

# Kinetics of Surface Processes for Mo(CO)<sub>6</sub> on Partially Dehydroxylated Alumina and Hydroxylated Alumina. Observation of Mo(CO)<sub>5</sub>(ads)

Karuna P. Reddy and Theodore L. Brown\*

Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois, 61801

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**Abstract:** The adsorption of Mo(CO)<sub>6</sub> on partially dehydroxylated alumina (PDA) and hydroxylated alumina (HA) has been studied using IR and UV–vis spectroscopy. The results from these experiments suggest that the initially physisorbed Mo(CO)<sub>6</sub> coordinates to two distinct Lewis acid sites on the surface of PDA, one much more abundant than the other, with an apparent single rate constant  $2.3 \times 10^{-3} \text{ s}^{-1}$  at 298 K. The Mo(CO)<sub>6</sub>(ads) in turn loses CO reversibly, with an apparent single rate constant  $1.8 \times 10^{-4} \text{ s}^{-1}$  at 298 K to form Mo(CO)<sub>5</sub>(ads). Upon removal of gas phase CO released in the first step, Mo(CO)<sub>5</sub>(ads) loses two additional COs to form Mo(CO)<sub>3</sub>(ads). Alternatively, on HA physisorbed Mo(CO)<sub>6</sub> undergoes nucleophilic attack by hydroxyl groups, which results in cis-labilization of a carbonyl group, leading in turn to the formation of Mo(CO)<sub>5</sub>(L), where L is a surface hydroxyl. The Mo(CO)<sub>5</sub>(L) so formed loses additional carbonyls to form a lower subcarbonyl. The decarbonylation process appears to be faster than on PDA. The experimental data indicate that there are no Al<sup>3+</sup> exposed on HA. All the observed decarbonylation processes are reversible under CO at room temperature on both HA and PDA. The addition of CO<sub>2</sub> to the subcarbonyl on HA results in the formation of a bicarbonate, with displacement of the subcarbonyls.

## Introduction

The chemistry of transition metal carbonyl complexes supported on metal oxide surfaces has attracted the attention of many researchers in the past several years, in part because it is possible to generate catalysts of high activity at low temperatures. Mo(CO)<sub>6</sub> supported on  $\gamma$ -alumina represents one of the first examples of a catalyst formed by reaction of a transition metal carbonyl compound with an oxide support.<sup>1</sup> Several studies have been undertaken to elucidate the surface reactions which convert Mo(CO)<sub>6</sub> adsorbed on  $\gamma$ -alumina into an active catalyst.<sup>2</sup>

Davie, Whan, and Kemball described a preliminary IR study of Mo(CO)<sub>6</sub> supported on alumina. A lowering in symmetry evidenced in the IR bands upon activation of the catalyst by heating for 1 h in vacuo at 373 K was attributed to a loss of CO with formation of a molybdenum subcarbonyl species, Mo(CO)<sub>6-x</sub>, assumed to be responsible for the catalytic activity.<sup>21</sup> However, the actual nature of the catalyst was not defined.

Initial IR spectroscopic studies by Howe and co-workers on fully hydroxylated  $\gamma$ -alumina (HA) indicated that activation of supported Mo(CO)<sub>6</sub> at 318 K causes decomposition, with removal of some carbonyl ligands to form several unidentified

molybdenum subcarbonyl species.<sup>2k</sup> It was also suggested that upon removal of all carbonyl ligands at temperatures of 473 K, the initially-formed Mo(0) is subsequently oxidized to a higher oxidation state species, which is the active form.<sup>2b</sup> In contrast, Brenner, Burwell, and co-workers<sup>2f,h,3</sup> showed that temperatures above 573 K are necessary for removal of all the carbonyl ligands at a reasonable rate from Mo(CO)<sub>6</sub> adsorbed on *partially* dehydroxylated alumina (PDA). They further postulated that the Mo(0) atoms released on decarbonylation may be oxidized by reduction of surface hydroxyl groups on a  $\gamma$ -PDA surface. In the absence of the OH groups, in fully dehydroxylated alumina (DA), the Mo atoms aggregate as metal clusters. Recent ESCA data also indicate that metallic Mo crystals form on Mo(CO)<sub>6</sub>/DA, whereas Mo<sup>4+</sup>, Mo<sup>2+</sup>, and Mo(0) are present on Mo(CO)<sub>6</sub>/PDA.<sup>4</sup>

