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Oxidation and Reduction of MoO_2–MoO_3 Studied by Infrared Emission Spectroscopy

Akifumi UENO* and Carroll O. BENNETT†

National Chemical Laboratory for Industry, 2-19-19, Mita, Meguro-ku, Tokyo 153

† *Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06268*

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A sample preparation technique was developed for the study of infrared emission spectroscopy. The emission spectrum of MoO_3 showed peaks at 987 and 925 cm^{-1} in the temperature range of 185 through 505 °C. Peak intensities were proportional to the sample weight. The background intensity in the emission spectrum was measured at 1050 cm^{-1} and it was also proportional to the sample weight. In order to apply emission spectroscopy to the study of reaction kinetics, the reduction of MoO_3 by H_2 and the oxidation of MoO_2 by O_2 were chosen as model reactions. These reactions were studied at 425 to 485 °C and the activation energy for the reduction of MoO_3 was 43 kcal/mol and that for the oxidation of MoO_2 was 38 kcal/mol. The activation energy for the formation of the terminal Mo=O bond was, however, 71.2 kcal/mol.

Oxides of molybdenum are important as oxidation catalysts. In connection with a recent study[1)] of the partial oxdation of methanol on MoO_3–Fe_2O_3, attempts were made to investigate the state of the surface of the catalyst by infrared spectroscopy. As a first step it seemed logical to work with pure MoO_3, but we found that it was not possible to prepare a suitable disk of this material for study by the usual scattered transmission tehnique. Although the catalytic behavior of some noble metals such as platinum seem little affected by supports, such is not the case for most transition metals, and *a fortiori* for metal oxides. Thus we have searched for a means of studying unsupported MoO_3. Previous infrared work[2,3)] on molybdenum oxides has been done on supported catalysts or by the Nujol method. Vanadium oxides have been studied in KBr disks.[4)] These methods are obviously not suited to the observation of the catalyst during catalysis, our ultimate goal.

Although it seems attractive to use emission spectroscopy to observe catalysts at reaction temperatures, typically 200—500 °C, few papers have been published on this subject. Eischens and Pliskin[5)] observed the spectrum of a thin layer of oleic acid on an aluminum rod at 200 °C. Low and Inoue[6)] used an aluminum plate as the sample substrate. In an ideal arrangement only the sample would be heated, but radiation from the polished heated aluminum is small. Koga *et al.*[7)] have used an infrared beam to heat their sample, so that the rest of the cell remained cooler, and interfering radiation was minimized. They observed the emission spectrum of formate ions on the surface of Al_2O_3. Dewing[8)] deposited bismuth molybdate on a heated gold foil and observed the emission spectrum of the solid. Cavallini *et al.*[9)] showed the utility of infrared emission spectroscopy as applied to the study of the oxidation of metal surfaces.

The experimental arrangement which we have used to obtain the infrared spectrum of CO_2 adsorbed on unsupported NiO[10)] is readily adapted to the emission mode. If the temperature is higher than about 200 °C, the source can be turned off and emission spectra obtained. As pointed out by Dewing,[8)] a thin layer (about 1 mg/cm^2) of solid must be used so that the black-body radiation of the solid does not overwhelm the emission peaks. For the study of MoO_3, we have evaporated on a stainless-steel mirror a suspension of finely divided (≈ 5 μm particles) oxide. This sample gives a good emission spectrum of MoO_3 or, after reduction, MoO_2. However, its surface area is so small that there is not enough adsorbed CH_3OH, for example, on the solid to give a spectrum of adsorbed species. In future work it should be possible to use highly divided oxide (100—200 Å) prepared in a flame reactor[11)] to permit the observation of adsorbed species. Such solids were not available to us at the time of the work reported here.

Infrared spectroscopy can be used to study the kinetics of changes of solids and species adsorbed on solids by the use of the transient method.[9,12,13)] In the work reported here we have applied this method to the reduction and oxidation of the system MoO_3–MoO_2.

Experimental

Sample Preparation. MoO_3 was obtained by the decomposition of ammonium molybdate at 340 °C in air. It was ground to less than 200 mesh. These finely divided particles were suspended in water, and some of the finest part of the suspension was pipetted onto a well polished stainless steel mirror (1.0 cm^2) and then dried at 110 °C. The mean particle size of the sample was about 5 μm, measured by optical microscopy. After weighing, the mirror coated with catalyst was placed in the reaction cell and heated at 485 °C for 16 h with oxygen flow.

