise. We report some results obtained with adsorbates known to be good Raman scatterers, and the first results from a supported oxide catalyst system using this technique.

EXPERIMENTAL METHODS

The support material used was porous Vycor glass (Corning No. 7930) with a surface area ca. $200\text{ m}^2\text{ g}^{-1}$. A major problem in obtaining Raman spectra of adsorbed species on silicas is the high background fluorescence. Egerton *et al.* (1) have recently shown how this may be eliminated from Vycor by heating in oxygen

at 500°C . We used a different method which seems to be equally satisfactory and is simpler.

Pieces of the glass were heated to ca. 100°C in a strongly oxidizing solution until all trace of coloration vanished: they were then washed several times in deionized water. The oxidizing solution was either 30% hydrogen peroxide or concentrated nitric acid to which a few crystals of potassium perchlorate had been added.

All cleaning and adsorption operations were carried out on a conventional vacuum line with grease-free taps. Cells containing the adsorbent were of a design similar to that of Kagel (2) and were coupled to the line by O-ring seals. Vycor was used in pieces ca. $16 \times 5 \times 1\text{ mm}^3$.

Spectra were recorded using Coderg Phl or PhO instruments with 632.8, 488.0, or 514.5 nm excitation. In general a focused laser beam was used striking the sample at an angle of ca. 45° . A typical spectrum of cleaned Vycor is shown in Fig. 1 and is

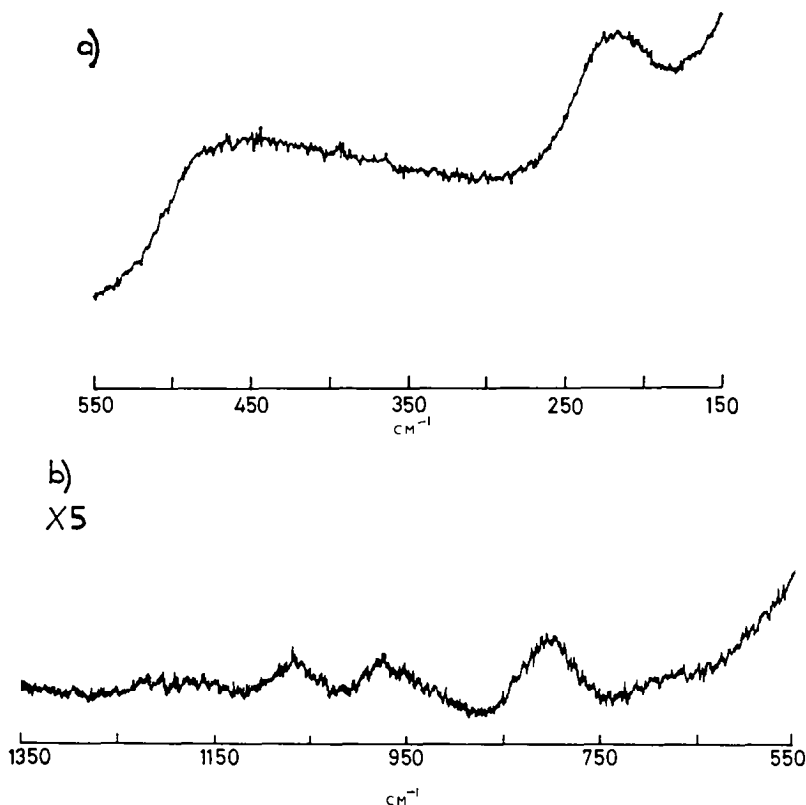


FIG. 1. Raman spectrum of clean Vycor glass, 488.0 nm excitation, ca. 50 mW at sample, spectral slit width 6 cm^{-1} . Gain in (b) is five times that in (a).

generally similar to that reported by Buechler and Turkevitch (3) except that their sharp 604 cm^{-1} band was much reduced in relative intensity in our spectra. This may be due to differences in slit width: unfortunately these authors report only that they used slit widths in the range 5–15 cm^{-1} , precluding specific comparisons. The stability of the spectra of adsorbed species over several hours under these conditions showed that the heating effect did not damage the layers.

