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Photoreducibility of Mo/SiO_2 Catalysts with CO

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The photoreduction of supported Mo/SiO_2 catalysts by CO has been investigated at room temperature as a function of Mo coverage and wavelength of the incident UV irradiation. The CO adsorbed on photoreduced Mo ions has been investigated by IR spectroscopy. In the literature, it has been reported that CO photoreduction of Mo/SiO_2 catalysts leads to the formation of Mo^{4+} and Mo^{5+} ions. Results of this study indicate that CO photoreduction also leads to the formation of Mo ions in valence states lower than Mo^{4+}. In particular, the pairs of IR bands observed at 2100, 2135 cm^{-1} and 2075, 2125 cm^{-1} were attributed to pairs of CO molecules adsorbed on Mo^{4+} or Mo^{3+}, and Mo^{2+} sites, respectively. These sites are assumed to be formed from the CO photoreduction of dimeric surface molybdates. Another IR band observed at 2035 cm^{-1} may be attributed to the stretching vibrations of a CO molecule adsorbed in a bridged configuration between two adjoining Mo^{2+} or to a single CO adsorbed linearly on Mo^{2+} sites. Thus, our results indicate that the low-temperature CO photoreduction is a complex process and that Mo ions in several valence and coordination states may be formed simultaneously during CO photoreduction in Mo/SiO_2 catalysts.

INTRODUCTION

Supported molybdena catalysts are of considerable current interest. Study of the valence state, coordination of Mo ions on these catalysts, and how the surface changes with pretreatment and reduction is often useful in the understanding of various reactions promoted by these catalysts. Thermal reduction properties of these catalysts have been investigated widely (*1–8*). High-temperature (400–600°C) reduction of Mo/Al_2O_3 (*1–4*) and Mo/SiO_2 (*5–8*) catalysts by H_2, CO, or hydrocarbons has been shown to lead to the formation of Mo ions in different coordination and valence states (Mo^{5+}, Mo^{4+}, Mo^{3+}, Mo^{2+}). On the other hand, it has been reported that Mo/SiO_2 catalysts could be reduced selectively to Mo^{5+} or Mo^{4+} state by the low-temperature photoreduction with H_2 or CO (*9–11*). It was suggested that the photoreduced Mo^{5+} (H_2, $\lambda > 320$ nm) and Mo^{4+} (CO, $\lambda < 340$ nm) are in tetrahedral coordination and it was inferred that the corresponding Mo^{6+} ions in the oxidized catalyst are also in tetrahedral coordination. The tetrahedral configuration of Mo^{4+} ions on CO-photoreduced catalysts was assumed to be maintained by strongly adsorbed CO molecules occupying the oxygen vacancies.

The properties of low-temperature CO-photoreduced Mo/SiO_2 catalysts have been shown to differ significantly from thermally reduced catalysts (*9–11*). The CO-photoreduced Mo/SiO_2 catalysts have been shown to exhibit very strong reducing properties (*9–11*). The strong reducing properties of these catalysts are evidenced by their ability to reduce N_2O at −120°C, CO_2 at 90°C, and H_2O at 150°C (*9–11*). It was suggested that the very high reducing properties of these catalysts are due to the unique properties of Mo^{4+} ions formed during CO photoreduction, and that the differences between the thermally and CO-photoreduced catalysts are due to the differences in the coordination state of reduced Mo ions (*9–11*).

The photocatalytic properties of supported molybdena catalysts have been investigated by several workers (*12–16*). It has been shown that these properties are

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sensitive to coordination of Mo ions in the surface molybdates and it was suggested that these properties may be used for the characterization of the surface (*12–16*).

The work reported herein investigates the CO photoreducibility of Mo/SiO$_2$ catalysts at room temperature as a function of Mo coverage and wavelength of the incident irradiation and gives IR spectroscopic results of CO adsorbed on photoreduced Mo ions.

EXPERIMENTAL

Catalyst Preparation

The details of the methods used in catalyst preparation are described elsewhere (*17*). Two series of Mo/SiO$_2$ catalysts were prepared using commercial-grade SiO$_2$ (Fisher S-662) with 99.9% minimum purity. The total pore volume was 0.35 cm^3 g^{-1}. The SiO$_2$ variety used exhibits a very narrow pore size distribution in the region of narrow pores with a sharp maximum at 2.0 nm.

The first series of catalysts was prepared by the conventional pore volume impregnation technique (impregnated catalysts) using aqueous solutions of high purity $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Anachemia AC-630). The second series of catalysts was prepared by the reaction of $Mo(\eta^3\text{-}C_3H_5)_4$ complex in pentane (certified, Fisher, P-393) with the superficial OH groups of the SiO$_2$ support at ambient temperature (fixed catalysts). The two series of catalysts were dried first (impregnated catalysts at 130°C and fixed catalysts at room temperature under vacuum) and then calcined at 500°C in air for 15 h.

UV Diffuse Reflectance Spectroscopy

The catalysts were characterized by UV diffuse reflectance spectroscopy using a Perkin–Elmer 559 UV–Vis spectrophotometer equipped with a diffuse reflectance attachment B-258. The catalyst samples were prepared by grinding the catalyst and pressing the powder at 8000 psi into 12-mm-diameter and 2-mm-thick pellets. Spectra were recorded just after calcination of the sample pellets at 500°C for 1 h in the range 210–500 nm against a pure SiO$_2$ reference subjected to the same pretreatment procedure as the sample.

CO Photoreduction

CO photoreduction experiments were conducted in a vibrofluidized bed annular quartz reactor irradiated in the UV region by a medium-pressure mercury lamp (Hanovia 673A36, 550 W). The lamp was enclosed in a water-cooled jacket made of quartz ($\lambda \geq 180$ nm) or Pyrex ($\lambda \geq 280$ nm). The water jacket materials served as filters for the incident UV irradiation. The inlet gas to the reactor was a 10% CO in argon mixture free of O$_2$ and CO$_2$ traces. The transient CO$_2$ signal that appeared at the reactor outlet was monitored continuously by leak valve admission to a quadrupole mass spectrometer (UTI-1000 C) (*18*).

IR Spectroscopy

The nature of the CO adsorbed on CO-photoreduced catalysts was investigated by IR spectroscopy. For these studies a vacuum-tight IR cell was used. Provisions were made so that the IR cell could be attached to a vacuum system during sample treatment. The catalyst samples were investigated in the form of self-supported wafers. These wafers were prepared by grinding 10 mg of precalcined catalyst and pressing the powder in a commercial dye under 20,000 psi in a hydraulic press. The sample wafers can be placed in an aluminium holder which can be supported freely on two glass beams inside the cell. The sample cell could be moved up to the heating section of the cell or it could be positioned between the CaF$_2$ IR windows for spectral recording by simply slanting the cell (*18*). The sample wafers were first calcined *in situ* at 500°C in O$_2$ for 1 h. The IR cell was then evacuated to a pressure below 10^{-5} Torr and was refilled with CO (Matheson Research Grade) up to 10 Torr. The sample wafers were irradiated by a UV beam focused at the sample through the CaF_2 ($\lambda \geq 180$ nm) window in the IR cell. The effect of the wavelength of the incident UV irradiation was investigated by using a Pyrex filter ($\lambda \geq 280$ nm) attached to the CaF_2 windows during the run.