Reaction Cell and Optics of Spectrometer. The reaction cell used is the same as the one used in the previous work,[3)] except that it was fitted with a BaF_2 window instead of an IRTRAN 6(CdTe) window; the BaF_2 window allows us to use higher temperatures than 300 °C. The window was glued into a stainless steel holder with Vacseal, although this adhesive was prone to leak after some exposure to temperatures above 400 °C. The cell was always used under positive pressure.

The optics of the infrared spectrometer is also the same as previously used,[10)] except that the infrared radiation source was turned off to obtain the emission spectrum. The slits were not programmed in the present work and were set at 4.0 mm for all experiments.

In the present experiments, not only the emission from the sample but also that from the stainless steel mirror were recorded. Therefore, a correction was always made by the subtraction of the emittance due to the mirror from that recorded due to the mirror with its sample. The emission spectrum of the mirror was not sensitive to its degree of polish for all those tested.

The intensities of the emission spectra were expressed in terms of μV on the lock-in amplifier (P.A.R. Model 128).

Chemicals. The gases used in the present experiments were obtained from Matheson. A cooling trap at −50 °C was used for H_2 and O_2 to remove water, and for Ar a Hydrox purifier was used to eliminate water and oxygen. These gases were introduced into the reaction cell with a flow rate of 3.0 ml/s, which corresponds to about 1 s of residence time in the reaction cell.

Procedure for Measurement of Reaction Rates. In order to obtain the reduction rate of MoO_3 by H_2 and the oxidation rate of MoO_2 by O_2, the wave numbers of the emission spectrum were fixed at 1050, 987, and 925 cm^{-1}, and the changes in the emission intensities were recorded separately for each experimental run. The emission spectrum of MoO_3 has peaks at 987 and 925 cm^{-1}, and they represent the termical Mo=O bond and the Mo–O–Mo net plane vibration.[3,9] For the experimental convenience, the increase in the background intensity at 1050 cm^{-1} is chosen to represent the change of bulk MoO_3 to MoO_2 and *vice versa*. The background intensity was sensitive to the oxidation states of molybdenum oxides at the higher wave numbers, and at the lower wave numbers around 825 cm^{-1} it became less sensitive (see Fig. 5). Therefore, the peak heights at 987 and 925 cm^{-1} were calculated by linear interpolation as follows every 1.0 min for the reduction of MoO_3 or every 5.0 s for the oxidation of MoO_2.

$$I_{987}(t) - \left(\frac{987-825}{1050-825}\right) I_{1050}(t) = P_{987}(t) \qquad (1)$$

$$I_{925}(t) - \left(\frac{925-825}{1050-825}\right) I_{1050}(t) = P_{925}(t) \qquad (2)$$

where $I_{987}(t)$ represents the intensity emitted from the sample at time t after the addition of H_2 (or O_2) at 987 cm^{-1}, and $I_{1050}(t)$, $I_{925}(t)$ also represent the emission at 1050 and 925 cm^{-1} respectively. From $P_{987}(t)$ and $P_{925}(t)$, the rates of reduction or oxidation could be obtained.

X-Ray Diffraction. The identification of MoO_2 and the Mo metal was obtained by X-ray powder diffraction by using Mo or Cu tubes with 40 kV and 20 mA. When the sample was studied by X-ray diffraction, it was exposed to air at room temperature. We confirmed that the sample was not oxidized by air at room temperature as follows: MoO_3 set in the reaction cell was reduced by the addition of H_2 at 485 °C, but the reduction stopped when H_2 was switched to Ar, as determined by the emission spectrum. Then the temperature was decreased to room temperature, keeping the sample in Ar, and its infrared transmission spectrum was observed. This spectrum did not change at all even when exposed to pure O_2 for several days at room