Temperature-programmed decarbonylation (TPDE) studies by Brenner, Burwell, and co-workers<sup>2h</sup> indicate that when the decarbonylation is carried out in a closed vessel, the decomposition of Mo(CO)<sub>6</sub> adsorbed on  $\gamma$ -PDA terminates very approximately at Mo(CO)<sub>5</sub>(ads) with resulting development of a partial pressure of CO. However, a helium sweep at 100 °C results in the loss of three COs with the formation of Mo(CO)<sub>3</sub>(ads). Exposure of Mo(CO)<sub>3</sub>(ads) to CO at –17 °C converts it to Mo(CO)<sub>4</sub>(ads). The TPDE data suggest that decomposition of Mo(CO)<sub>6</sub> is reversible in discernible steps by appropriate treatment with CO. Formation of Mo(CO)<sub>3</sub>(ads) as a relatively stable species is strongly supported by quantitative measurements of the amounts of CO evolved during catalyst activation

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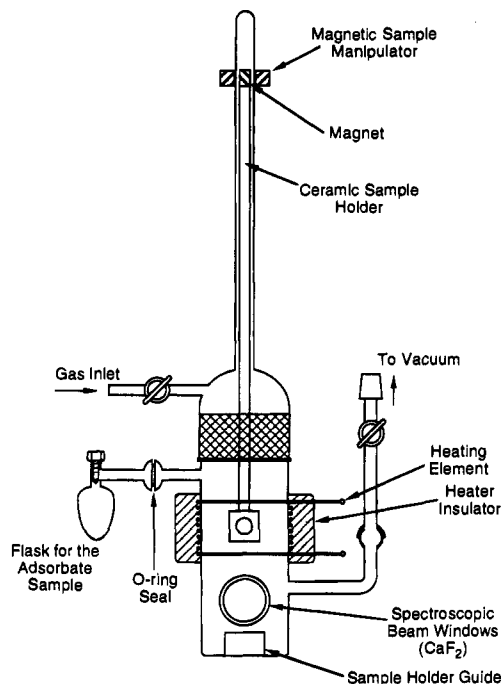


Figure 1. Diagram of the IR cell.

at 100 °C<sup>2h</sup> as well as by the TPDE results.<sup>2j</sup> An IR study by Howe<sup>2k,5</sup> of Mo(CO)<sub>6</sub> between 243 and 318 K on hydroxylated  $\gamma$ -alumina was reported to be in agreement with the formation of subcarbonyl species as suggested by Brenner and Burwell.<sup>2h</sup> However, there was disagreement as to the molecular form of Mo(CO)<sub>3</sub>(ads).<sup>2k,3e,5</sup>

Unlike earlier reports in which the surface chemistry was monitored by IR spectroscopy at higher temperatures (>298 K), Zecchina et al.<sup>6</sup> recently carried out a study and analysis of the IR spectra obtained from Mo(CO)<sub>6</sub> adsorbed on DA preparations at room temperature. The carbonyl was added in small successive doses and removed slowly by desorption. The authors argued that the principal bands could be divided into two sets of quartets ascribed to undissociated Mo(CO)<sub>6</sub>, bonded through the oxygen of a ligand CO to an aluminum ion in either an octahedral or a tetrahedral surface site. On extended evacuation, a monomeric subcarbonyl, similarly bound, was proposed to account for a third, lower-frequency quartet which replaced the others.

The behavior of Mo(CO)<sub>6</sub> and related metal carbonyl compounds on alumina has also been studied using solid-state NMR methods.<sup>7</sup> These studies also provide evidence for the presence of subcarbonyl species; however, the compositions of such species cannot be inferred from the NMR results alone.

It is evident from the considerable body of published work that the behavior of Mo(CO)<sub>6</sub> supported on  $\gamma$ -alumina depends on the degree of surface hydroxylation. To clarify the initial processes that occur upon adsorption of Mo(CO)<sub>6</sub>, we have undertaken a study of the time dependence of the IR spectra upon adsorption of Mo(CO)<sub>6</sub> on PDA (525 °C activation) and HA (225 °C activation) at room temperature. In addition, we have obtained for the first time UV-vis spectra as a function of time for Mo(CO)<sub>6</sub> adsorbed on PDA and HA.