RESULTS

UV Diffuse Reflectance Spectroscopy

The UV spectra of freshly calcined impregnated and fixed Mo/SiO_2 catalysts are given in Figs. 1 and 2. Both types of catalysts exhibit similar absorption bands. Three principal bands are observed. These are centered at 240–260 nm, 260–300 nm, and 300–340 nm. All three bands are observed only at high Mo coverage. At low coverage absorption bands above 300 nm are practically absent, and at very low Mo coverage only the 240- to 260-nm band is present.

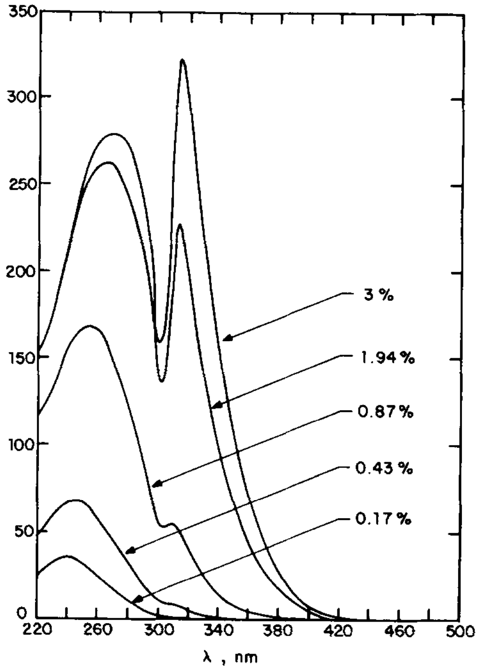


FIG. 2. UV diffuse reflectance spectra of calcined (500°C/air/1 h) fixed Mo/SiO_2 catalysts of various Mo contents.

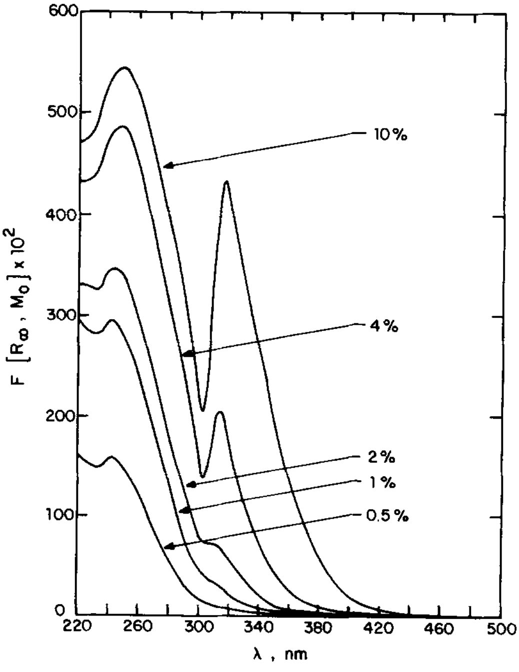


FIG. 1. UV diffuse reflectance spectra of calcined (500°C/air/1 h) impregnated Mo/SiO_2 catalysts of various Mo contents.

It is now generally accepted that tetrahedrally coordinated isolated Mo^{6+} absorb around 220–280 nm and octahedrally coordinated Mo^{6+} as in polymolybdates absorb around 300–340 nm. Elsewhere (*13, 14*) we have suggested that the band at 240–260 nm should be identified with tetrahedrally coordinated isolated Mo^{6+}, the 260- to 300-nm band with the terminal Mo=O groups of surface polymolybdates and/or dimers, and the 300- to 340-nm band with charge transfers involving the Mo–O–Mo bridged groups of the surface polymolybdates. Thus, according to the reported spectra for calcined Mo/SiO_2 catalysts, isolated tetrahedral monomers are abundant at low Mo coverage while surface polymolybdates with Mo in octahedral coordination predominate at high Mo coverage in the freshly calcined catalysts.

Elsewhere (*18–22*) we reported that on hydrated Mo/SiO_2 catalysts, the surface molybdates which are dependent on the Mo coverage include isolated monomers with Mo in tetrahedral coordination, a highly dispersed phase of tridimensional isopolymolybdates, and silicomolybdic acid species with Mo in octahedral coordination and crystalline MoO$_3$. On these catalysts the symmetry within the isopolymolybdates, and silicomolybdic acid species is destroyed during O$_2$ calcination at 500°C and may be restored by rehydration of the catalysts at room temperature. The collapse of these polymolybdate clusters is accompanied by a change in the coordination symmetry of Mo ions from octahedral to tetrahedral according to the interpretation of the UV spectra suggested above. However, calcination is not expected to lead to a complete destruction of the polymolybdate structures, since this would necessitate the surface diffusion of molybdates to reform the original structures during hydration at ambient temperature. Thus, it was suggested that the change in the coordination symmetry of Mo ions from octahedral to tetrahedral as seen by UV is due to severe distortions in the octahedral symmetry resulting from the collapse of the tridimensional clusters.

Photoreduction by CO

The CO photoreduction data for impregnated Mo/SiO$_2$ catalysts are shown in Figs. 3–6. The transient CO$_2$ concentration signal observed at the outlet of the reactor as a function of Mo loading is given in Fig. 3 for unfiltered light ($\lambda \geq 180$ nm). The effect of filtering the incident UV irradiation ($\lambda \geq 280$ nm) on the transient CO$_2$ signal is given in Fig. 4 for a 2 wt% Mo/SiO$_2$ catalyst. It can be immediately noticed that filtered light ($\lambda \geq 280$ nm) gives rise to a considerably lower photoreduction of the surface. The total number of surface oxygens (N[O]) photoextractable as CO$_2$ is calculated by

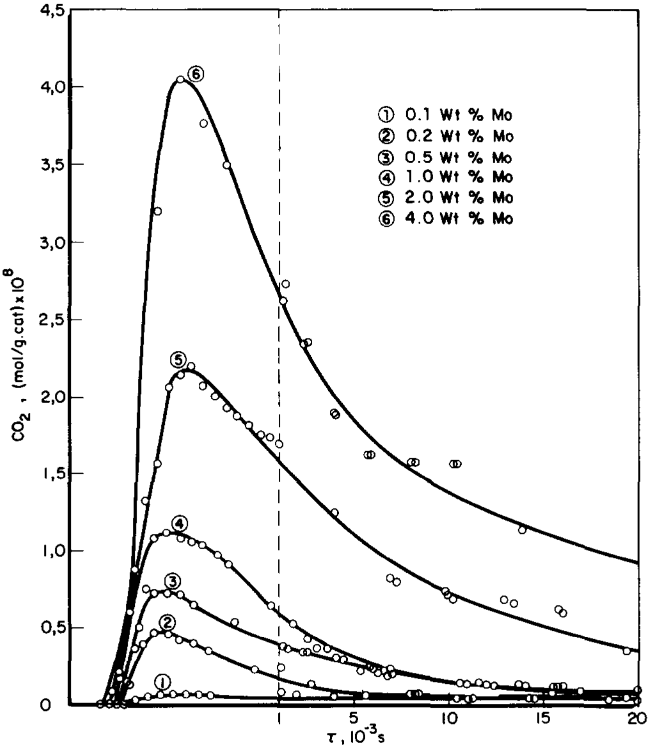


FIG. 3. Transient CO$_2$ response curves obtained during CO photoreduction of impregnated Mo/SiO$_2$ catalysts with unfiltered light ($\lambda \geq 180$ nm) at various Mo contents. (Dotted line indicates the change in scale of the time axis.)