RESULTS AND DISCUSSION

1. Surface $-\text{OH}$ Groups on Vycor

The spectroscopic consequences of the dehydration of Vycor are shown in Fig. 2. When the pores of the glass are filled with water the Raman spectrum (Fig. 2a) is

indistinguishable from that of liquid water. The rather sharp band at 3716 cm^{-1} is higher than $\nu(\text{OH})$ in water but comparable in position to what is found in equivalent ir studies (4). Heating and evacuation at 250°C revealed a further component at 3743 cm^{-1} and there could well be at least one more band within the envelope. The ir spectrum of this material given similar treatment shows a single band close to 3743 cm^{-1} . The relative sharpness of these Raman bands, and of the equivalent ir band, indicate that they are both due to non-hydrogen-bonded species. Two sets of workers have, indeed, claimed to have resolved the ir band into three components (5, 6), although the claim has been contested (7, 8). A plausible explanation of these results is that the 3716 cm^{-1} band is associated with $\nu(\text{OH})$ motions of groups

in an environment in which they do not generate an ir band. Subsequent dehydration leads to a modified surface for which ir and Raman results are comparable. This result suggests, however, that the further study of simple reactions at this surface (e.g., with ammonia) may reveal hitherto unsuspected features.

The most probable origin of these bands is in $\nu(\text{OH})$ motion of either B-OH or Si-OH groups on the Vycor surface. Without further experiments we cannot distinguish between these possibilities. The possibility arises (as suggested by a referee) that our cleaning procedure may have developed a preponderance of surface B-OH groups; this should be checked by carrying out a parallel experiment with Vycor cleaned by the procedure of Egerton *et al.* (1).

2. Vycor-Supported Molybdenum Hexacarbonyl

The high catalytic activity of supported metal carbonyls is well known and the formation of subcarbonyl species of $\text{Mo}(\text{CO})_6$ on various oxide supports has been detected (9). We have obtained the Raman

spectrum of $\text{Mo}(\text{CO})_6$ adsorbed on Vycor, Fig. 3. In outline the spectrum resembles that of a solution of this compound, and is notably different from that of the crystalline solid (10). The higher frequency $\nu(\text{CO})$ band (A_g in O_h) is at a position (2117 cm^{-1}) intermediate between those of the solid (2112 cm^{-1}) and the vapor (2124 cm^{-1}) (11) and comparable with that for solution in a solvent of high dielectric constant, such as dichloromethane. The lower band, which originates in the E_g $\nu(\text{CO})$ vibration of the isolated molecule, clearly shows unresolved structure which is characteristic neither of a solution nor of the crystalline solid: it also is intermediate in position between solution and vapor frequencies.

With increasing surface loading this spectrum increased in intensity but was otherwise unchanged at the highest loadings that could be obtained, which corresponded to ca. four layers. Heating the loaded samples *in vacuo* simply cleaned the glass; no evidence was found of any subcarbonyl species.

The small pore size of Vycor frustrated attempts at increasing the surface loading further and hence at observing a transition

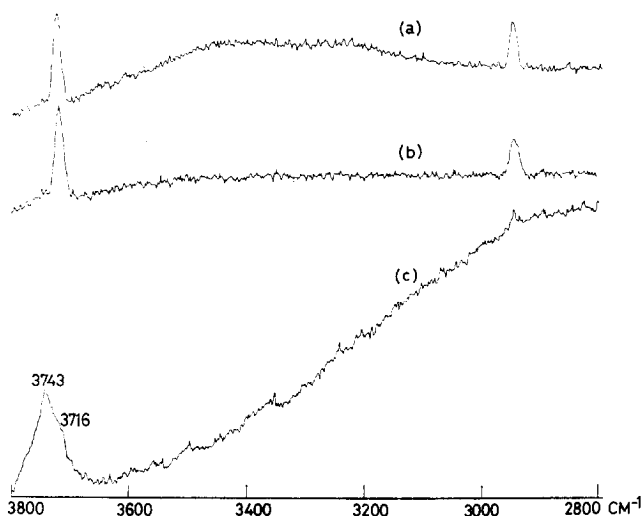


FIG. 2. Raman spectra of Vycor glass, 488.0 nm excitation, 100 mW at sample, spectral slit width 4 cm^{-1} . (a) Showing multilayer absorption of water. After heating *in vacuo* for (b) 1 hr at 65°C , (c) 5.5 hr at 250°C .

to crystalline packing. The layers formed are most reasonably described as glass-like. Their spectra are broadly similar to solution spectra and even show similar polarization behavior. The structure of the lower band, which has at least three components, shows that there is some breakthrough from the T_{1u} mode and that the mutual exclusion rule no longer holds. This implies a very low site symmetry on the surface.