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## Experimental Section

Alumina purchased from Degussa was pretreated by making a slurry with distilled water and drying overnight at 150 °C. The alumina obtained after drying was ground with a mortar and pestle; then 60–80 mesh size particles were separated using sieves. The 60–80 mesh alumina was then pressed into pellets 18 mm in diameter by applying a pressure of 46 000 psi ( $3.2 \times 10^5$  kPa). The alumina pellet was then placed into the sample holder and activated at 800 or 425 K, under vacuum for 2 h in the oven section of the cell described in Figure 1, to obtain PDA and HA, respectively. The sample holder was then moved into the window region. The IR and UV-vis spectra were collected *in situ* utilizing a Model 1710 Perkin-Elmer FTIR spectrometer and Model 8452A Hewlett-Packard diode array spectrometer, respectively. Deuterated alumina was prepared *in situ* by activating the alumina at 800 K, exposing it to D<sub>2</sub>O vapor, equilibrating it for 1 h, and repeating the process twice to ensure complete deuteration, after which it was activated at 425 K to form fully hydroxylated (deuterated) alumina for further studies. Mo(CO)<sub>6</sub> was purchased from Strem and sublimed prior to use, while CO and CO<sub>2</sub> were purchased from Matheson and MG industries, respectively. The CO was purified by being passed through a column of charcoal activated at 180 °C and then through a column of activated charcoal which was cooled in a dry ice/acetone bath, while CO<sub>2</sub> was passed through a column of activated 3A molecular sieves.

## Results and Discussion

Because alumina is highly transparent in the carbonyl region, IR spectroscopy provides an excellent tool for probing the chemical changes occurring upon adsorption of a metal carbonyl compound. It has been established that the surface of PDA presents the incoming nucleophile with mainly two distinct types of coordinatively unsaturated Lewis acid sites associated with Al<sup>3+</sup>.<sup>8</sup> Gruver and Fripiat<sup>9</sup> have shown recently that there are approximately 10<sup>20</sup> Lewis acid sites per 300 m<sup>2</sup> on alumina activated at 600 °C, which represents 4% of the total surface aluminum content, while the ratio between the two types of Lewis acid sites was reported to be ~4.5. These acid sites together with the remaining hydroxide group coverage, and the oxide ions also present at the surface, confer on the alumina surface an acid-base character.

When Mo(CO)<sub>6</sub> is adsorbed on Al<sub>2</sub>O<sub>3</sub>, the IR spectra change as a function of time as shown in Figure 2. The initial strong absorption at 1998 cm<sup>-1</sup> can be associated with a weakly adsorbed Mo(CO)<sub>6</sub>, because of the close similarity of the IR band to the IR-active T<sub>1u</sub> mode in gas-phase<sup>10</sup> or solution-phase Mo(CO)<sub>6</sub>.<sup>10b</sup> The initial absorption decreases in intensity over several minutes. The IR bands that arise in its place can be deconvoluted as a pair of superimposed quartets (Table 1). We interpret these sets as due to Mo(CO)<sub>6</sub> coordinated through the oxygen of CO to two distinct Lewis acid sites, labeled I and II. The interpretation of the IR spectral changes over the first several minutes following adsorption as due to migration of an initially-physisorbed Mo(CO)<sub>6</sub> to Lewis acid sites is supported by analysis of the time dependence of the UV-vis spectra, as discussed below.

Our results are similar to those reported by Zecchina and co-workers, who worked with fully dehydroxylated alumina.<sup>6</sup> The

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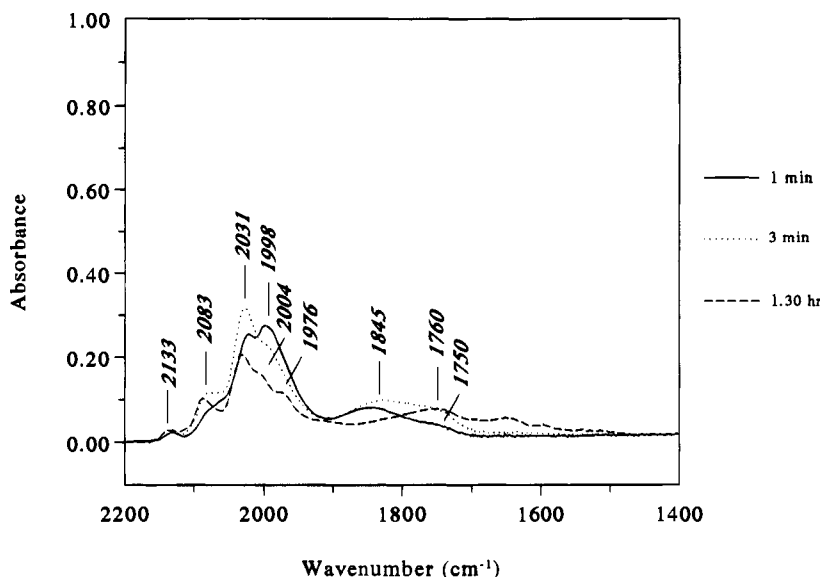


Figure 2. FTIR spectra for Mo(CO)<sub>6</sub> adsorbed on PDA as a function of time.