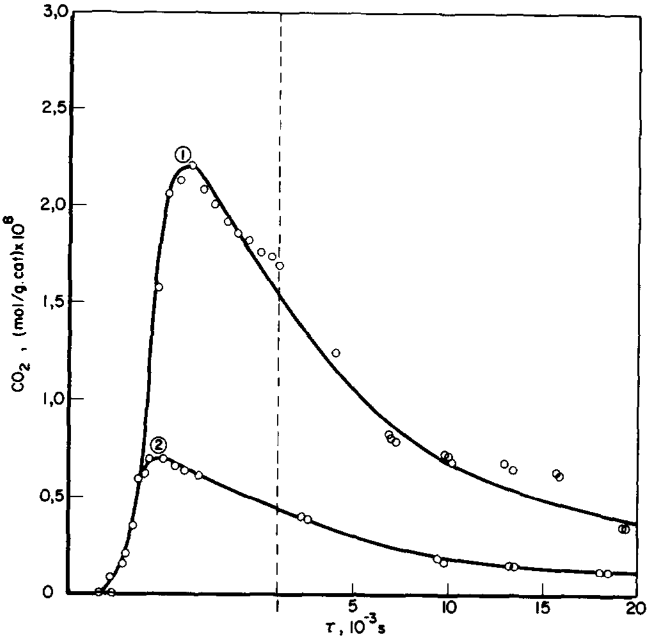


FIG. 4. Transient CO_2 response curves obtained during CO photoreduction of a 2 wt% impregnated Mo/SiO_2 catalyst. (1) Unfiltered light ($\lambda \geq 180$ nm). (2) Filtered light ($\lambda \geq 280$ nm). (Dotted line indicates the change in scale of the time axis.)

integrating the transient CO_2 concentration signal up to 2×10^4 s. These results are shown in Fig. 5 as a function of Mo loading for both filtered and unfiltered light. These data are also represented in terms of the number of surface oxygens photoextractable per Mo atom (N[O]/N[Mo]) and in terms of the average oxidation number as a function of Mo loading in Fig. 6.

As can be seen in Fig. 5, the amount of photoextractable surface oxygen increased up to 4 wt% Mo and then decreased with loading for both filtered and unfiltered light. This behavior results in a net decrease in the N[O]/N[Mo] ratio with increasing loading (Fig. 6A) and is also reflected in the decrease in the degree of reduction (increase in the average oxidation number) with Mo loading.

Figure 6 also shows that significantly more surface oxygen atoms per Mo could be photoextracted by CO photoreduction of the Mo/SiO_2 catalysts with unfiltered light ($\lambda \geq 180$ nm) than with filtered light ($\lambda \geq 280$ nm). At the lowest Mo coverage, about one surface oxygen atom per Mo could be photoextracted with unfiltered light ($\lambda \geq 180$ nm), while at the same Mo coverage only about 0.4 surface oxygen atoms per Mo could be photoextracted with filtered light ($\lambda \geq 280$ nm).

IR Spectroscopy

UV irradiation of Mo/SiO_2 catalysts in the presence of CO ($P_{CO} = 10$ Torr) with unfiltered ($\lambda \geq 180$ nm) or filtered light ($\lambda \geq 280$ nm) gives rise to two intense IR bands centered at 2075 and the 2125 cm^{-1} and to a third weak band at 2035 cm^{-1} (Figs. 7–9). Irradiation of pure SiO_2 wafers in the presence of CO does not lead to the appearance of similar IR bands. Evacuation of the catalyst samples removed the first two bands (2075 and 2125 cm^{-1}) but not the weak band at 2035 cm^{-1} which in fact increased in intensity considerably (Figs. 7, 8). The 2075- and 2125-cm^{-1} bands reappeared upon exposure of the evacuated

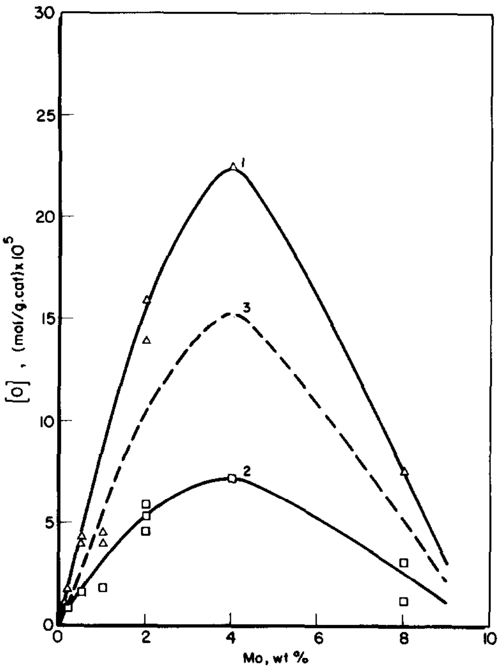


FIG. 5. Amount of oxygen atoms photoextractable as CO$_2$ during CO photoreduction of impregnated Mo/SiO$_2$ catalysts as a function of Mo loading. (1) Unfiltered light ($\lambda \geq 180$ nm). (2) Filtered light ($\lambda \geq 280$ nm). (3) Difference curve [(1) − (2)].

sample to fresh CO in the dark and the intensity of the 2035-cm^{-1} band decreased concomitantly. The intensities of the 2075- and 2125-cm^{-1} bands that reappeared upon exposure of the evacuated samples to fresh CO are somewhat less intense than the original bands and may be increased by reirradiating the sample. These data indicate that the observed IR bands stem from CO adsorbed on photoreduced Mo sites. The effect of filtering the incident UV irradiation on the observed IR spectra is reported in Fig. 9. Filtering of the incident UV irradiation using a Pyrex filter ($\lambda \geq 280$ nm) caused a significant decrease in the intensity of the 2075- and 2125-cm^{-1} bands, while no new bands are observed (Fig. 9). This indicates that similar CO adsorption sites (reduced Mo sites with the same oxidation state and the coordination environment) are formed during CO photoreduction of Mo/SiO$_2$ catalysts with both filtered ($\lambda \geq 280$ nm) and unfiltered light ($\lambda \geq 180$ nm).