These results are consistent with those of Howe *et al.* (9). Using infrared spectroscopy, they concluded that, although alumina and magnesia were capable of stabilizing subcarbonyls of molybdenum $\text{Mo}(\text{CO})_n$ ($6 > n > 0$), the spectrum of silica-supported $\text{Mo}(\text{CO})_6$ showed little evidence for such stabilization. Associated catalytic studies indicated that the active species formed on heating $\text{Mo}(\text{CO})_6/\text{SiO}_2$ was not molybdenum metal but possibly some higher oxidation state. Their infrared spectra for $\text{Mo}(\text{CO})_6$ on silica can, however,

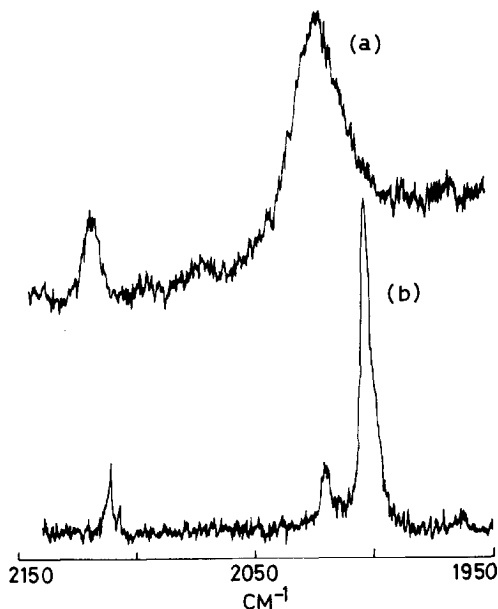


FIG. 3. Raman spectra of molybdenum hexacarbonyl, (a) adsorbed on Vycor glass, (b) solid in capillary tube. Both spectra recorded at 8 cm^{-1} spectral slit width using 24 mW 632.8 nm excitation. The higher of the two bands in (a) is almost totally polarized.

be quite plausibly interpreted in terms of the model outlined above.

3. Adsorption on Vycor-Supported Nickel Oxide

No Raman spectra have yet been reported for species adsorbed on the kind of supported metal oxide catalyst so commonly studied by ir methods. In our attempts to rectify this omission we have obtained many negative results and it is clear that the signal levels are generally much lower than those found for simple adsorption on Vycor.

Samples were prepared by standard methods. Cleaned Vycor pieces were immersed in aqueous nickel nitrate solutions, dried, and heated *in vacuo* to yield the metal oxide. The color of the product often varied, indicating a degree of nonstoichiometry. The nickel oxide thus prepared varied in color from pale yellow, through green, to black but showed no differences detectable by Raman spectroscopy, and only the most minor differences from that of Vycor itself. A study was made of the adsorption of pyridine on this material.

At very low loadings of nickel oxide (as judged by the concentration of the nickel nitrate solution used), the spectra of pyridine were closely similar to those obtained for pyridine on clean Vycor. When samples were prepared from highly concentrated or saturated nickel nitrate solutions no Raman spectra could be obtained but at intermediate surface loadings of nickel oxide multilayer adsorption of pyridine resulted in detection of peaks at 1007 and 1034 cm^{-1} typical of the liquid state. Following heating *in vacuo* at 60°C for 30 min these peaks decreased in intensity and disappeared after 3 hr at 110°C , leaving a broad band centered at 1012 cm^{-1} , Fig. 4.

Ni^{2+} ions on a surface will present sites of greater Lewis acidity than does Vycor alone and it is therefore reasonable to

expect there to be coordination to nickel. The coordination complex NiCl_2py_2 shows (12) a prominent band at 1013 cm^{-1} with a shoulder at 1017 cm^{-1} ; the parallel with our observations is very close and implies that we are indeed seeing a band due to pyridine adsorbed on the supported nickel oxide. Infrared spectra (13, 14) of pyridine adsorbed on silica-supported nickel oxide can similarly be interpreted in terms of Lewis bonding on Ni^{2+} ions and hydrogen-bonding on silica $-\text{OH}$ groups. The absence of a band at ca. 1550 cm^{-1} shows that there is no appreciable Brønsted acidity on the nickel oxide/silica surface.