Table 1: IR Frequencies for Mo(CO)<sub>6</sub> and Subcarbonyl Species (cm<sup>-1</sup>)

| complex  | IR frequencies   | refs      |
|--|--|-----------|
| Mo(CO) <sub>6</sub> [solid]                          | 2114, <sup>a</sup> 2005, <sup>a</sup> 1990 <sup>b</sup>                      | 24        |
| Mo(CO) <sub>6</sub> [in KBr]                         | 2112, 2022, 2003   | 10        |
| Mo(CO) <sub>6</sub> [supported on alumina]           | 2115, 2025, 2000   | 10        |
| Mo(CO) <sub>6</sub> [site I on PDA]                  | 2133 (vw), 2083 (w), 2031 (s), 1755 (br) <sup>c</sup>                        | this work |
| Mo(CO) <sub>6</sub> [site II on PDA]                 | 2133 (vw), 2029 (s), 1998 (s), 1845 (br) <sup>c</sup>                        | this work |
| Mo(CO) <sub>5</sub> (ads) [on PDA]                   | 2083 (w), 2031 (s), 2004 (m), 1976 (m), 1760 (br) <sup>c</sup>               | this work |
| Mo(CO) <sub>5</sub> <sup>d</sup> (Nujol mull)        | 2089, 1962, 1927   | 15        |
| Mo(CO) <sub>5</sub> (ads) [on PDA]                   | 2018 (m), 1992 (m), 1945 (m), 1690 (br), <sup>c</sup> 1595 (br) <sup>c</sup> | this work |
| Mo(CO) <sub>6</sub> (physisorbed)                    | 2119 (vw), 2030 (m), 1998 (s)  | this work |
| Mo(CO) <sub>5</sub> (L) [site I on HA] <sup>e</sup>  | 2085 (vw), 1945 (s), 1850 (br) <sup>c</sup>                                  | this work |
| Mo(CO) <sub>5</sub> (L) [site II on HA] <sup>e</sup> | 2075 (vw), 1912 (s), 1790 (br) <sup>c</sup>                                  | this work |
| lower subcarbonyl [on HA]                            | 2030 (w), 1945 (m), 1790 (br), <sup>c</sup> 1710 (br) <sup>c</sup>           | this work |

<sup>a</sup> Raman active. <sup>b</sup> IR active. <sup>c</sup> IR frequencies rounded to nearest 5 cm<sup>-1</sup> due to broad nature of the bands. <sup>d</sup> The vacant coordination site is occupied by a loosely bound solvent molecule. <sup>e</sup> L represents surface hydroxyl groups.

interaction of Mo(CO)<sub>6</sub> with the surface can be rationalized in terms of the established basicity of the carbonyl oxygen in metal carbonyl compounds and the availability of Lewis acid sites on the alumina surface. The presence of two broad IR bands centered at 1845 and 1755 cm<sup>-1</sup>, which can be assigned to the CO oxygen-bonded to the Al<sup>3+</sup> acid sites, lends support to this interpretation. CO groups O-bonded to Lewis acids are known to exhibit stretching frequencies in the 1600 to 1900 cm<sup>-1</sup> region.<sup>11</sup>

In agreement with Zecchina et al., we notice a kinetic selectivity; binding occurs somewhat more rapidly to the 1755 cm<sup>-1</sup> binding site. However, the two sites do not appear to be equally abundant. Figure 3 shows a series of IR spectra, each taken about 1 min following a succession of Mo(CO)<sub>6</sub>(g) additions to the system at 298 K. The major IR absorbances increase in a continuous way with the amount of Mo(CO)<sub>6</sub> added to the system. On the other hand, the band at 1755 cm<sup>-1</sup>, which increases with addition of Mo(CO)<sub>6</sub> at low levels of addition, saturates at a comparatively low absorbance, whereas the absorbance at 1845 cm<sup>-1</sup> continues to increase. The absorbance at 1998 cm<sup>-1</sup> increases more rapidly than the other absorptions

upon successive additions of Mo(CO)<sub>6</sub> because the migration of physisorbed Mo(CO)<sub>6</sub> to the Lewis acid sites is slower overall than the rate of addition of Mo(CO)<sub>6</sub> to the system. When the time interval between each addition of Mo(CO)<sub>6</sub> and observation of the spectrum is increased to 3 min (Figure 4), the bands characteristic of Mo(CO)<sub>6</sub> bound to the Lewis acid centers are relatively more intense. In this case, the saturation of the absorbance at 1755 cm<sup>-1</sup> is even more evident.

