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# An Infrared Study of Methanol and Ammonia Adsorption on Molybdenum Trioxide

Molybdenum trioxide is an effective catalyst for the selective oxidation of methanol to formaldehyde (*1–3*). Although various oxidation mechanisms have been proposed (*1–3*) direct evidence of reaction intermediates has been lacking. To date no relevant infrared work has been done at energies greater than 2000 $cm^{-1}$, primarily because the samples used have been too opaque to measure (*4, 5*). Herein we report infrared studies of surface species formed by adsorbing methanol and ammonia onto oxidized $MoO_3$.

Polycrystalline $MoO_3$ was prepared by decomposition of molybdenum oxalate. The oxalate was synthesized by dissolving $MoO_3$ (Fisher) in hot oxalic acid and evaporating the saturated solution to dryness. The resulting blue product was crushed and ground. It was then decomposed in the presence of flowing oxygen at 450°C. The powder turned white and X-ray diffraction studies showed a single-phase $MoO_3$ pattern. The powder was then sieved to exclude particles larger than 35 $\mu$m. The sieved fraction was composed of agglomerates 10–20 $\mu$m in size. The crystallites that formed the agglomerates were less than a micrometer in diameter and had a rounded morphology. Emission spectra showed the impurities: Si, 100–500 ppm; Ca, 50–250 ppm; Cu, 50–250 ppm; and Mg, 10–50 ppm. Self-supporting pellets for transmission infrared studies were pressed between Mylar polyester film disks in an 11-mm die from 5 to 10 mg of starting material. Typical conditions were 20–40 min at $2–5 \times 10^8$ N/$m^2$ (15–36 tons/in.$^2$). Allowing for sample losses when removing the Mylar after pressing, this usually resulted in a 5 to 7-mg pellet about 10 mm diameter by $3 \times 10^{-3}$ cm thick. The BET krypton surface area of the starting material was 10 $m^2$/gm. Pelleting typically decreased the surface area by 1–2 $m^2$/gm in all cases. After several weeks of experimentation, the pellets were removed from the infrared cell and the surface areas remeasured, giving values in the range 6–8 $m^2$/g.

The infrared cell and gas-mixing manifold were part of a metal ultrahigh vacuum system pumped by a 30 liter/s Vacion pump together with a Leybold–Heraeus Model NT550M turbomolecular pump. After introducing an oxidized sample into the infrared cell, the entire system was baked under vacuum at 300°C for 16–60 h before any further experimentation was done. Typically during this initial bakeout, the samples became opaque due to sample reduction by adventitious organic contamination. The original sample transmission was readily restored by introducing oxygen at temperatures above 250°C.

Interferograms were obtained with a Nicolet 7001P interferometer and processed with a PDP11/55 computer to give single-beam spectra with 4 $cm^{-1}$ resolution. Typically 1000–3000 scans were required to achieve adequate signal to noise. Spectra were calculated in the usual manner, i.e., by taking the negative logarithm of a "sample" spectrum ratioed with a "reference" spectrum obtained by removing the heated sample from the infrared beam. Since the "reference" spectrum is obtained without otherwise disturbing either the cell windows or the gas phase, spectra can be obtained even in the presence of fairly strong infrared absorbing gases. Subtracting two

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such spectra results in a "difference" spectrum which shows the net changes taking place at the sample, including its surface.

The inset to Fig. 1 shows a typical infrared spectrum of a sample which had been heated overnight in 10 Torr (1 Torr = 133.3 N/m$^2$) oxygen at 400°C and cooled under vacuum to 70–100°C, the temperature at which most of the spectra reported herein were obtained. Although silica is the most abundant impurity, we saw no evidence for the characteristic silica hydroxyl vibration at 3750 cm$^{-1}$ suggesting that its surface concentration was negligible or that it was chemically inert.

Spectral quality was limited by increased absorbance both at (i) high energies due to scattering losses, and (ii) energies below 1000 cm$^{-1}$ due to the lattice vibrations which are 100–1000× more intense than any features appearing in Fig. 1. The main features of the inset to Fig. 1 are the bands at 1960–1890, 1132 and 1082 cm$^{-1}$ which probably arise from overtones and/or combinations of the intense lattice vibrations. A band sometimes appears at 2350 cm$^{-1}$ which is probably due to intercalated $CO_2$[1,2] remaining from the oxalate decomposition. Its intensity relative to the other observed bands varies from sample to sample and with successive redox cycles of the samples. However, no changes in any of these bands were observed during any of the experiments reported herein, so no further reference will be made to them.

