

# Monolayer dispersion of molybdenum on silica

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Laser Raman spectroscopy (LRS) was used to characterize the hydrated and dehydrated states of surface-supported  $\text{Mo}^{6+}$  on Davison 952 silica gel. Silica-supported Mo samples were prepared from  $\text{MO}_2(\eta^3\text{-C}_3\text{H}_5)_4$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ . Metal loadings of 5.1–7.8 wt% Mo were studied. Crystallites of  $\text{MoO}_3$  were not observed at these high loadings. An upper limit for dispersing dehydrated, isolated  $\text{Mo}^{6+}$  was found at about 1 Mo atom/ $\text{nm}^2$ , which corresponds to the isolated silanol density of silica.

**Keywords:** Spreading; dehydration; molybdenum oxide; silica; infrared spectroscopy; Raman spectroscopy; preparation of oxides

## 1. Introduction

There has been a considerable interest in the literature regarding the synthesis and characterization of silica-supported molybdena. The utility of molybdena on silica catalysts has driven research toward the production of catalysts that have a high percentage of molybdena in a dispersed state while at the same time minimizing the formation of crystalline  $\text{MoO}_3$  [1–3]. Recent studies conducted by Williams et al. [2] have shown, at 6.4 wt% Mo, that  $\text{Mo}^{6+}$  will undergo a transformation from a hydrated polyanionic structure to a dehydrated isolated species over silica when the catalyst is dehydrated.

Raman spectroscopy has been used to characterize the hydrated polyanionic and dehydrated, isolated surface  $\text{Mo}^{6+}$  structures on silica, as well as crystalline  $\text{MoO}_3$  [2–4]. Raman studies have shown that  $\text{MoO}_3$  crystallites do not spread on the surface of  $\text{SiO}_2$  [1,5]. Stampfl et al. [1] have reasoned that the  $\text{MoO}_3\text{-SiO}_2$

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interaction is not sufficient to allow an appreciable amount of  $\text{MoO}_3$  to disperse. When  $\text{Mo}/\text{SiO}_2$  was prepared from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ , the formation of crystalline  $\text{MoO}_3$  was observed at very low weight loadings (0.4 wt% Mo) [2]. Less conventional techniques involving non-aqueous organometallic precursors can be employed to suppress the formation of crystallites. Various researchers have employed  $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$  and  $\text{Mo}_2(\eta^3\text{-C}_5\text{H}_5)_4$  on  $\text{SiO}_2$  to synthesize catalysts that have higher dispersions and at the same time no crystalline  $\text{MoO}_3$  [2,6–9]; Williams et al. [2] reported no crystallites up to 6.4 wt% Mo. De Boer et al. [3] avoided crystallite formation at 3.7 wt% Mo by exchanging  $\text{Mo}^{3+}$  with silica.

Morrow and McFarlan [10] have determined that, regardless of the type of silica used, the isolated surface silanol concentration is approximately  $1.1/\text{nm}^2$ . In terms of Mo, a loading of 6.4 wt% translates to a density of  $1.3/\text{nm}^2$ . It has been determined that isolated surface silanol groups play a direct role in the spreading of  $\text{Mo}^{6+}$  with H being displaced from the silanol group by the Mo cation [11]. These two studies [10,11] suggest an upper limit for dispersing  $\text{Mo}^{6+}$ . Our synthetic techniques involving organometallic precursors, namely  $\text{Mo}_2(\eta^2\text{-C}_3\text{H}_5)_4$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$  yield high dispersions of  $\text{Mo}^{6+}$  on  $\text{SiO}_2$  with no crystallite formation, permitting us to quantify the Mo loading at which a monolayer coverage of the Mo cation can be attained. We report here a relation between isolated silanol density and monolayer dispersion of  $\text{Mo}^{6+}$ .