Over a longer period of time, about 1.3 h, the bands due to Mo(CO)<sub>6</sub>(ads) decline in intensity, as shown in Figure 2; new bands appearing in their place can be assigned to Mo(CO)<sub>5</sub>(ads) (Table 1). The loss of CO from Mo(CO)<sub>6</sub>(ads) is not surprising; the bonding of a CO group of a metal carbonyl to a strong Lewis acid site confers on the CO group a stronger  $\pi$ -acid character than the other CO groups with respect to the metal center. A stronger  $\pi$ -acid ligand gives rise to labilization of the *trans* ligand with respect to dissociation.<sup>12</sup> The coordinatively unsaturated species formed via CO loss should be capable of facile rearrangement, placing the vacant coordination site *cis* to the CO bound to the surface acid site and permitting the binding of a basic hydroxide or oxide site. A pattern of IR absorptions characteristic of *cis*-M(CO)<sub>4</sub>LL' (where L is the oxygen-coordinated CO and L' is the oxy or hydroxy function) is to be expected. Indeed, the correspondence with the spectra of authentic examples with *cis* geometry is good.<sup>13</sup>

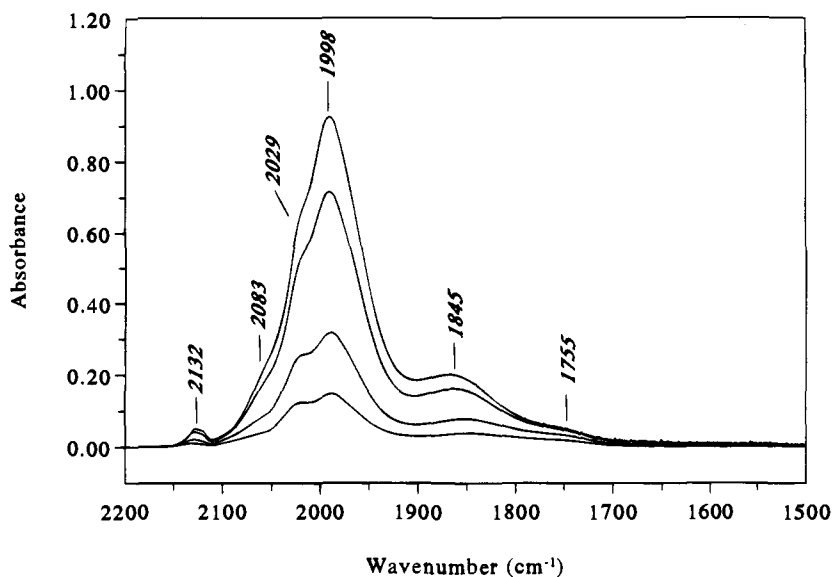
Our results differ from those of Zecchina et al. who studied Cr(CO)<sub>6</sub> and Mo(CO)<sub>6</sub> on DA<sup>6</sup> and found that decarbonylation occurs only under pumping. The difference in observations may relate to variations in the surfaces, or to the fact that their experiments were conducted under higher loading. In addition, it should be noted that Mo(CO)<sub>6</sub> is generally more labile than Cr(CO)<sub>6</sub> toward thermal CO loss.<sup>12a</sup>

The observed IR bands for the subcarbonyl Mo(CO)<sub>5</sub>(ads) are shifted to slightly lower frequencies in comparison with Mo(CO)<sub>6</sub>(ads), in agreement with the increase in electron density

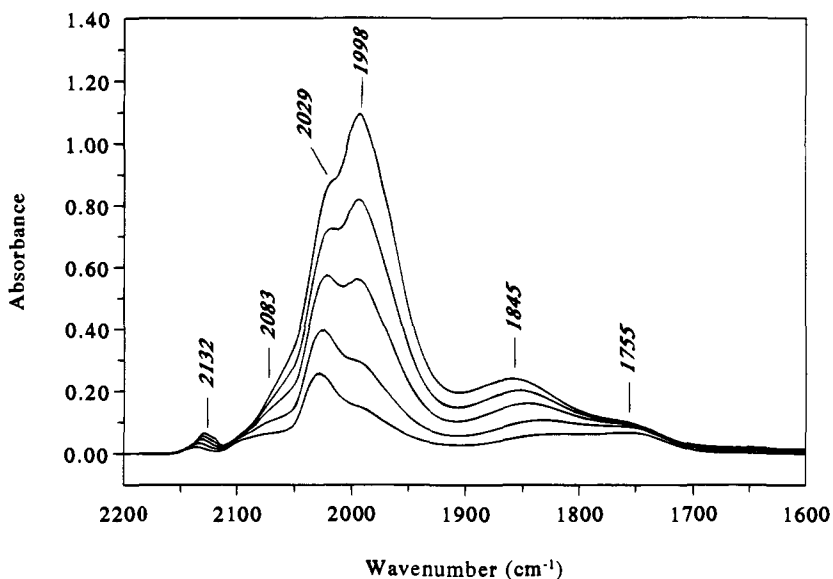
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**Figure 3.** FTIR spectra, each taken after 1 min following a succession of  $\text{Mo}(\text{CO})_6$  additions to PDA.