## RESULTS

Figure 1 shows a difference spectrum for oxidized $MoO_3$ at 100°C before and after introducing 1 Torr methanol. Since the lattice contributions and gas-phase methanol have been spectrally subtracted out the vertical scale is about 10× more sensitive than that of the inset. Bands are observable in the OH and CH stretching regions (3600–2800 cm$^{-1}$), CH and OH deformation region (1440, 1365 cm$^{-1}$), and CO stretching region (1100–1000 cm$^{-1}$).

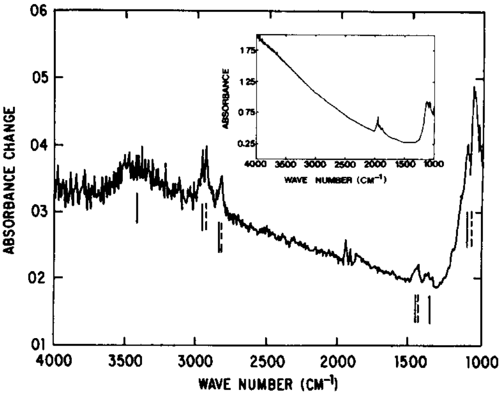

FIG. 1. Infrared spectral changes taking place with oxidized $MoO_3$ at 100°C in 1 Torr methanol, (—) volatile species, (---) nonvolatile species. Inset: Infrared spectrum of oxidized $MoO_3$ before methanol introduction.

Subsequent evacuation of the infrared cell caused the following spectral changes to Fig. 1: the bands marked by the solid lines disappear leaving behind the bands marked by the dashed lines, i.e., the bands at 3600–3200, 2960, and 1365 cm$^{-1}$ disappear, those at 2850–2825 and 1100–1000 cm$^{-1}$ sharpen, and the band at 1440 cm$^{-1}$ decreases to about ½ its original intensity. Essentially the same behavior was noted (i.e., the same bands remained) for starting pressures ranging from $10^{-4}$ to 10 Torr. The positions of bands (both volatile and nonvolatile species) for methanol ($-d_0$, $-d_3$, $-d_4$) exposures are summarized in Table 1.

Figure 2 shows a spectrum of changes taking place when oxidized $MoO_3$ at 70°C is placed in 1 Torr ammonia. In this case the sample had been preexposed to $10^{-4}$ Torr $H_2O$ for 100 s. Clear cut bands are observed in the NH stretching region (3400–3200 cm$^{-1}$) and NH deformation region (1600, 1450, and 1250 cm$^{-1}$). The only observable effect of the water exposure was to enhance the intensity of the 1450-cm$^{-1}$ band by about 3×, i.e. Our sensitivity was insuffi-

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[1] Measurements at higher resolution suggest that this band is really a composite of 3–5 separate bands.

[2] It is unlikely that this band arises from molybdenum hydride since its frequency is about 100 cm$^{-1}$ too high for a metal hydride.

TABLE 1

Principle Adsorbed Methanol (-$d_0$, -$d_3$, -$d_4$) Bands on $MoO_3$

| Adsorbate (cm$^{-1}$) | | | Functional group (cm$^{-1}$) | |
|---|---|---|---|---|
| $CH_3OH$ | $CD_3OH$ | $CD_3OD$ | Nonvolatile | Volatile |
| 3660 | 3660 | 2700 | | —$OH^{str}$ |
| 2960 | 2225 | 2225 | | —$CH_3^{AS}$ |
| 2925 | | 2185 | —$CH_3^{AS}$ | |
| 2850 | 2080 | 2080 | | —$CH_3^{SYM}$ |
| 2825 | 2070 | 2065 | —$CH_3^{SYM}$ | |
| 1440 | | 1098 | —$CH_3^{def}$ | —$CH_3^{def}$ |
| 1365 | 1335 | | | —$OH^{def}$ |
| 1065 | | 1050 | —O—C | —O—C |

cient to detect any changes produced by the water exposure alone Subsequent evacuation of the infrared cell caused the 1450-cm$^{-1}$ band to disappear and decreased the 1600- and 1250-cm$^{-1}$ bands to about $\frac{2}{3}$ their original intensities Additional changes appearing in the 3400 to 3200-cm$^{-1}$ bands could not be quantified because the noise was too great

## DISCUSSION

### *Methanol Adsorption*

The nonvolatile species in Fig 1 is undoubtedly a surface methoxy The bands at 2925, 2825 and 1440 cm$^{-1}$ are assigned to methyl asymmetric stretch, symmetric stretch, and deformation vibrations, respectively, and the 1065-cm$^{-1}$ band to CO stretch The low frequency for the methyl symmetric stretch (2825 cm$^{-1}$) indicates (*6*) that the methyl group is attached directly to an oxygen The absence of an —OH feature also suggests that this group is a surface methoxy