The general behavior of the 2075-, 2125-, and 2035-cm^{-1} bands indicates a close rela-

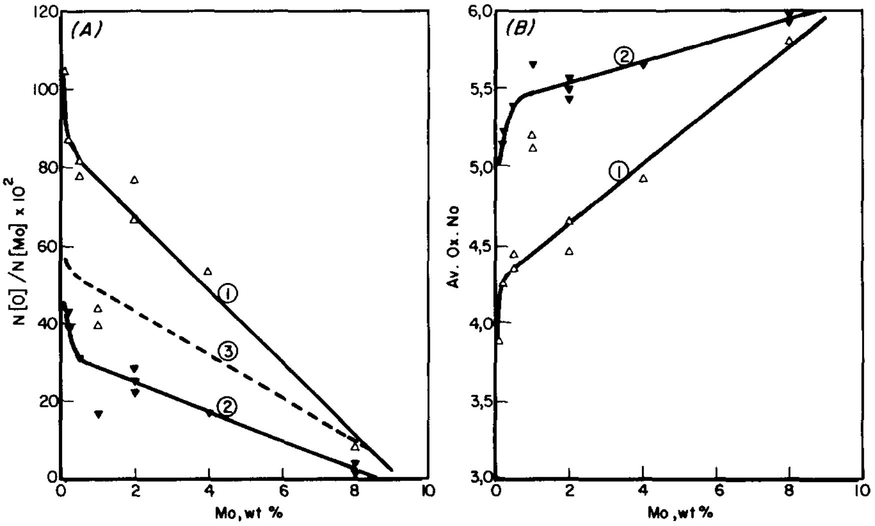


FIG. 6. Co photoreduction data for impregnated Mo/SiO$_2$ catalysts. (A) The molar ratio N[O]/N[Mo] (oxygen atoms photoextractable as CO$_2$ per Mo atom) as a function of Mo loading. (B) The average oxidation number of photoreduced Mo/SiO$_2$ catalysts as a function of Mo loading. (1) Unfiltered light ($\lambda \geq 180$ nm). (2) Filtered light ($\lambda \geq 280$ nm). (3) Difference curve [(1) − (2)].

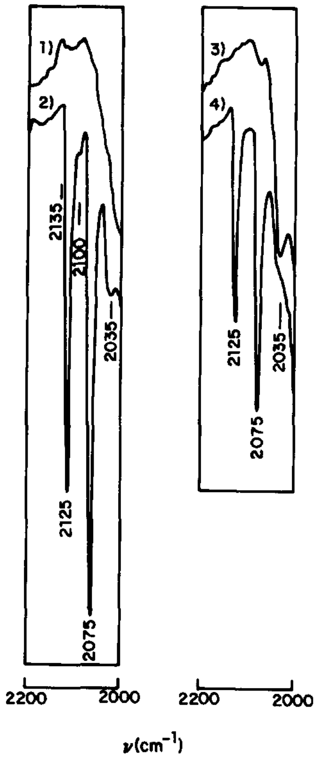
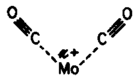


FIG. 7. IR spectra of CO adsorbed on a photoreduced impregnated 4 wt% Mo/SiO_2 catalyst. (1) Calcined catalyst sample in CO (P_{CO} = 10 Torr). (2) After irradiation of the catalyst sample with unfiltered light (λ ≥ 180 nm) for 1 h in CO. (3) Sample evacuated of CO. (4) CO reintroduced (P_{CO} = 10 Torr).

tionship between these bands. The two intense bands at 2075- and 2125-cm^{-1} appear and disappear simultaneously and are predominant at high CO pressures while the 2035-cm^{-1} band predominates at low CO pressures. Figure 10 shows the variation of the adsorbance ratio of the two bands at 2075 and 2125 cm^{-1} as a function of loading for both fixed and impregnated Mo/SiO_2 catalysts. Given the experimental scatter of the points in Fig. 10, this ratio appears to be constant at 0.77 ± 0.06. Given the large variation observed in the oxidation number for CO-photoreduced impregnated Mo/SiO_2 catalysts with loading (Fig. 6B), the insensitivity of the peak absorbance ratio A_{2125}/A_{2075} to loading and to the mode of catalyst preparation suggests that these two bands have a common origin, and they may stem from pairs of CO molecules adsorbed on the same photoreduced Mo^{x+} sites. The two bands could be attributed to the symmetric and antisymmetric stretching vibrations of these two molecules (*18, 22, 23*).



The 2035-cm^{-1} band that is predominant at low CO pressures may stem from single CO molecules adsorbed on the same photoreduced Mo^{x+} sites as the pairs of CO are removed during evacuation of the sample at room temperature. Since the removal of a

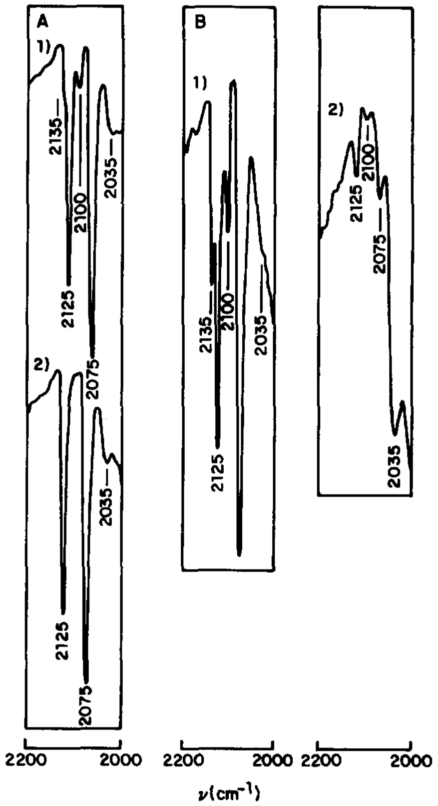


FIG. 8. IR spectra of CO adsorbed on a photoreduced, fixed 5.3 wt% Mo/SiO_2 catalyst. (A) After irradiation of the catalyst sample with unfiltered light (λ ≥ 180 nm) in CO (P_{CO} = 10 Torr). (1) After 1 h; (2) after 2 h. (B) After irradiation of the catalyst sample with filtered light (λ ≥ 280 nm) in CO (P_{CO} = 10 Torr). (1) After 1 h; (2) sample evacuated of CO for 5 min.

CO molecule from an adsorbed pair on the same site should result in a decrease in the ν_{C-O} for the remaining adsorbed CO molecule, the 2035-cm^{-1} band may be associated with a linearly bonded CO on the same site. It is also equally possible that this band results from a single CO adsorbed on two Mo^{x+} sites in a bridged configuration (*23*).

Figure 11 shows the variation of the peak absorbances for the 2125- and 2075-cm^{-1} bands as a function of loading for both fixed and impregnated Mo/SiO$_2$ catalysts. The spectra were recorded after UV irradiation of the samples for 1 h in CO (P_{CO} = 10 Torr). Longer irradiation times did not lead to any significant increase in the peak intensities. Surprisingly, the observed variation in the peak absorbances of the 2125- and 2075-cm^{-1} bands for impregnated Mo/SiO$_2$ catalysts resembles very closely the variation of the CO$_2$ evolved per gram catalyst with loading (compare Figs. 5 and 11). Both these curves show a maximum around 4 wt% Mo. The peak absorbance values, which are proportional to the concentration of reduced Mo^{x+} sites holding CO, decrease with loading at high Mo coverage for both fixed and impregnated Mo/SiO$_2$ catalysts. This indicates that the reduced Mo^{x+} sites holding CO are not formed from the photoreduction of octahedrally coordinated Mo in the collapsed polymolybdates, since UV spectroscopic analysis of these catalysts (Figs. 1 and 2) shows that octahedrally coordinated Mo^{6+} increase with loading.

Apart from the IR absorption bands observed at 2125, 2075, and 2035 cm^{-1}, two other bands centered at 2135 and 2100 cm^{-1} are observed at random (Figs. 7–9). The appearance and the intensity of these bands could not be predicted with any certainty. When these bands are present they can be removed from the spectrum either by prolonged irradiation (Fig. 8) or by evacuation of the sample at room temperature (Fig. 8).