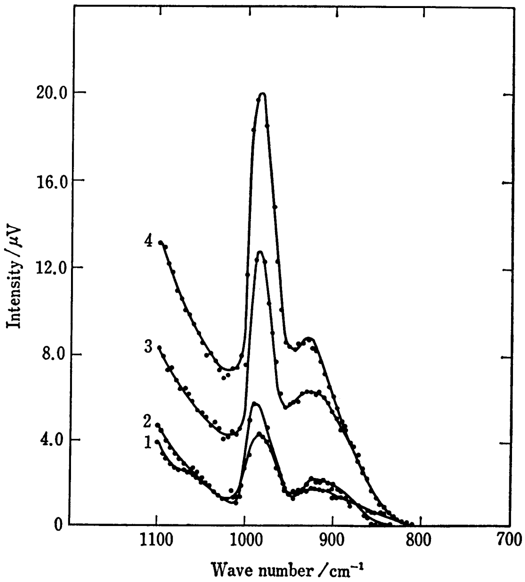

Fig. 1. Emission spectra of MoO_3 at 485 °C.
Sample weights: 1: 0.2 mg, 2: 0.4 mg, 3: 0.8 mg, 4: 1.1 mg.

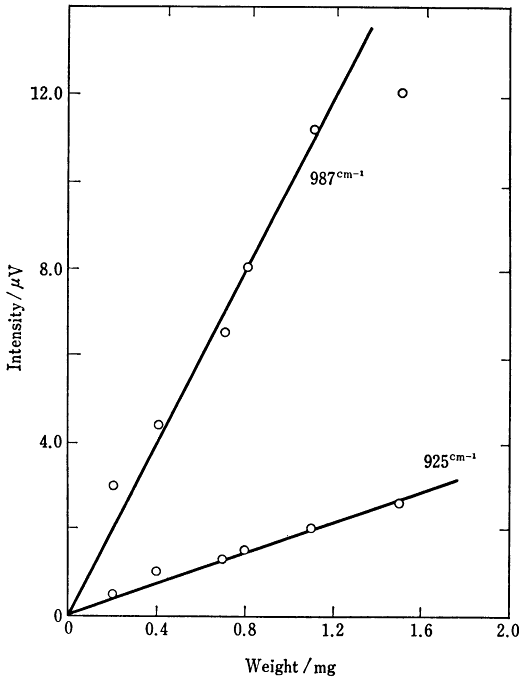

Fig. 2. Relation of emission intensities to sample weight at 485 °C.

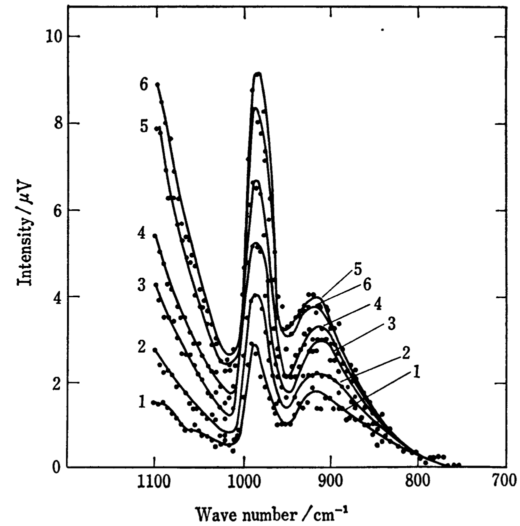

Fig. 3. Emission spectra of MoO_3 at various temperatures for 0.7 mg of sample.
1: 185 °C, 2: 245 °C, 3: 335 °C, 4: 365 °C, 5: 425 °C, 6: 485 °C.

temperature.

Results

Emission Spectra. Figure 1 shows the emission spectra at 485 °C for various sample weights deposited on the mirror. The intensities, corrected for radiation from the mirror, are plotted in Fig. 2 as a function of sample weight. Up to 0.8 mg/cm^2 a linear relation is obtained; such curves facilitate the comparison of spectra obtained from different samples. Higher sample loadings may show some effect of the submergence on the individual bands by black body radiation for thick samples. This effect is often mentioned, for example by Dewing.[8)]

The effect of temperature on the emission spectra is shown in Fig. 3, and the intensities of the various bands vary with temperature as shown in Fig. 4. The surprising linearity of these relations is not in disagreement with the fourth-power law of radiation, as illustrated by the following analysis.