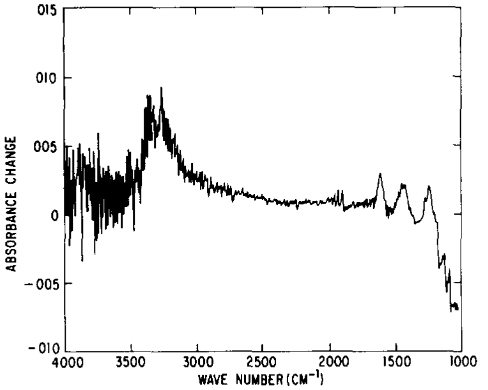

FIG 2 Infrared spectral changes taking place with oxidized $MoO_3$ at 70°C placed in 1 Torr ammonia The sample had been preexposed to $H_2O$

The volatile species appears to be undissociated methanol, determined by using the above assignments for the volatile bands analogous to methoxy, and assigning the 1365-cm$^{-1}$ band to the methanol OH in-plane deformation The band at 3660–3200 cm$^{-1}$ suggests that the hydroxyl end of the molecular methanol is involved in a hydrogen bond The OH in-plane deformation is shifted to higher energies relative to the gas phase (*7*) by 22 and 45 cm$^{-1}$ for methanol-$d_0$ and -$d_3$, respectively, an observation consistent with hydrogen bond formation Using the empirical relationship of Novak (*8*) for the frequency shift between a free and hydrogen bonded hydroxyl, we estimate an oxygen–oxygen bond distance about 2 8–3 0 Å between the two oxygen atoms participating in the (OH O) bond

Using $\varepsilon$(methyl) ~ 3 × $10^{-19}$ cm$^2$/molecule[3] we find a surface methoxy concentration of 3–4 × $10^{13}$ cm$^{-2}$ Assuming an adsorption site density $10^{15}$ cm$^{-2}$, this suggests a 3–4% surface coverage, in reasonable agreement with that estimated from temperature-programmed desorption studies (*11*) on the same starting material It thus appears that methoxy gives rise to the "$\beta$-peak" observed at 220°C in temperature-programmed desorption studies (*11*) It would obviously be desirable to determine the temperature dependence of the methoxy concentration to compare directly with TPD results (*11*) However, this could not be done since, once a sample was exposed to methanol, heating it above 125°C

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[3] Obtained from the methylene extinction coefficient (Ref (*9*)) and the fact that methyl antisymmetric stretching vibration at 2925 cm$^{-1}$ is typically 2–3× stronger than the comparable methylene absorption (Ref (*10*))

resulted in overall absorbance increases indicating that sample reduction was occurring These changes in overall absorbance made it impossible to obtain the required sensitivity by spectral subtraction such as shown in Fig 1

### *Ammonia Adsorption*

Ammonia coordinated to metal atoms (*12*) typically gives rise to symmetric deformation vibrations in the range 1170–1370 cm$^{-1}$ Also the doubly degenerate bending mode which occurs at 1627 cm$^{-1}$ in the gas is shifted to slightly lower frequencies for coordinated ammonia (*13*) Hence from Fig 2, we conclude that coordinately bonded ammonia is present, assigning the 1613- and 1250-cm$^{-1}$ bands to $\delta_d(NH_3)$ and $\delta_s(NH_3)$, respectively

The presence of ammonium ion in Fig 2 is indicated by the ammonium bending mode, $\delta_d(NH_4^+)$, at 1450 cm$^{-1}$ (*12, 13*) Since preadsorbed water significantly enhances ammonium formation, one expects that ammonia interacts with available surface hydroxyls to form ammonium ion The process is evidently reversible since subsequent evacuation removes all traces of $NH_4^+$

Unfortunately our signal to noise is insufficient to detect "free" (i e , nonhydrogen bonded) surface hydroxyls or even to see changes in free surface hydroxyl concentrations during water, methanol and ammonia exposures Hence little else can be said about the state of surface hydroxylation

The existence of coordinately bonded ammonia suggests the presence of metal-atom-like sites thus suggesting a small amount of surface reduction [4]

## CONCLUSIONS

We have used infrared spectroscopy to identify surface species on $MoO_3$ resulting from methanol and ammonia adsorption Methanol adsorption results in 2 surface species methoxy $-OCH_3$ and molecular methanol, weakly chemisorbed through a hydrogen bond to a lattice oxygen Ammonia adsorption results in strongly held coordinately bonded ammonia and weakly adsorbed ammonium ion

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[4] Cooling the sample (after oxidation at 400°C) before evacuating the oxygen resulted in the same spectra following methanol and ammonia adsorptions Hence it seems unlikely that sample reduction occurred in evacuation