Role of silanol groups in dispersing Mo(VI) on silica

R.D. Roark, S.D. Kohler and J.G. Ekerdt *

Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

Received 13 May 1992; accepted 10 June 1992

Infrared spectroscopy was used to follow the intensity of the isolated silanol stretching mode during the reversible transformation of supported molybdenum between the hydrated, polymolybdate structure and the dehydrated, isolated Mo^{6+} structure. The isolated silanol absorbance intensity was attenuated upon dehydration and spreading of Mo^{6+}. The Si–OH (or Si–OD) silanol band was regenerated by rehydration with H_2O (or D_2O). A model for spreading is proposed in which the surface silanol groups are the sites for attachment of the isolated Mo^{6+} cation.

Keywords: Spreading; dehydration; molybdenum oxide; silica; infrared spectroscopy

1. Introduction

Recent publications have shown that when special methods are used to prepare Mo^{6+}/SiO_2, it is possible to avoid crystallite formation up to loadings of 6.4 wt% Mo [1,2]. Through the use of Raman spectroscopy, these publications have also shown that the Mo^{6+} is present in two forms depending on the degree of hydration. Silica exposed to ambient air adsorbs water and this adsorbed water acts to solvate the Mo^{6+} cations, leading to the formation of O_h Mo^{6+} clusters [1]. The most likely cluster is the heptamolybdate polyanion, $Mo_7O_{24}^{6-}$, with a characteristic Raman Mo=O band at 944–965 cm^{-1}. The heptamolybdate structure was not stable after heating to remove water and the Mo^{6+} cations migrated onto the silica support. An isolated Mo^{6+} cation, with the Raman Mo=O band at 986–998 cm^{-1}, was proposed to form [1]. On the basis of EXAFS studies, the isolated Mo^{6+} was proposed to have octahedral symmetry [2]. De Boer et al. [2] also suggested that the presence of surface Si–OH groups benefitted the spreading.

The heptamolybdate Raman band has been reported by various groups for silica-supported Mo^{6+} [3–7]. For aqueous preparation methods that employ Mo^{6+} cations, MoO_3 crystallites have been observed at loadings as low as 0.4%

* To whom correspondence should be addressed.

molybdenum [1]. Spreading has not been observed when the molybdenum was present as MoO_3 crystallites prior to the removal of water [8]. Since silica-supported molybdenum is likely to be subjected to a pretreatment procedure that involves heating under an oxidizing or inert atmosphere prior to use in a catalytic reaction, it seems reasonable to suggest that some or all of the heptamolybdate phase is transformed into the isolated Mo^{6+} form during this pretreatment procedure. Isolated Mo^{6+}, untransformed Mo polyanions, and MoO_3 crystallites may all be present during catalysis and one or more of these forms may contribute to the catalytic reaction.

This communication addresses the formation of isolated Mo^{6+} on silica. We show that the isolated Mo^{6+} is directly related to the isolated silanol groups on silica and that at least H is lost from the silanol groups during dehydration of the samples and the formation of isolated Mo^{6+}.

2. Methods

Transmission infrared (IR) spectra were obtained with a Digilab FTS-15/90 FTIR spectrometer. Spectra were obtained after 50 scans at a resolution of 2 cm^{-1}. A stainless steel cell connected to a quartz furnace, capable of 1273 K, was used. A magnetically coupled sample transfer arm was used to move the samples from the heated zone to the zone where IR spectra were recorded at room temperature. CaF_2 optics were used. The cell could be purged with a gas mixture at a pressure of 1 atm or evacuated with a mechanical pump.

The samples were pressed into self-supporting wafers and placed in a disk support ring. Wafers were pressed at 5000 psi and a typical wafer was 60 mg with a diameter of 1.7 cm. Following installation in the IR cell, the wafers were examined with IR (designated as ambient samples) and heated in helium (99.99 + %) or hydrocarbon-free air (Liquid Carbonic, zero air). For rehydration experiments, the helium was diverted through a 273 K liquid bubbler filled with H_2O (deionized, distilled) or D_2O (Sci-Graphics, 99.8% D) prior to entering the IR cell; the wafer was at 298 K during rehydration.