## 2. Experimental

Davison 952 silica gel ( $280 \text{ m}^2/\text{g}$ ) was used in the preparation of the  $\text{Mo}^{6+}/\text{SiO}_2$  samples after it had been washed in dilute sulfuric acid to remove calcium and sodium impurities [12]. Following acid-washing, the surface area of the silica gel was  $330 \text{ m}^2/\text{g}$ .  $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$  was prepared from  $\text{C}_3\text{H}_5\text{MgBr}$  and  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$  following the procedure of Candlin and Thomas [8]. The  $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$  was synthesized from  $\text{Mo}(\text{CO})_6$  (Aldrich, 98%) and glacial acetic acid. Additional details of this synthesis have been described elsewhere [2]. The  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$  precursor was prepared from  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$  (Aldrich, 98%) as prescribed by Curtis et al. [13].

The silica was evacuated at  $375^\circ\text{C}$  for 30 min followed by Ar (Liquid Carbonic, 99.999%) purge at similar conditions to remove all physisorbed water and to render all surface silanols isolated. The  $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$  catalysts were prepared according to Williams et al. [2]. Solid  $(\eta^2\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$  was dissolved in anhydrous benzene that had been dried for several days over sodium/benzophenone. This solution was then introduced to the pretreated silica at  $25^\circ\text{C}$  and allowed to react for 1 h during which the benzene was allowed to evaporate by purging the mixture with Ar (Liquid Carbonic, 99.999%). The sample was then ramped at  $10^\circ\text{C}/\text{min}$  in pure  $\text{H}_2$  (Liquid Carbonic, 99.999%) to

550°C and held at this temperature for 1 h. After cooling, the samples were calcined in pure O<sub>2</sub> (Liquid Carbonic, 99.999%) at 500°C for 1 h.

The procedure and apparatus used to determine the Mo content of the samples prepared from Mo<sub>2</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>4</sub> and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub> are described elsewhere [2]. Weight loadings obtained from these preparations ranged from 5.1 to 7.8 wt% Mo. The techniques for obtaining the hydrated and dehydrated Raman spectra are described by De Boer et al. [3].

Transmission infrared (IR) spectra were obtained with a Digilab FTS-15/90 FTIR spectrometer. Spectra were obtained at a resolution of 2 cm<sup>-1</sup> after 50 scans. A stainless steel cell coupled to a quartz furnace, capable of thermal treatments up to 1000°C, was employed. A magnetically coupled sample transfer wand was used to manipulate the sample from the heated zone to the IR beam where samples could be collected at room temperature. The cell could be