**Figure 4.** FTIR spectra, each taken after 3 min following a succession of  $\text{Mo}(\text{CO})_6$  additions to PDA.

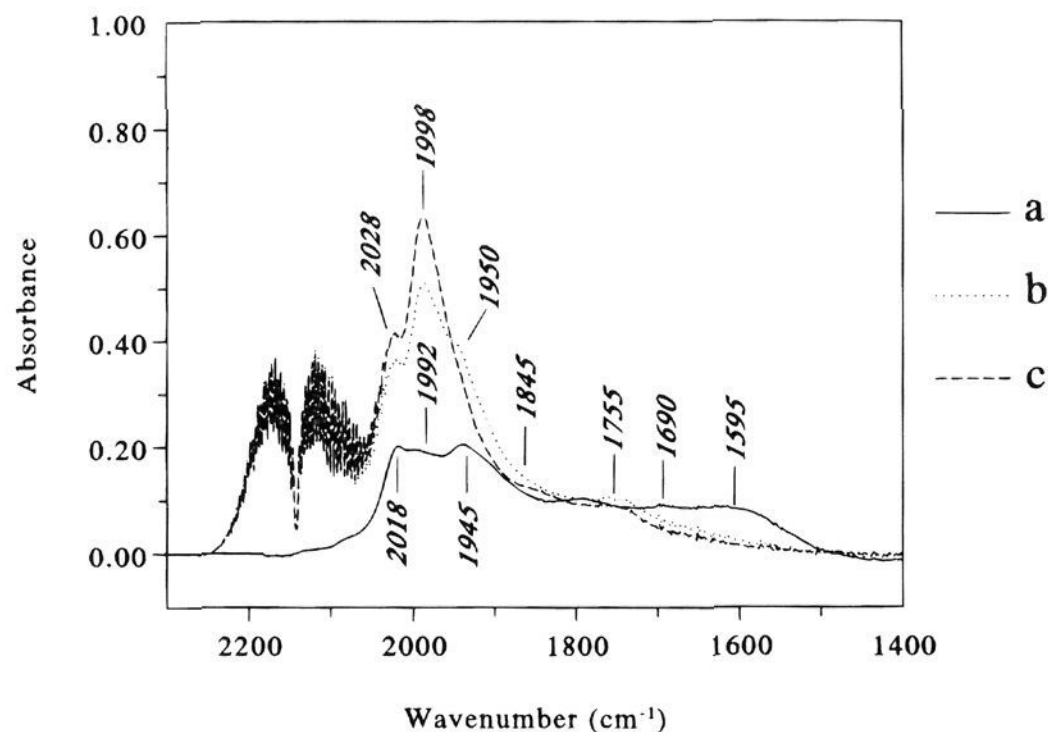
on the metal arising from replacement of a CO group by an oxo or hydroxo group. A weak band due to adsorbed CO is seen at  $2133\text{ cm}^{-1}$ . The IR bands due to the CO groups of  $\text{Mo}(\text{CO})_5(\text{ads})$  coordinated to surface Lewis acid sites should be shifted to lower frequencies relative to those in  $\text{Mo}(\text{CO})_6(\text{ads})$ . We observe a band at  $1760\text{ cm}^{-1}$ , which may correspond to the band at  $1845\text{ cm}^{-1}$  in  $\text{Mo}(\text{CO})_6(\text{ads})$ . A second, lower-frequency coordinated CO bound to the second, less abundant, type of Lewis acid site is not discernible; it may be shifted to still lower frequency and may not be distinguishable from absorptions in the  $1640\text{ cm}^{-1}$  region resulting from the growth over an extended period of time of surface hydroxyl groups due to adsorption on the alumina of trace water vapor that desorbs off the glass surface of the apparatus.