Davison 952 silica gel (280 m^2/g) was used as the support; it was treated in dilute sulfuric acid to remove calcium impurities [9]. Molybdenum (6.4 wt%) was attached to the silica using $Mo_2(\eta^3\text{-}C_3H_5)_4$. The preparation, pretreatment, and hydrated and dehydrated Raman spectra of this sample have been described elsewhere [1].

3. Results

Figs. 1 and 2 present spectra of the hydroxyl stretching region for Davison 952 after heating to the indicated temperatures for 1 h. Consistent with published

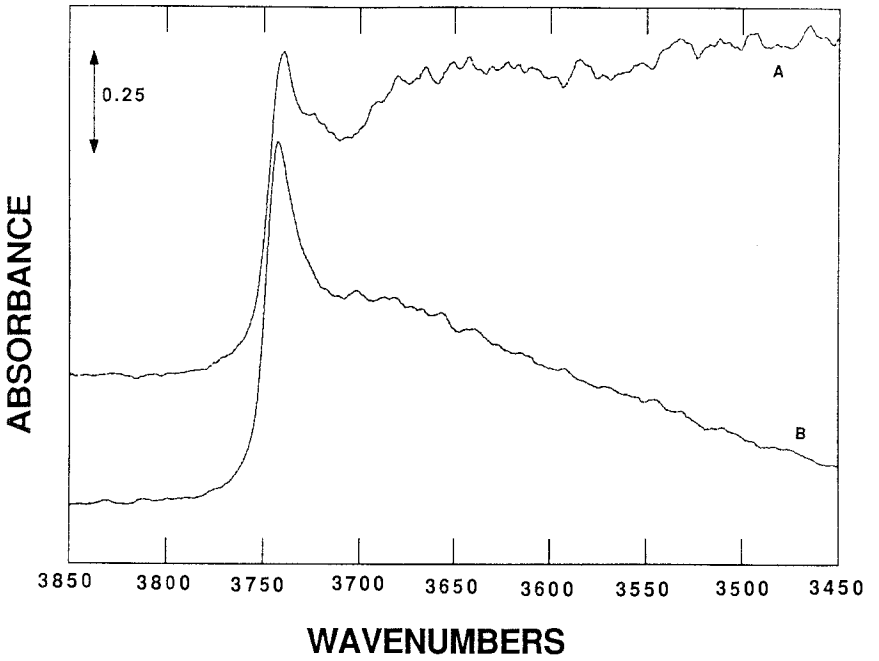

Fig. 1. Infrared spectra of Davison 952 silica in helium: (A) as pressed and without heating (ambient), and (B) after heating to 673 K.