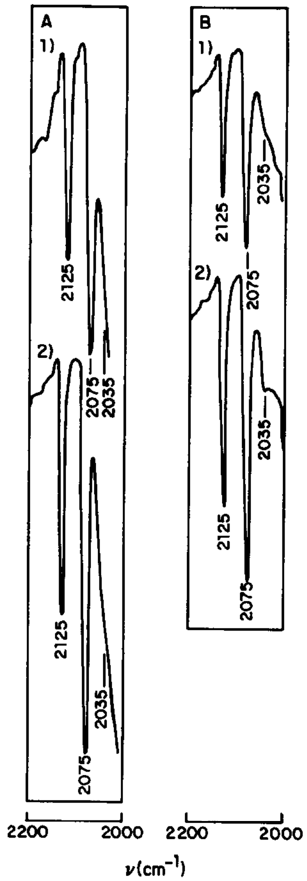


FIG. 9. (A) IR spectra of CO adsorbed on a photoreduced, fixed 1.94 wt% Mo/SiO$_2$ catalyst. (1) After irradiation of the catalyst sample with filtered light ($\lambda \geq 280$ nm) for 1 h in CO (P_{CO} = 10 Torr). (2) After irradiation of the same sample for another hour with unfiltered light ($\lambda \geq 180$ nm). (B) IR spectra of CO adsorbed on a photoreduced, fixed 3 wt% Mo/SiO$_2$ catalyst. (1) After irradiation of the catalyst sample with filtered light ($\lambda \geq 280$ nm) for 1 h in CO (P_{CO} = 10 Torr). (2) After irradiation of a fresh catalyst sample with unfiltered light ($\lambda \geq 180$ nm) for 1 h in CO (P_{CO} = 10 Torr).

The general behavior of these bands parallels the behavior of the 2075- and 2125-cm^{-1} bands. This would suggest that these bands may also have a common origin and may stem from pairs of CO molecules adsorbed on reduced Mo sites (*23*). The frequencies of these bands indicate that the valency states of the reduced Mo sites are higher than those of the Mo^{x+} sites responsible for

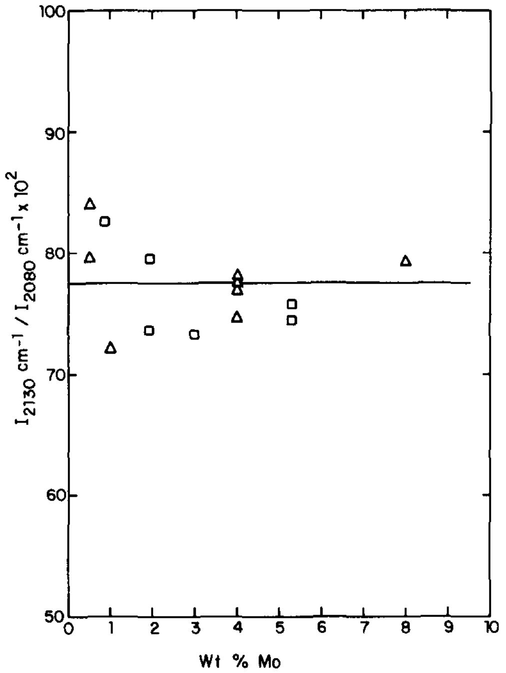


FIG. 10. The peak absorbance ratio (A_{2125}/A_{2075}) of CO stretching bands on Mo/SiO$_2$ catalysts as a function of Mo loading. (△) Impregnated catalysts; (□) fixed catalysts.

the 2075- and 2125-cm^{-1} bands. The lability and the poor reproducibility of these bands indicate the transient nature of the oxidation state of Mo responsible for these bands.

DISCUSSION

Low-temperature photoreductions of Mo/SiO$_2$ catalysts have been studied extensively by Pershin *et al.* (*9*), Shelimov *et al.* (*10*), and Kazansky *et al.* (*11*). Photoreduction of Mo/SiO$_2$ catalysts by H$_2$ ($\lambda \geq 320$ nm) was shown to lead to the reduction of Mo^{6+} states selectively to Mo^{5+} states. From ESR data they concluded that the Mo^{5+} ESR signal with $g_1 = 1.811$, $g_2 = 1.919$, and $g_3 = 1.952$ at 77 K stems from Mo^{5+} ions in distorted tetrahedral coordination, and it was inferred that the corresponding Mo^{6+} ions in the oxidized catalysts are also in tetrahedral coordination. Reduction of Mo/SiO$_2$ catalysts with H$_2$ using unfiltered light ($\lambda \leq 320$ nm) leads to the formation of a mixture of Mo^{4+} and Mo^{5+} ions. On the basis of quantitative measurements of CO$_2$ evolved and the O$_2$

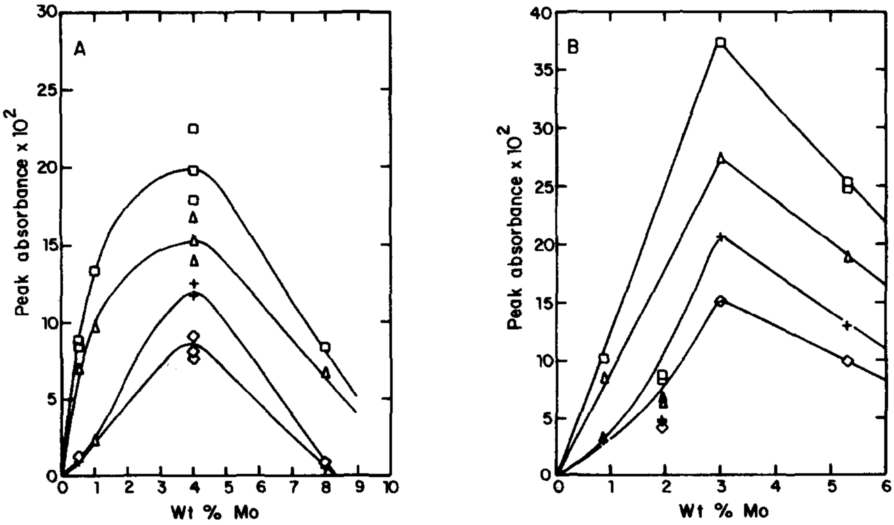
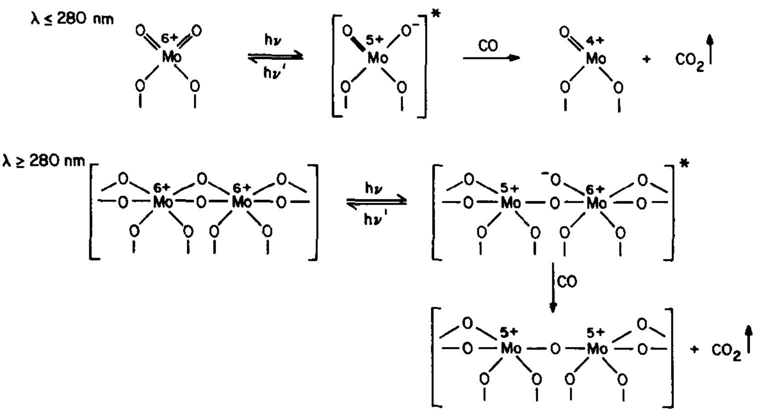


FIG. 11. Variation in the peak absorbance for CO adsorbed on photoreduced Mo/SiO$_2$ catalysts as a function of Mo loading. (A) Impregnated catalysts. (B) Fixed catalysts. Unfiltered light: (△) 2125 cm^{-1}, (□) 2075 cm^{-1}. Filtered light: (◇) 2125 cm^{-1}, (+) 2075 cm^{-1}.