A simple balance of radiant energy at the detector equates the energy received from the sample at T to that lost to the surroundings at ambient temperature T_0:

$$K_1(T^4 - T_d^4) = K_2(T_d^4 - T_0^4) \tag{3}$$

were T_d is the temperature of the detector. The signal depends on T_d, given by

$$T_d = \left(\frac{K_1T^4 + K_2T_0^4}{K_1 + K_2}\right)^{1/4} \tag{4}$$

K_1 and K_2 depend on view factors and emissivities in a complicated fashion, but to a first approximation

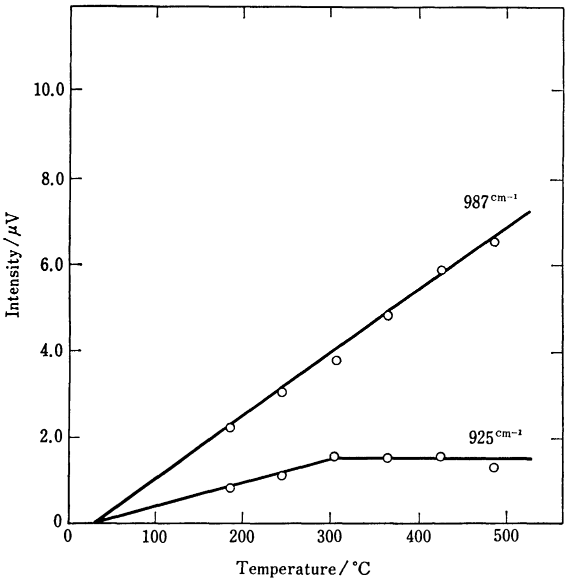

Fig. 4. Effect of temperature on emission intensity.

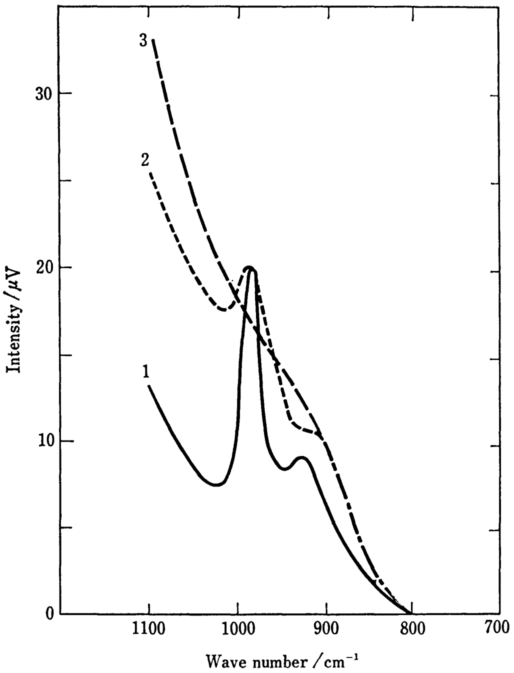

Fig. 5. Changes in emission spectrum of MoO_3 caused by addition of H_2 at 485 °C and 1 atm.
1: In O_2 (1 atm), 2: in H_2 for 2 min, 3: in H_2 for 10 min.

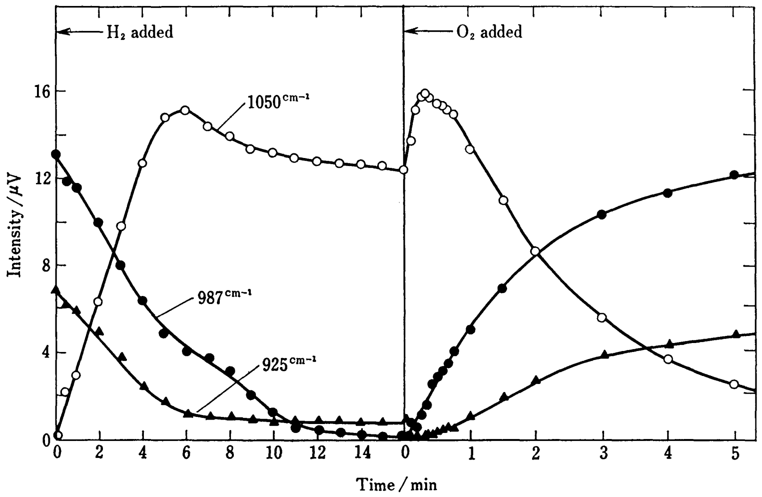

Fig. 6. Variation of emission intensities during reduction and oxidation at 485 °C. Reduction past MoO_2 toward Mo.