After overnight pumping to remove initially-released CO,  $\text{Mo}(\text{CO})_5(\text{ads})$  loses additional CO to form  $\text{Mo}(\text{CO})_3(\text{ads})$  (Table 1), a species that has been recognized in previous work. The presence of two bands in the low-frequency region, at  $1595$  and  $1690\text{ cm}^{-1}$ , can be ascribed to CO groups oxygen-bonded to two distinct Lewis acid sites on the surface. Howe and co-workers have speculated that the spectrum of  $\text{Mo}(\text{CO})_3(\text{ads})$  is consistent with a dimeric form.<sup>2k,5</sup> However, our spectra were obtained under much more dilute conditions than in the earlier

work, without a significant difference in the relative intensities of the observed bands. Thus, a dimeric form does not seem likely. Rather, the spectrum can be more readily associated with the presence of two distinct acid sites on the surface with a resulting multiplicity of bands, though not all of these can be resolved.

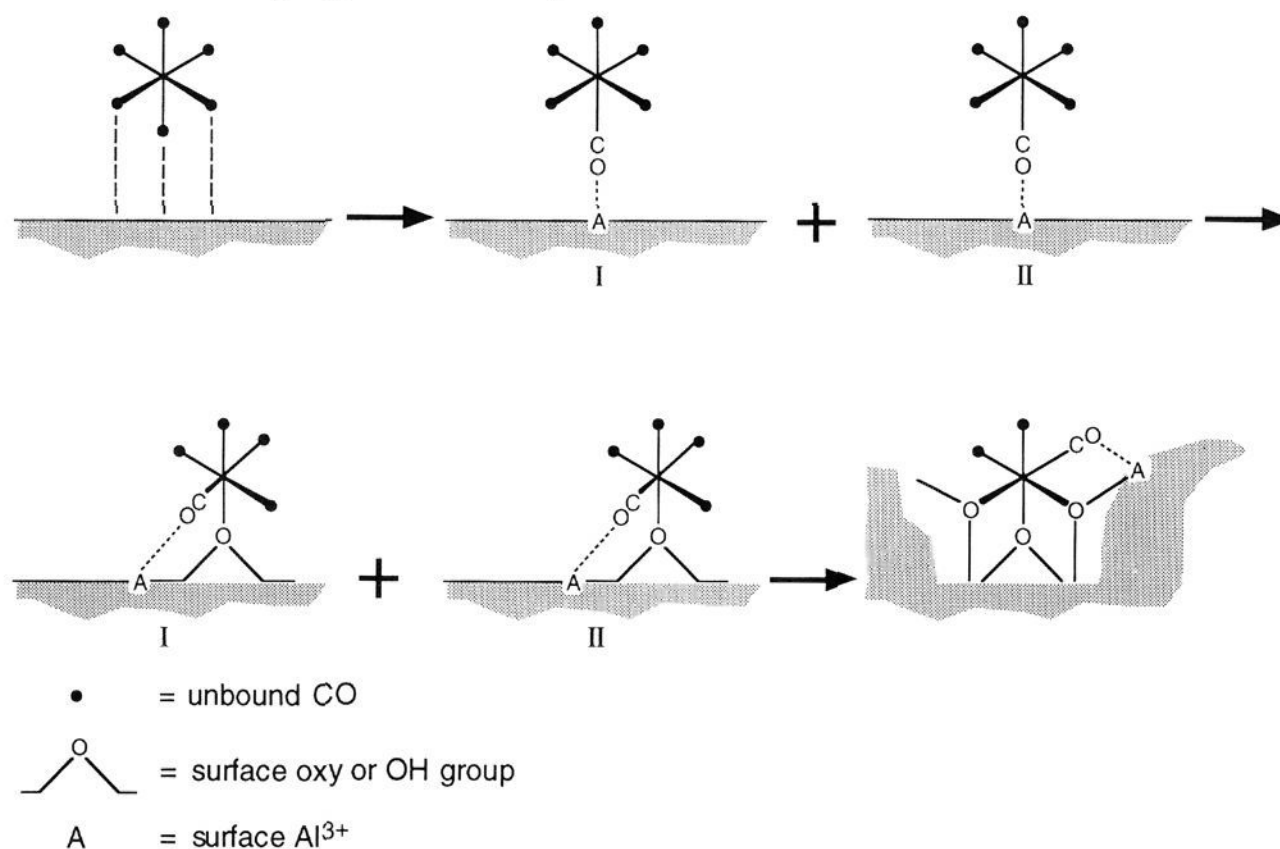
Our experimental results are in agreement with the TPDE experiments, which indicate that the decarbonylation of  $\text{Mo}(\text{CO})_6$  on PDA terminates approximately at  $\text{Mo}(\text{CO})_5(\text{ads})$  upon treatment in a closed vessel, with the resulting development of a partial pressure of  $\text{CO}(\text{g})$ . The helium sweep in the work of Brenner, Burwell, and co-workers, and pumping under vacuum in our work, have the same effect of shifting the equilibrium toward the species with lower CO content,  $\text{Mo}(\text{CO})_3(\text{ads})$ . The overall behavior of  $\text{Mo}(\text{CO})_6$  upon adsorption on PDA is illustrated in Scheme 1.