uptake by the reduced catalysts during reoxidation Kazansky *et al.* (*9–11*) concluded that the surface of a 1 wt% Mo/SiO_2 catalyst could be photoreduced quantitatively to the Mo^{4+} state by CO ($\lambda \leq 340$ nm). From UV spectroscopic data of the reduced catalysts they concluded that the Mo^{4+} ions are in tetrahedral coordination. The tetrahedral coordination of the Mo^{4+} ions was assumed to be maintained via the adsorption of a CO molecule. However, it should be mentioned that the interpretation of UV spectroscopic data of reduced supported molybdena catalysts is complex and there are no reliable literature data available to date, on the optical spectra of Mo^{4+} ions in tetrahedral coordination, to substantiate such an assignment. Furthermore, Kazansky *et al.* (*9–11*) also reports that some Mo^{5+} ions in octahedral coordination are also formed during CO photoreduction ($g_\perp = 1.947$, $g_\parallel = 1.875$). They indicate, however, that the concentration of these ions is below 1% of the total Mo content. It is well documented that only a fraction of the reduced Mo^{5+} ions is detected by ESR (*1, 4*). Some Mo^{5+} ions present in a reduced system can escape detection by ESR due to antiferromagnetic coupling in Mo^{+5}–O–Mo^{+5} species that would quench the ESR signal (*1, 4*). This would suggest that the concentration of Mo^{5+} ions present on CO-photoreduced catalysts may be significantly higher than what is reported by Kazansky *et al.* (*9–11*) and also, the possibility of the formation of lower-valent Mo ions through further photoreduction of octahedrally coordinated Mo^{5+} cannot be completely ruled out. Recently, Guglielminotti and Giamello (*23*) have shown that Mo^{2+} sites are formed during CO photoreduction of Mo/SiO_2 catalysts previously reduced thermally (H_2/4 h/450°C).

CO photoreducibility data obtained by us (Fig. 5) show that the amount of photoextractable surface oxygen per gram catalyst decreases with loading at high Mo coverage (>4 wt% Mo). From previous Raman spectroscopic investigations of these catalysts we have shown that on impregnated Mo/SiO_2 catalysts MoO_3 is formed at loadings as low as 2 wt% Mo and its concentration was seen to increase with increasing Mo coverage. Thus the decrease in the amount of photoextractable surface oxygen with loading at high Mo coverage (Fig. 5) should be partly attributed to an increase in the concentration of MoO_3 on the surface. Furthermore, CO photoreducibility data obtained with impregnated Mo/SiO_2 catalysts indicate that significantly more surface oxygen atoms per Mo could be photoextracted with unfiltered light ($\lambda \geq 180$ nm) than with filtered light ($\lambda \geq 280$ nm) (Fig. 6A). Kazansky *et al.* (*9–11*) have shown that CO photoreduction of Mo/SiO_2 catalysts leads to the formation of Mo^{4+} ions in tetrahedral coordination and to some Mo^{5+} ions in octahedral coordination. These results would suggest that during CO photoreduction Mo^{4+} ions are formed from the photoreduction of isolated tetrahedral monomers and Mo^{5+} from the photoreduction of octahedrally coordinated Mo^{6+} ions in polymolybdates. Tetrahedrally coordinated Mo^{6+} isolated monomers absorb around 240–260 nm (Figs. 1 and 2) (*21*) and as a consequence CO photoreduction of these catalysts using filtered light ($\lambda \geq 280$ nm) should not lead to the reduction of Mo^{6+} isolated monomers. With filtered light only the species absorbing above 280 nm are excited and could be photoreduced by CO. The majority of the species absorbing in this region are the octahedrally coordinated Mo^{+6} in polymolybdates. These species may be expected to be CO photoreduced via charge transfer complexes involving Mo–O–Mo bonds. Thus the observed differences in the CO photoreducibility of impregnated Mo/SiO_2 catalysts by unfiltered ($\lambda \geq 180$ nm) and filtered ($\lambda \geq 280$ nm) light (Figs. 5 and 6) may be attributed to an absence of any photoreduction of Mo^{6+} isolated monomers by CO with filtered light. Accordingly, the CO photoreduction process may be viewed as follows:



According to the above interpretation, the difference between the two curves in Figs. 5 and 6 for filtered and unfiltered light (dashed curves) should yield the concentration of tetrahedrally coordinated Mo^{6+} monomers on the surface as a function of loading. Thus, according to Fig. 6A (curve 3) the fraction of the tetrahedral monomers is at a maximum at the lowest Mo coverage (60%), and falls sharply to a value of ~5% at the highest Mo coverage studied.

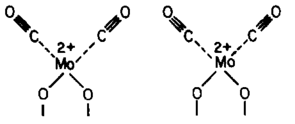
In the Results section, we attributed the major IR bands observed at 2125, 2075, and 2035 cm^{-1} to pairs of CO adsorbed on CO photoreduced Mo^{x+} sites and to a single CO molecule adsorbed on similar sites in a linear or bridged configuration. Similar IR bands are observed on CO-photoreduced Mo/SiO_2 catalysts by both filtered ($\lambda \geq 280$ nm) and unfiltered ($\lambda \geq 180$ nm) light. Thus, it may be concluded that the photoreduced Mo^{x+} sites holding CO are not necessarily formed from the photoreduction of isolated tetrahedral monomers. Furthermore, our data (Fig. 11) also revealed that these sites are probably not formed from the photoreduction of octahedrally coordinated Mo^{6+} in the collapsed polymolybdates (Fig. 11). Thus, the Mo^{x+} sites holding CO could have formed from the CO photoreduction of surface molybdates that absorb in the region 260–300 nm and are excited by both filtered ($\lambda \geq 280$ nm) and unfiltered light ($\lambda \geq 180$ nm). The surface molybdates that absorb in this region may be identified with dimeric molybdates and terminal Mo=O in polymolybdates (*13, 14*).

A special feature of the CO adsorption on transition metal cations is the possibility to derive the valence state and coordination of the adsorbing metal cation from the IR frequency data of the adsorbed CO molecules. Peri (*24*) and Caceres *et al.* (*25*) attributed the IR bands of adsorbed CO on thermally reduced Mo/Al_2O_3 catalysts observed at 2040–2025 cm^{-1} to CO adsorbed on Mo^0 sites and the band at 2185–2190 cm^{-1} to CO on Mo^{4+} sites. Recently, Delgado *et al.* (*26*) and Zaki *et al.* (*27*) also reported the presence of a band around 2186 cm^{-1} for CO adsorbed on thermally reduced supported molybdena catalysts with different support materials and this band has been attributed to Mo^{+4}–CO complexes. CO adsorbed on thermally (CO/1 h/400°C) and CO-photoreduced V^{5+}/SiO_2 catalysts yields a pair of IR bands at 2170–2174 and 2185–2189 cm^{-1} (*28, 29*). These bands have been attributed to CO adsorbed on V^{3+} sites. On reduced Cr^{6+}/SiO_2 catalysts a band observed at 2095 cm^{-1} (*30*) or at 2035 cm^{-1} (*31*) has been attributed to CO species adsorbed in a bridged configuration on two Cr^{2+} sites. Generally, the IR bands of CO adsorbed on metal cations below 2100 cm^{-1} are seen to arise for CO held either linearly (2000–2030 cm^{-1}) or in a double-bridged configuration (1800–2000 cm^{-1})

on fully reduced metal sites (M^0) (*24, 32*). IR bands above 2100 cm^{-1} have been usually attributed to CO held on ionic metal sites (*32*).