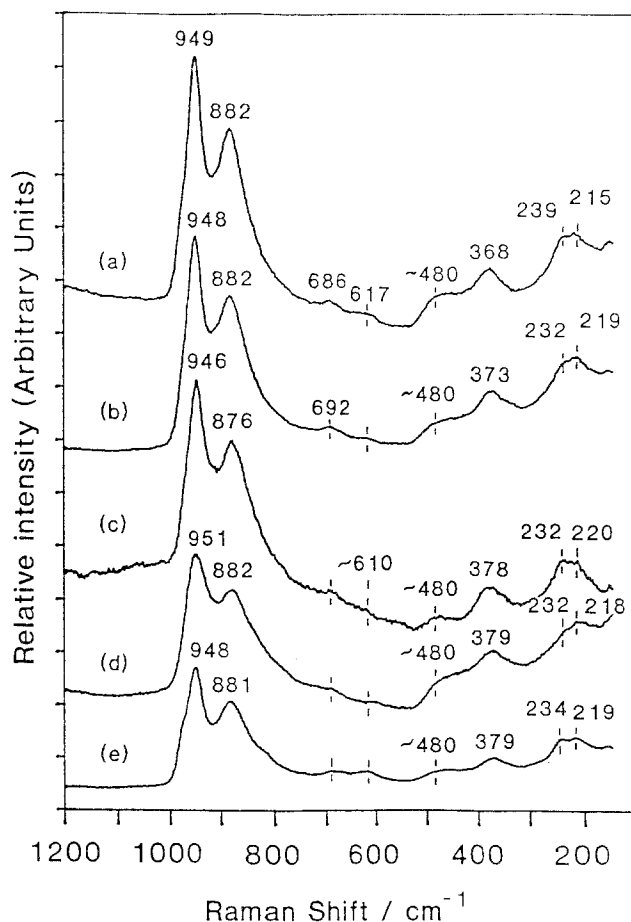


Fig. 1. Raman spectra of Mo<sup>6+</sup>/SiO<sub>2</sub> under ambient conditions prepared from Mo<sub>2</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>4</sub>: (a) 7.8 wt% Mo<sup>6+</sup>/SiO<sub>2</sub>, (b) 6.7 wt% Mo<sup>6+</sup>/SiO<sub>2</sub>, (c) 6.4 wt% Mo<sup>6+</sup>/SiO<sub>2</sub>, (d) 5.1 wt% Mo<sup>6+</sup>/SiO<sub>2</sub>, and prepared from (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub> (e) 5.1 wt% Mo<sup>6+</sup>/SiO<sub>2</sub>.

purged with a gas mixture at a pressure of 1 atm or evacuated with a mechanical pump.

Approximately 60 mg of each sample was pressed at a pressure of 5000 psi into self-supporting wafers with diameters of 1.7 cm. The wafers were then placed in a disk support ring. Following installation in the IR cell, the wafers were dehydrated at 650°C for 1 h in He (99.99 + %).

### 3. Results

In order to facilitate interpretation of the results, the Raman absorbances for the surface Mo structures are assigned below.  $\text{Mo}^{6+}/\text{SiO}_2$  species have been identified as follows. The  $\text{Mo}_7\text{O}_{24}^{6-}$  species associated with the hydrated, ambi-

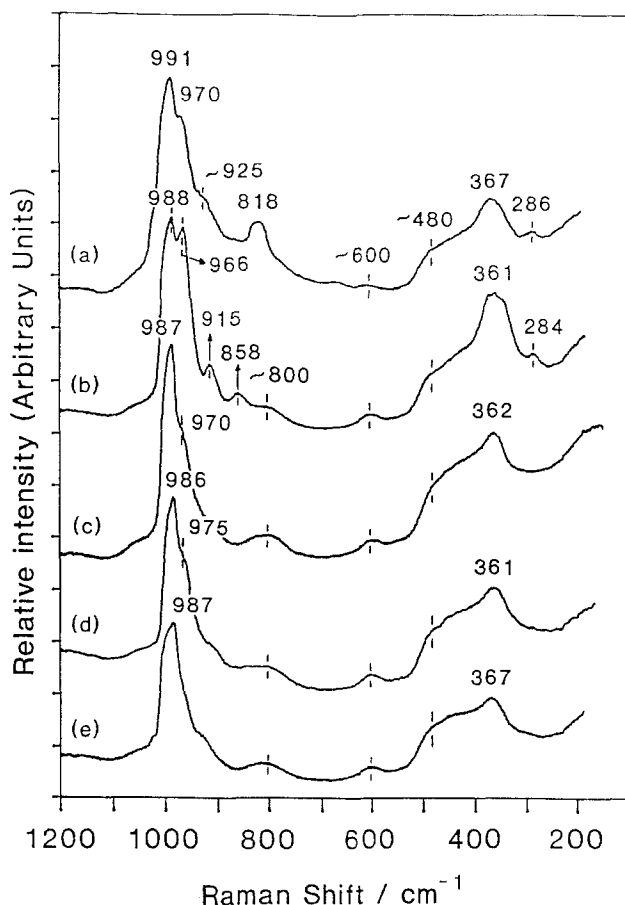


Fig. 2. Raman spectra of  $\text{Mo}^{6+}/\text{SiO}_2$  under dehydrated conditions prepared from  $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ : (a) 7.8 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , (b) 6.7 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , (c) 6.4 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , (d) 5.1 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , and prepared from  $(\eta^5\text{-C}_3\text{H}_5)_2\text{Mo}_2(\text{CO})_4$  (e) 5.1 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ .

ent conditions has been characterized as having broad features at 965–944, 880, 380–370, and 240–210  $\text{cm}^{-1}$  [2]. When  $\text{Mo}^{6+}/\text{SiO}_2$  undergoes dehydration to isolated  $\text{Mo}^{6+}$ , an intense absorbance is observed at 986–991  $\text{cm}^{-1}$  [2,3]. The silica support exhibits Raman absorbances at  $\approx 820$  and 457  $\text{cm}^{-1}$  associated with siloxane linkages and 605 and 488  $\text{cm}^{-1}$  due to three- and four-fold siloxane rings [3].

Figs. 1 and 2 present the Raman spectra of  $\text{Mo}^{6+}/\text{SiO}_2$  samples with Mo loadings ranging from 5.1 to 7.8 wt%. The spectra of fig. 1 represent samples in the hydrated, or ambient, state. The spectra (fig. 1) are characteristic of the supported heptamolybdate species [2,3]. The Mo–O bending and stretching modes are identified by absorbances at 368–379  $\text{cm}^{-1}$  and 946–951  $\text{cm}^{-1}$ , respectively. The Mo–O–Mo modes can be identified by bands at 880  $\text{cm}^{-1}$  (asymmetric stretching) and 220  $\text{cm}^{-1}$  (bending). Crystalline  $\text{MoO}_3$  exhibits sharp absorbances at 995, 819, 666, 417, 377, 338, 291, 248, 217, 198, and 160  $\text{cm}^{-1}$  with the band at 819  $\text{cm}^{-1}$  being the most intense. The absence of this intense absorbance at 819  $\text{cm}^{-1}$  in figs. 1 and 2 verifies that these samples are totally devoid of crystalline  $\text{MoO}_3$  in both the ambient and in situ states.

The spectra of fig. 2 represent samples in the dehydrated state. The appearance of the strong absorbance at 986–991  $\text{cm}^{-1}$ , corresponding to the isolated  $\text{Mo}^{6+}$  species, signals the destruction of the large polymolybdate structures and

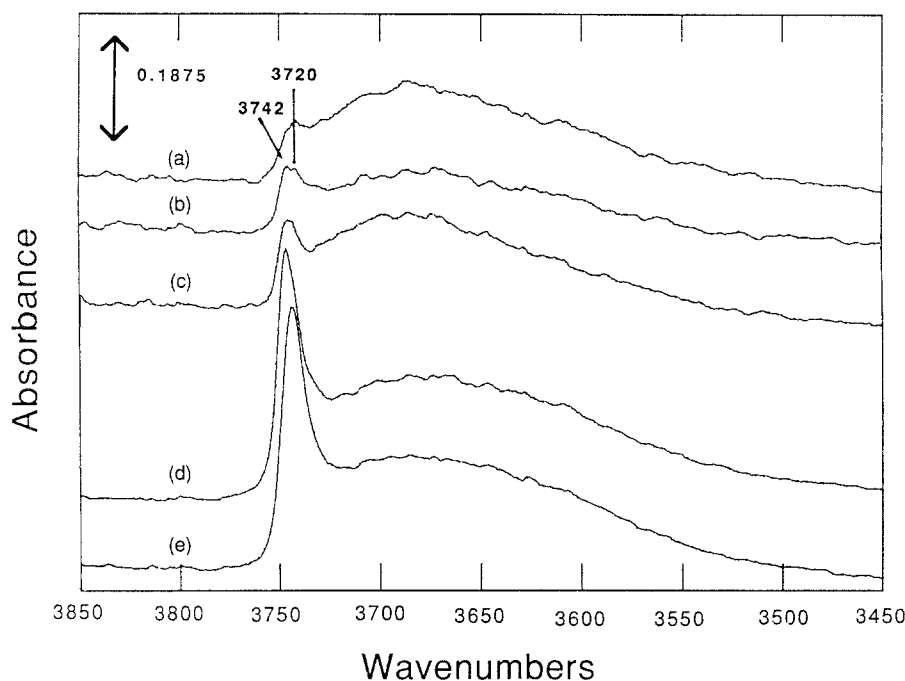


Fig. 3. FTIR spectra  $\text{Mo}^{6+}/\text{SiO}_2$  under dehydrated conditions prepared from  $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ : (a) 7.8 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , (b) 6.7 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , (c) 6.4 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , (d) 5.1 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ , and prepared from  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$  (e) 5.1 wt%  $\text{Mo}^{6+}/\text{SiO}_2$ .