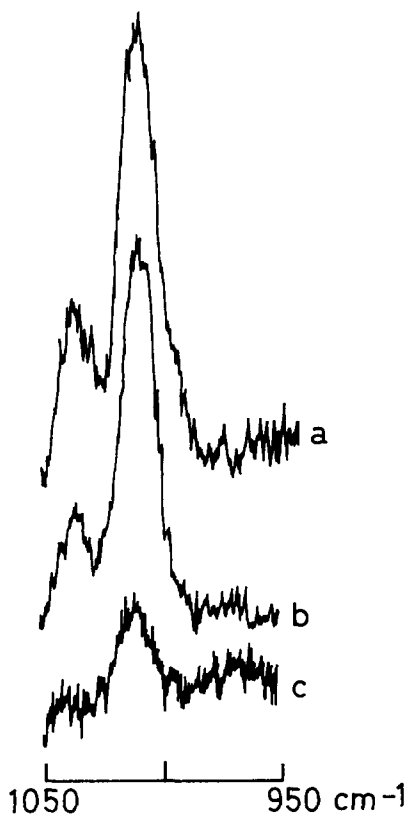


FIG. 4. Raman spectrum of pyridine adsorbed on Vycor-supported nickel oxide. Spectral slit width with 4 cm^{-1} , 50 mW 488.0 nm excitation at the sample. (a) After initial adsorption of pyridine; (b) after evacuation at 60°C for 0.5 hr ; (c) after evacuation at 110°C for 3 hr .

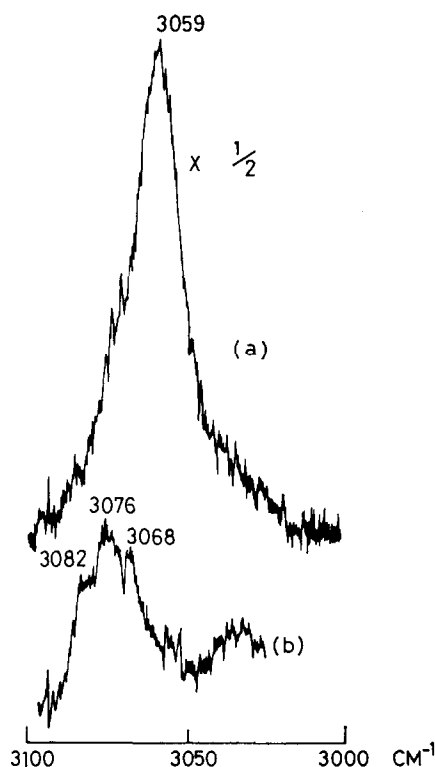


FIG. 5. Raman spectrum of pyridine adsorbed on Vycor glass. (a) After initial exposure to pyridine vapor; (b) after evacuation at 50°C for 1 hr . 488.0 nm excitation, 30 mW at sample; spectral slit width 4 cm^{-1} (a), 8 cm^{-1} (b).

4. Other Results

In common with others (15) we found that adsorption of organic vapors on Vycor in monolayer concentrations or above yields Raman spectra indistinguishable from low-resolution spectra of the corresponding liquids. All such adsorbates are readily removed by evacuation at up to 100°C and are clearly physically adsorbed. We have confirmed this for many simple adsorbents but report only the following points of difference from, or addition to, earlier work.

Pyridine on Vycor. Egerton *et al.* (1) report that initial adsorption on this glass (cleaned and outgassed at 500°C) gave a layer responsible for a band at 3072 cm^{-1} and that further adsorption led to develop-

ment of a band at 3056 cm^{-1} . Our results, Fig. 5, suggest that our initial surface loading is higher than theirs: the spectrum is dominated by the "liquid" band at 3059 cm^{-1} , on which a high-frequency shoulder ca. 3072 cm^{-1} is evident. Evacuation at 50°C for 1 hr resulted in the more complex spectrum of Fig. 3b of a surface species with at least three $\nu(\text{C-H})$ bands (3068 , 3076 , and 3082 cm^{-1}), all at frequencies greater than in liquid pyridine. It is probable that these were beneath the strong "liquid" band initially. These new bands are accompanied by strong scatter at 1007 cm^{-1} known to be associated with adsorption on Brønsted acid sites and hence helps to complete the characterization of pyridine in that situation.

Benzene on Vycor. In contrast with Egerton *et al.* (1) we found that the spectrum of benzene on Vycor shows a prominent shoulder at ca. 3052 cm^{-1} on the main band at 3065 cm^{-1} : this corresponds quite well with the spectrum they obtained after standing the initially prepared sample for 12 days. The discrepancy could be due simply to different initial surface loadings, theirs being the lighter, or perhaps to our different methods of cleaning Vycor. Buechler and Turkevich (3) apparently found a single band at 3056 cm^{-1} for this system but that may be a misprint for 3065 cm^{-1} . It is evident that this system warrants further attention.

CONCLUSIONS

Raman spectroscopy of adsorbed species is a difficult and unpredictable technique

not yet capable of routine application to systems other than those involving good Raman scatterers. The use of spectrum accumulation methods could significantly improve its capabilities.

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