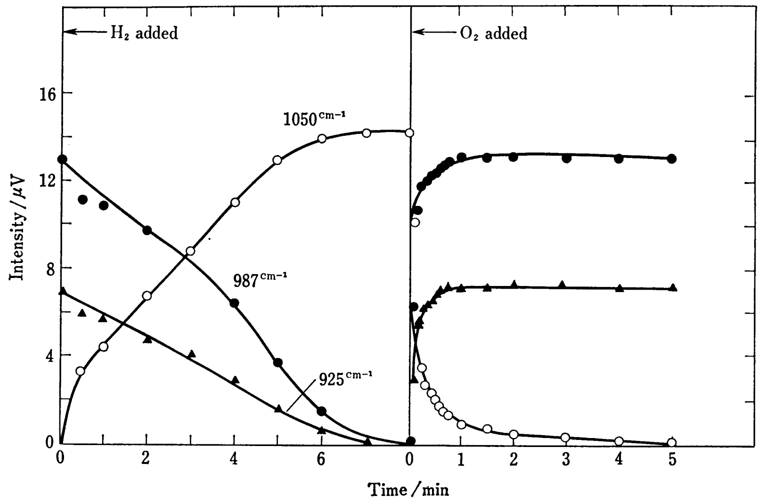

Fig. 7. Variation of emission intensities during reduction of MoO_3 to MoO_2 and during oxidation of MoO_2 to MoO_3, at 485 °C.

they are equal. We then have

$$T_d = \left(\frac{T^4+T_0^4}{2}\right)^{1/4} \qquad (5)$$

For $T_0=300$ K and T varying from 450 K to 750 K, the relation between T_d and T is almost linear. When T equals T_0, T also equals T_d, and there is no signal. No explanation is offered for the break in the curve for 925 cm⁻¹ in Fig. 4.

Application to Kinetics. The MoO_3 sample was exposed to CO over the temperature range 25—485 °C but no adsorption bands nor reduction of the catalyst was observed. CO_2, CH_3OH, HCOOH, and HCHO also had no effect. However, exposure to hydrogen reduced the catalyst to MoO_2 and eventually partly to Mo. The emission spectra changed as shown in Fig. 5; the Mo=O (987 cm⁻¹) and Mo–O–Mo (925 cm⁻¹) bands are removed as the sample is reduced. Flow rates of all these gases were about 3 ml/s.

A quantitative study of the kinetics of reduction by hydrogen (≈1 atm) and oxidation by oxygen (≈1 atm) was made. The intensities at 987 cm⁻¹ and 925 cm⁻¹ were calculated from Eqs. 1 and 2, and the displacement of the background at 1050 cm⁻¹ was measured, taking MoO_3 as zero. These intensities were measured as a function of time during reduction and oxidation at various temperatures. A typical result at 485 °C is shown in Figs. 6 and 7. At various times the sample was "frozen" by switching to argon and cooling as already described. The X-ray diffraction peaks obtained are shown in Fig. 8. We interpret the maximum in the background (1050 cm⁻¹) to be the point where the MoO_3 is exhausted and where Mo metal starts to appear, reducing the emissivity of the sample. We decided to limit our quantitative studies to the interconversion of MoO_3 and MoO_2 only, as shown in Fig. 7. The reduction is stopped when the intensity at 1050 cm⁻¹ reaches its maximum.

The experiments described above were repeated at 425, 445, 465, 485, and 505 °C. From the initial slopes of curves such those of Fig. 7 the initial rate can be calculated in arbitrary units such as μV/s. These rates at various temperatures are used to construct the Arrhenius-type diagrams of Figs. 9 and 10. For the reduction of MoO_3 all three lines give an activation energy of 43 kcal/mol (179.7 kJ/mol). For the initial rate of oxidation of MoO_2, the activation energies are different for the three bands: 38.3 kcal/mol for 1050 cm⁻¹; 37.6 kcal/mol for 925 cm⁻¹; and 71.2 kcal/mol for 987 cm⁻¹. The rate of oxidation is so fast that these results are probably less precise than