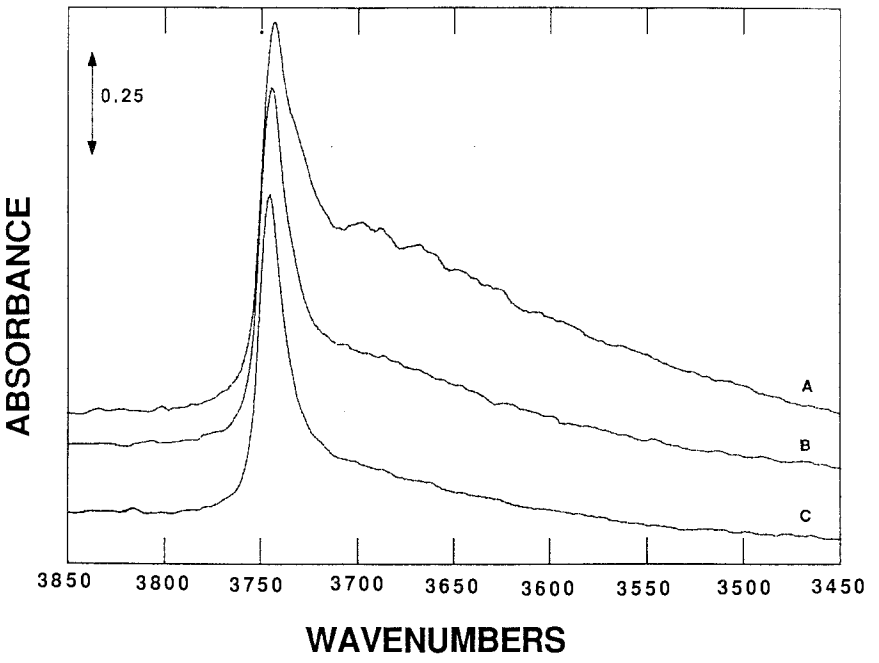

Fig. 2. Infrared spectra of Davison 952 silica in helium after heating to (A) 773, (B) 873, and (C) 923 K.

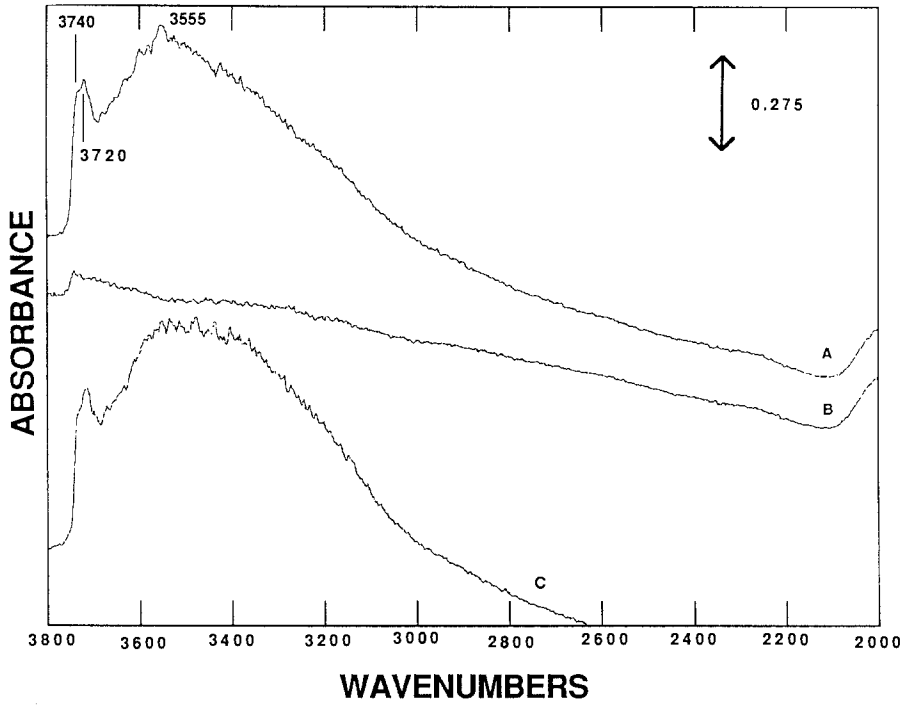

Fig. 3. Infrared spectra of 6.4 wt% Mo/SiO_2: (A) after pressing the wafer and placing in the IR cell in the hydrated (and ambient) state, (B) after heating to 873 K in hydrocarbon-free air, and (C) after rehydrating with H_2O vapor at 298 K.

results over silica gels [10,11], the broad feature observed for the ambient sample (fig. 1A) that is centered near 3500 cm^{-1} and has been associated with hydrogen-bonded silanols, was attenuated upon heating above 673 K. The intensity of the remaining absorbance at 3742–3745 cm^{-1} that is associated with isolated silanol groups [10] was not appreciably affected by heating to 923 K.