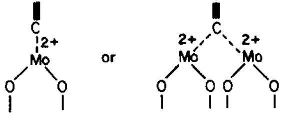
Thus, according to the literature data the observed IR bands on CO-photoreduced Mo/SiO_2 catalysts should stem from CO adsorbed on reduced Mo sites having valency states lower than Mo^{4+} (probably Mo^{3+} or Mo^{2+}). Since the average oxidation number for CO-photoreduced Mo/SiO_2 catalysts never falls below 4+, the fraction of these low-valent ions should be extremely small.

Kazansky *et al.* (*11*) reported that CO photoreduction of Cr^{6+}/SiO_2 catalysts leads to the formation of Cr^{2+} ions on the surface. They suggest that these species are formed from the CO photoreduction of bichromate surface complexes. Thus, it may be tentatively suggested that the observed IR bands at 2075 and 2125 cm^{-1} stem from pairs of CO molecules adsorbed on Mo^{2+} sites formed from the photoreduction of dimeric molybdates. This assumption is consistent with the previous deduction that the Mo^{x+} sites holding CO are formed from the photoreduction of certain surface molybdates that absorb in the 260- to 300-nm region and are therefore excited by both filtered ($\lambda \geq$ 280 nm) and unfiltered ($\lambda \geq$ 180 nm) light and that these species may be identified with dimeric molybdates (*13, 14*).



2075, 2125 cm^{-1}

The 2035-cm^{-1} band then may be attributed to a single CO molecule adsorbed linearly or in a double-bridged configuration on these two Mo^{2+} sites.

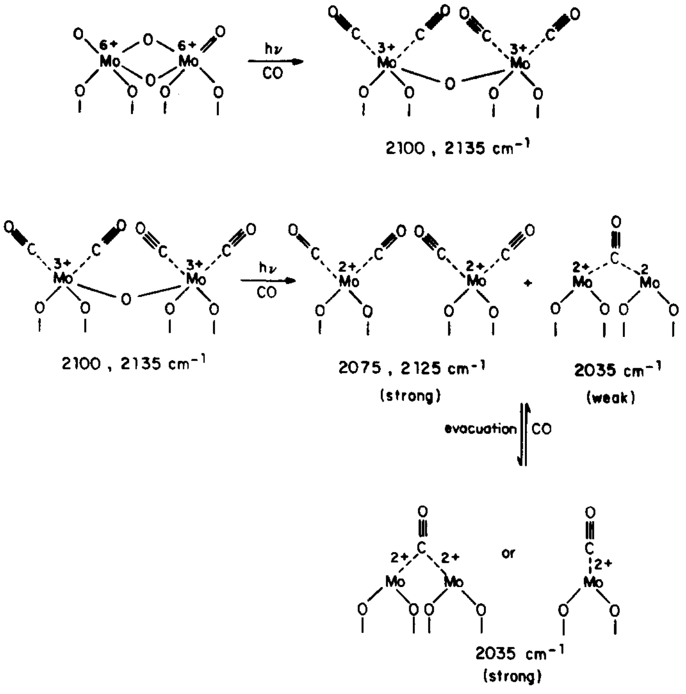


2035 cm^{-1}

Recently Guglielminotti and Giamello (*23*) reported very weak IR bands for CO adsorbed on thermally reduced Mo/SiO_2 catalysts (H_2/4 h/450°C) at 2203 and 2181 cm^{-1}. These bands were assigned to CO adsorbed on Mo^{5+} and Mo^{4+} ions, respectively. CO photoreduction of these thermally reduced catalysts leads to the appearance of two strong bands at 2128 and 2080 cm^{-1} and to a weak band at 2043 cm^{-1}. The position and the behavior of these bands parallel the IR bands that we observed. From isotopic ^{13}CO–^{12}CO exchange experiments, they concluded that the 2128- and 2080-cm^{-1} bands arise from pairs of CO adsorbed on photoreduced Mo^{2+} sites and the 2143-cm^{-1} band arises from a single CO adsorbed on two Mo^{2+} sites in a double-bridged configuration. These data are in excellent agreement with our results and provide additional support for our interpretation.

Similar to the IR bands that we observed at 2100 and 2135 cm^{-1}, Guglielminotti and Giamello (*23*) also observed two bands at 2108 and 2140 cm^{-1}. Interestingly, they also reported the lack of reproducibility of these bands. In their opinion, these bands arise from pairs of CO adsorbed on Mo^{4+} sites. Also, recently Zaki *et al.* (*27*) attributed two very similar weak IR bands at 2130 and 2105 cm^{-1} found for CO adsorbed on thermally reduced supported molybdena catalysts on various supports to dicarbonyl $Mo^{4+}(CO)_2$ species. However, according to data by the same author and others which ascribe a vibration at 2180–2190 cm^{-1} to $Mo^{4+}(CO)$, the reported stretching frequencies of 2100 and 2135 cm^{-1} would appear to be too low to be attributed to dicarbonyl $Mo^{4+}(CO)_2$ species. Thus, we believe that these bands at 2100 and 2135 cm^{-1} arise from pairs of CO adsorbed on Mo^{+3} sites which are intermediates in the CO photoreduction of Mo^{6+} in the dimeric surface molybdates to Mo^{2+}. Accordingly the CO photoreduction of dimeric molybdates may be viewed as in Scheme 1.

On the other hand, if the two IR bands at

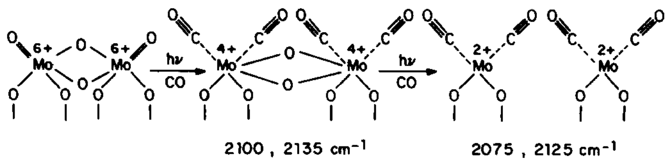


SCHEME 1.

2100 and 2135 cm^{-1} are attributed to dicarbonyl $Mo^{4+}(CO)_2$ species as suggested by Guglielminotti and Giamello (*23*) and Zaki *et al.* (*27*) then the bands at 2075 and 2125 cm^{-1} may be attributed to either $Mo^{3+}(CO)_2$- or $Mo^{2+}(CO)_2$-type species. However, the attribution of the latter IR bands to dicarbonyl $Mo^{2+}(CO)_2$ species may still be valid in view of the fact that Mo^{3+} ions have never been observed by ESR on CO-photoreduced catalysts (*9–11, 23*). Moreover, the reduced Mo^{x+} ions associated with the two IR bands at 2075 and 2125 cm^{-1} appear to be a final product of CO photoreduction of Mo/SiO_2 catalysts. According to this latter interpretation, the species responsible for the observed IR bands may be viewed as in Scheme 2.

Although, the IR spectroscopic data of CO adsorbed on photoreduced Mo/SiO_2 catalysts may be interpreted as indicating the presence of reduced Mo ions with oxidation states lower than 4+, the definite valence state of these ions cannot be established on the basis of IR spectroscopic data alone. Therefore, our data do not allow us to discriminate between the Schemes 1 and 2.