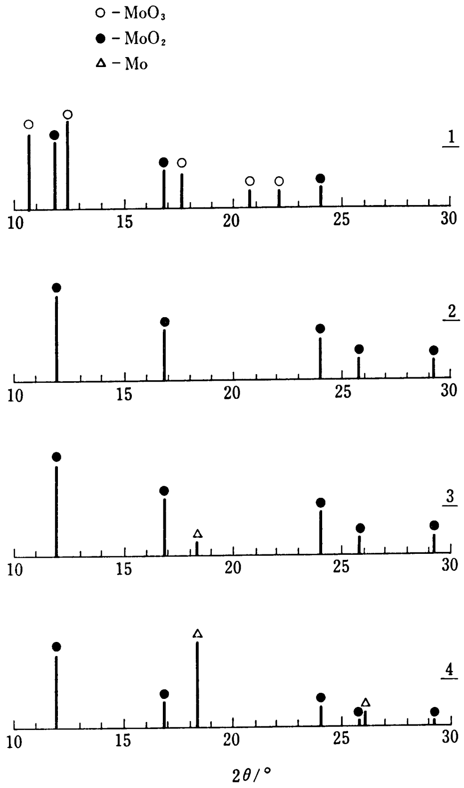

Fig. 8. X-Ray diffraction results during reduction of MoO_3 at 485 °C in H_2 for various times of exposure. 1: 3 min, 2: 6 min, 3: 8 min, 4: 20 min.

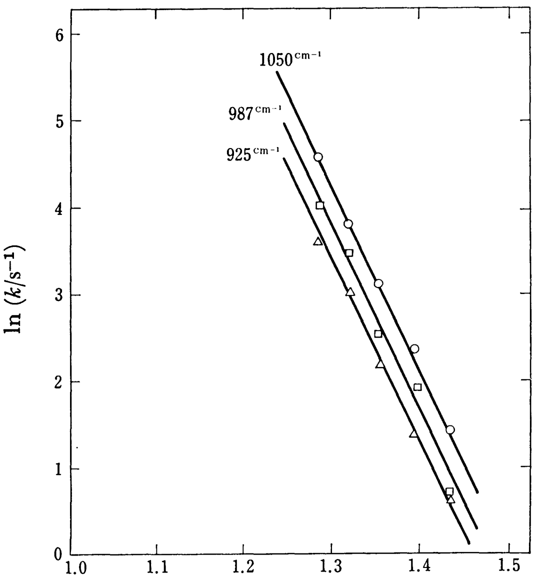

Fig. 9. Reduction rates of MoO_3.

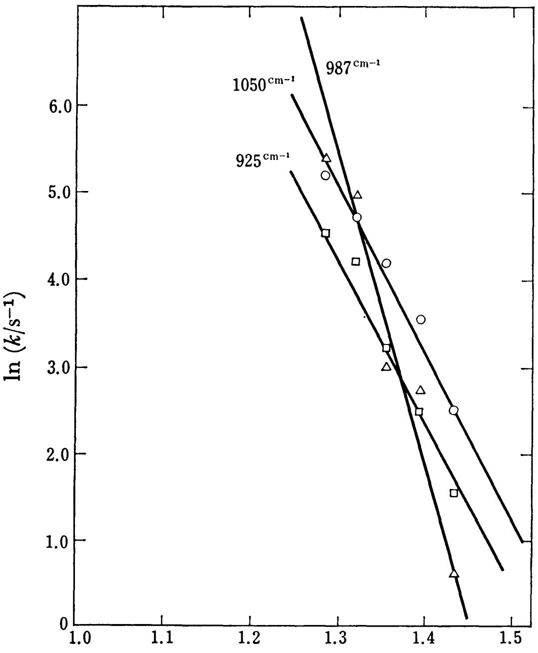

Fig. 10. Oxidation rates of MoO_3.

those for the reduction.

Earlier studies[14,15] of the reduction of MoO_3 by H_2 reported activation energies of 46—48 kcal/mol for the temperature range 365—445 °C, similar to our result of 43 kcal/mol. For the oxidation of MoO_2, Ramodorai *et al.*[15] report $E=40\pm2$ kcal/mol at about 465 °C, in qualitative agreement with our results based on the rate of change at 1050 cm^{-1} or 925 cm^{-1}. Possibly the formation of Mo=O starts only after most of the bulk is oxidized, so that our initial rates based on 987 cm^{-1} are too low. Recent studies[16-18] show that the system is quite complicated.

Summary

Emission spectroscopy can be used to study the structure and kinetics of reduction and oxidation of unsupported MoO_3–MoO_2, a system which has been difficult to study *in situ* by infrared techniques. In accord with Dewing,[8] we find that a sample loading of about 1 mg/cm^2 or less is suitable for the emission work. Infrared spectroscopy can now be used for kinetic measurements in catalysis.[2,3] For the MoO_3–MoO_2 system it furnishes a convenient method of measuring rates of reduction and oxidation.

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