Figs. 3 and 4 present the IR spectra recorded over Mo^{6+}/SiO_2 in the hydrated and in the dehydrated states. The samples were heated to 873 K for 1 h to dehydrate the molybdena. Spectrum 3A was recorded after loading the wafer into the IR cell; it is similar to spectrum 1A in that it has the isolated silanol band at 3740 cm^{-1} and the broad hydrogen-bonded feature centered at 3555 cm^{-1}. A second absorbance was observed at 3720 cm^{-1} for hydrated Mo/SiO_2 samples; this could be associated with Si–OH interacting with Mo_7 clusters. Heating silica alone to 873 K removed the hydrogen-bonded silanol feature but did not dehydroxylate the silica (fig. 2). Heating Mo^{6+}/SiO_2 to 873 K resulted in nearly complete attenuation of the isolated silanol band at 3740 cm^{-1}. Rehydration of the sample with H_2O restored both the isolated silanol and hydrogen-bonded silanol features (spectrum 3C). Dehydration of the sample a second time (spectrum 4A) led to attenuation of the isolated silanol absorbance band. Rehydration with D_2O led to the formation of absorbance bands

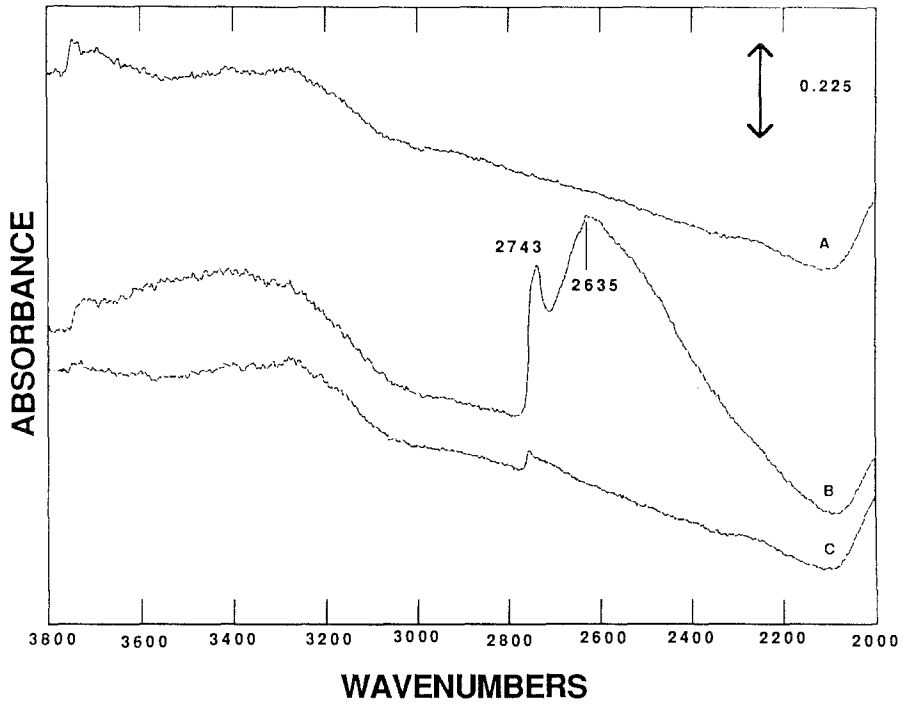

Fig. 4. Infrared spectra of 6.4 wt% Mo/SiO_2: (A) after dehydrating the rehydrated sample (fig. 3C) by heating in hydrocarbon-free air at 873 K, (B) after rehydrating the sample with D_2O vapor at 298 K, and (C) after dehydrating the D_2O-treated sample by heating to 873 K.

at 2743 and 2635 cm^{-1} that are associated with the deuterated analogs of the isolated silanol and hydrogen-bonded silanol groups. No appreciable isolated OH bands were observed following rehydration with D_2O. Dehydration of the D_2O-treated sample (spectrum 4C) resulted in loss of the OD absorbance modes and a spectrum that was similar to the other dehydrated spectra in figs. 3 and 4.