Pershin *et al.* (*9*), Shelimov *et al.* (*10*), and Kazansky *et al.* (*11*) reported that the



SCHEME 2

extremely high reducing properties of CO-photoreduced Mo/SiO$_2$ catalysts, such as the ability to reduce N_2O at −120°C, CO_2 at 90°C, and H_2O at 150°C, are turned on only after degassing the strongly adsorbed CO at 150°C. The only IR band that could not be removed from the IR spectrum after degassing the sample is the 2035-cm^{-1} band which is attributed to a single CO adsorbed linearly or in a double-bridged configuration on Mo^{2+} sites. Guglielminotti and Giamello (*23*) reported that the IR band pertaining to these species could be removed from the spectrum only after outgassing the sample at temperatures above 100°C. Thus, it may be possible that the strong reducing properties of CO-photoreduced Mo/SiO$_2$ catalysts as observed in (*9–11*) are associated with the low-coordinated Mo^{2+} ions rather than with the Mo^{4+} ions. Furthermore, Pershin *et al.* (*9*), Shelimov *et al.* (*10*), and Kazansky *et al.* (*11*) reported that the propylene metathesis activity of CO-photoreduced Mo/SiO$_2$ catalysts is not quenched after exposure of these catalysts to N_2O (CO-photoreduced catalysts are easily oxidized by N_2O even at temperatures as low as −120°C (*9–11*)). The IR bands attributed to CO adsorbed on Mo^{2+} sites are easily removed by exposure of the CO-photoreduced samples to O_2 at room temperature. This would suggest that metathesis activity of CO-photoreduced Mo/SiO$_2$ catalysts (*11*) resides with photoreduced Mo ions in higher valence states (probably Mo^{4+}) that are not oxidized by N_2O at room temperature. This is in agreement with previous observations (*23, 33, 34*) which suggest that very low-valent Mo ions are not active in metathesis.

REFERENCES

1. Hall, W. K., and Lo Jacono, M., *in* "Proceedings 6th Int. Congr. Catal., London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 247. The Chemical Society, London, 1977.
2. Massoth, F. E., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 27, p. 265. Academic Press, New York, 1978.
3. Zingg, D. S., Makovsky, L. E., Tischer, R. E., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **84,** 2898 (1980).
4. Hall, W. K., *in* "Proceedings 4th Int. Conf. on The Chemistry and Uses of Molybdenum, Golden, Colo." (H. F. Barry and P. C. H. Mitchell, Eds.), p. 224. Climax Molybdenum Co., Ann Arbor, MI, 1982.
5. Vorotyntzev, V. M., Shvetz, V. A., and Kazansky, V. B., *Kinet. Katal.* **12,** 1249 (1971).
6. Che, M., Figueras, F., Forisier, M., McAteer, J., Perrin, M., Portefaix, J. L., and Praliaud, H., *in* "Proceedings 6th Int. Congr. Catal., London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 261. The Chemical Society, London, 1977.
7. Vaghi, A., Castellan, A., Bart, J. C. J., and Giordano, N., *J. Catal.* **42,** 381 (1976).
8. Ward, M. B., Lin, M. J., and Lundsford, J. H., *J. Catal.* **50,** 306 (1977).
9. Pershin, A. N., Shelimov, B. N., and Kazansky, V. B., *Kinet. Katal.* **20,** 1298 (1979).
10. Shelimov, B. N., Pershin, A. N., and Kazansky, V. B., *J. Catal.* **64,** 426 (1980).
11. Kazansky, V. B., Pershin, A. N., and Shelimov, B. N., *in* "Proceedings 7th Int. Cong. Catal., Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), Part B, p. 1210. Elsevier, Amsterdam, 1981.
12. Kaliaguine, S., Mahay, A., and Roberge, P. C., *in* "Proceedings 2nd World Congr. Chem. Eng., Montreal, 1981," Vol. 3, p. 272.
13. Marcinkowska, K., Kaliaguine, S., and Roberge, P. C., *J. Catal.* **90,** 49 (1984).
14. Marcinkowska, K., Rodrigo, L., Kaliaguine, S., and Roberge, P. C., *J. Catal.* **97,** 75 (1986).
15. Mahay, A., Kaliaguine, S., and Roberge, P. C., *Canad. J. Chem.* **60,** 2719 (1980).
16. Lafrance, C. P., Kaliaguine, S., Roberge, P. C., and Pichat, P., *in* "Catalysis on the Energy Scene" (S. Kaliaguine and A. Mahay, Eds.), p. 309. Elsevier, Amsterdam, 1984.
17. Marcinkowska, K., M.Sc. thesis, Université Laval, Québec, 1983.
18. Rodrigo, L., Ph.D. thesis, Université Laval, Québec, 1986.
19. Rodrigo, L., Marcinkowska, K., Adnot, A., Roberge, P. C., Kaliaguine, S., Stencel, J. M., Makovsky, L. E., and Diehl, J. R., *J. Phys. Chem.* **90,** 2690 (1986).
20. Stencel, J. M., Diehl, J. R., D'Este, J. R., Makovsky, L. E., Rodrigo, L., Marcinkowska, K., Adnot, A., and Roberge, P. C., *J. Phys. Chem.* **90,** 4739 (1986).
21. Marcinkowska, K., Rodrigo, L., Roberge, P. C., and Kaliaguine, S., *J. Mol. Catal.* **33,** 189 (1985).
22. Rodrigo, L., Roberge, P. C., and Kaliaguine, S., Paper presented before the 10th Canadian Symposium on Catalysis, Kingston, Ontario, 1986.

23. Guglielminotti, E., and Giamello, E., *J. Chem. Soc. Faraday Trans. 1* **81,** 2307 (1985).

24. Peri, J. B., *J. Phys. Chem.* **86,** 1615 (1982).

25. Caceres, C. V., Fierro, J. L. G., Agudo, A. L., Blanco, M. N., and Thomas, H. J., *J. Catal.* **95,** 501 (1985).

26. Delgado, E., Fuentes, G. A., Herman, C., Kunzmann, G., and Knözinger, H., *Bull. Soc. Chim. Belg.* **83,** 735 (1984).

27. Zaki, M. I., Vielhaber, B., and Knözinger, H., *J. Phys. Chem.* **90,** 3176 (1986).

28. Rebenstorf, B., Berglund, M., Lykvist, R., and Larsson, R., *Z. Phys. Chem.,* N.F., **126,** 47 (1981).

29. Gerasimov, S. F., and Filimonov, V. N., *Kinet. Katal.* **22,** 469 (1981).

30. Zecchina, A., Garrone, E., Ghiotti, G., and Coluccia, S., *J. Phys. Chem.* **79,** 972 (1975).

31. (a) Rebenstorf, B., and Larsson, R., *J. Mol. Catal.* **11,** 247 (1981); (b) Rebenstorf, B., and Larsson, R., *Z. Anorg. Allg. Chem.* **478,** 119 (1981).

32. Mayfair, C. K., and Kung, H. H., *Catal. Rev. Sci. Eng.* **27,** 425 (1985).

33. Kuznetsov, B. N., Startsev, A. N., and Yermakov, Yu. I., *J. Mol. Catal.* **8,** 135 (1980).

34. Lombardo, E. A., Lo Jacono, M., and Hall, W. K., *J. Catal.* **64,** 150 (1980).