the dispersion of  $\text{Mo}^{6+}$  to an isolated structure. The lack of any absorbance at  $220\text{ cm}^{-1}$  also signifies the disappearance of the polyanions. When  $\text{Mo}^{6+}$  loadings approach and surpass 6.4 wt%, the anticipated coverage for complete surface silanol occupation, the emergence of a new band at  $\approx 970\text{ cm}^{-1}$  is noted. This is ostensibly due to the inability of the heptamolybdate species to spread because of the limited number of available silanols with which the Mo cation is able to react.

Fig. 3 presents the IR spectra of the  $\text{Mo}^{6+}/\text{SiO}_2$  samples in the dehydrated state with Mo loadings ranging from 5.1 to 7.8 wt%. During dehydration, when  $\text{Mo}^{6+}$  disperses on the silica surface, the complete consumption of surface silanols is observed at the higher Mo weight loadings. This phenomenon is manifest in the nearly complete attenuation of the isolated silanol absorbance at  $3742\text{ cm}^{-1}$ .

#### 4. Discussion

A model of the hydration/dehydration spreading phenomena of  $\text{Mo}^{6+}$  on silica has previously been reported [2,3]. A  $\text{Mo}^{6+}/\text{SiO}_2$  catalyst in the hydrated state contains adsorbed water that solvates the  $\text{Mo}_7\text{O}_{24}^{6-}$  species and renders a stable surface structure. When the sample is dehydrated and all adsorbed water is removed, the polyanion becomes unstable and hence disperses. As the amount of surface-supported  $\text{Mo}^{6+}$  approaches and exceeds  $\approx 1/\text{nm}^2$ , it becomes increasingly more difficult to spread the  $\text{Mo}^{6+}$  cation due to decreased probability of the cations finding available silanols to displace. The nearly complete attenuation of the surface silanol band at  $3742\text{ cm}^{-1}$  in the IR spectra of fig. 3 demonstrates that there are no more silanols with which the Mo cation can react.

The coordination of the isolated  $\text{Mo}^{6+}$  surface species is not immediately apparent from the Raman studies. At present, no conclusive evidence has been presented to support the existence of a tetrahedrally or octahedrally coordinated isolated  $\text{Mo}^{6+}$  structure. It has been proposed that the Mo cation assumes a distorted octahedral configuration [3].

The dehydrated  $\text{Mo}^{6+}$  cations are no longer in the  $\text{Mo}_7\text{O}_{24}^{6-}$  heptamolybdate, polyanionic structure as evidenced by the absence of any absorbance in the  $220\text{ cm}^{-1}$  (Mo–O–Mo bending mode) region and the emergence of a new Raman absorbance at  $960\text{--}975\text{ cm}^{-1}$ . We suggest that this absorbance may correspond to a heretofore uncharacterized Mo cluster that is different from the heptamolybdate anion that is present in the hydrated state and is stabilized by the adsorbed water.

These results provide evidence that the techniques of synthesis outlined in this paper yield dispersed molybdena on silica that are totally free of crystalline  $\text{MoO}_3$ . They also provide additional support of the model in which isolated

surface silanol groups facilitate the spreading of the  $\text{Mo}^{6+}$  cation [11]. In a previous publication, we furnished results that suggested a limit beyond which the dehydration/spreading phenomena should be observed. This paper quantifies this limit and yields insight into the behavior of the supported  $\text{Mo}^{6+}$  once the limit has been surpassed.

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