4. Discussion

Morrow and McFarlan have determined that hydroxylated silicas contain about 1.1 isolated silanols/nm^2 [11]. 6.4 wt% Mo/Davison 952 silica translates into about 1.3 Mo/nm^2. As shown in figs. 3 and 4, when the samples were dehydrated and the molybdena spread onto the silica to form isolated Mo^{6+} cations, the isolated Si–OH silanol absorbance intensity was completely attenuated. The similar isolated Mo^{6+} and isolated silanol surface densities, and the silanol absorbance attenuation with spreading indicate that the isolated Mo^{6+} cations titrate and occupy the isolated silanol sites. When D_2O was used to rehydrate the dehydrated/isolated Mo^{6+} sample, Si–OD rather than Si–OH

absorbance bands were formed. The formation of Si–OH from H_2O, and Si–OD from D_2O, indicates that the isolated silanol groups (Si–OH or Si–OD) were consumed during the spreading of Mo^{6+} onto the silica surface.

The results presented here provide direct evidence for the role of Si–OH in the spreading of molybdena onto silica and also support a model in which isolated silanols are the sites for attachment of isolated Mo^{6+} cations, with at least H (or D) being displaced from the silanol group during spreading/attachment. The facts that isolated silanol groups are consumed during spreading and that both aerosil and silica gel forms of SiO_2 have similar isolated silanol densities (1.1 nm^{-2}) suggest a limit beyond which spreading of Mo^{6+}, from the heptamolybdate cluster, should be observed on SiO_2. A silica surface possesses isolated silanols, interacting silanols and siloxane linkages. The IR results permit us to propose attachment at the isolated silanol sites, they do not reveal the manner of attachment. Since the isolated Mo^{6+} structures will have several linkages to the surface, the interacting silanols and possibly cleaved-siloxane linkages are likely to participate in the bonding.

Acknowledgement

This work was supported by the US Department of Energy, Office of Basic Energy Sciences.

References

[1] C.C. Williams, J.G. Ekerdt, J.-M. Jehng, F.D. Hardcastle, A.M. Turek and I.E. Wachs, J. Phys. Chem. 95 (1991) 8781.
[2] M. de Boer, A.J. van Dillen, D.C. Koningsberger, J.W. Geus, M.A. Vuurman and I.E. Wachs, Catal. Lett. 11 (1991) 227.
[3] H. Jeziorowski, H. Knözinger, P. Grange and P. Gajardo, J. Phys. Chem. 84 (1980) 1825.
[4] L. Rodrigo, K. Marcinkowska, A. Adnot, P.C. Roberge, S. Kaliaguine, J.M. Stencel, L.E. Makovsky and J.R. Diehl, J. Phys. Chem. 90 (1986) 2690.
[5] C.P. Cheng and G.L. Schrader, J. Catal. 60 (1979) 276.
[6] N. Kakuta, K. Tohji and Y. Udagawa, J. Phys. Chem. 92 (1988) 2583.
[7] R. Thomas, M.C. Mittelmeijer-Hazeleger, F.P.J.M. Kerkhof, J.A. Moulijn, J. Medema and V.H.J. de Beer, in: *Proceedings of the Climax 3rd International Conference on Chemistry and Uses of Molybdenum*, Climax Molybdenum Co., Ann Arbor, MI, 1979, p. 85.
[8] J. Leyrer, D. Mey and H. Knözinger, J. Catal. 124 (1990) 349.
[9] N. Spencer, J. Catal. 109 (1988) 187.
[10] A.J. McFarlan and B.A. Morrow, J. Phys. Chem. 95 (1991) 5388.
[11] B.A. Morrow and A.J. McFarlan, Langmuir 7 (1991) 1695.