As reported by others,<sup>2b,h,k,5</sup> the loss of CO is reversible at room temperature. An IR spectrum obtained 2 min following addition of CO is compared in Figure 5 with that just prior to addition. The low-frequency bands at  $1595$  and  $1690\text{ cm}^{-1}$  due to oxygen-bonded CO in  $\text{Mo}(\text{CO})_3(\text{ads})$  disappear, with concurrent increase in the bands due to  $\text{Mo}(\text{CO})_5(\text{ads})$ . A spectrum obtained 26 min following addition of CO shows full conversion



**Figure 5.** FTIR spectra after pumping under vacuum overnight to generate  $\text{Mo}(\text{CO})_3(\text{ads})$  species followed by addition of CO: (a) pumping under vacuum for 14.30 h after addition of  $\text{Mo}(\text{CO})_6$ ; (b) 2 min after addition of CO (0.1 atm) to the sample shown in (a); (c) 26 min after addition of CO.

**Scheme 1.** Surface Processes of  $\text{Mo}(\text{CO})_6$  Adsorbed on  $\gamma$ -PDA



to the original  $\text{Mo}(\text{CO})_6(\text{ads})$ , as evidenced by the appearance of bands at  $1845$  and  $1755\text{ cm}^{-1}$  due to oxygen-bonded CO and at  $1998$  and  $2028\text{ cm}^{-1}$  in the terminal CO region.

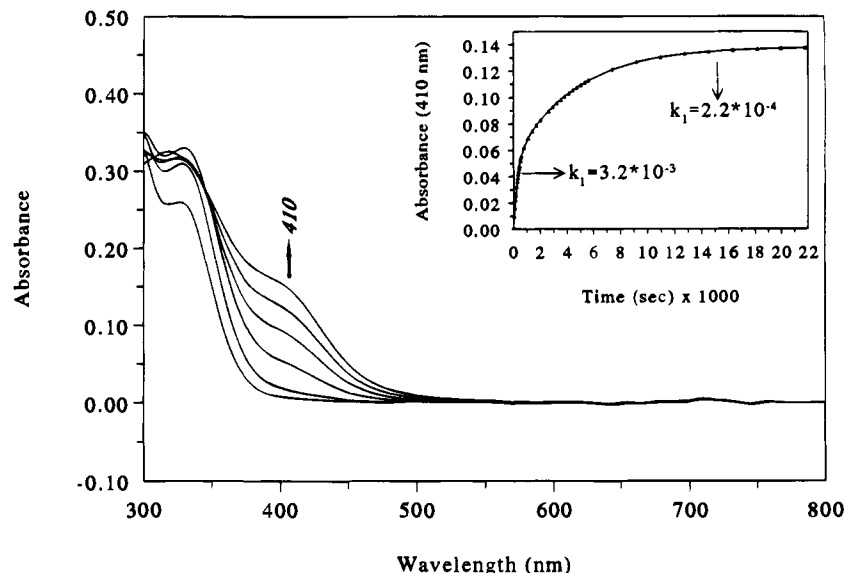
Figure 6 shows the UV-vis spectra as a function of time for  $\text{Mo}(\text{CO})_6$  adsorbed on PDA. Initially, an overall shift of the spectrum to longer wavelengths is evident. At still longer times, an absorbance centered at  $410\text{ nm}$  becomes increasingly intense. The overall shift in absorbance to longer wavelengths corresponds in time to the shifts in the IR spectra which we have associated with migration of physisorbed  $\text{Mo}(\text{CO})_6$  to Lewis acid binding sites. Although the IR evidence indicates that there are two such acid sites, the rates at which  $\text{Mo}(\text{CO})_6$  binds to them do not appear to be greatly different. Furthermore, the acid site giving rise to the CO band at  $1845\text{ cm}^{-1}$  is substantially more abundant than the one at  $1755\text{ cm}^{-1}$ . Thus, it is unlikely that the presence of two distinct kinetics processes could be extracted from the absorbance change data at short times. Instead, we assume that the overall process of migration from the physisorbed to chemisorbed states can be treated in terms of a single first-order rate constant.

Several examples of compounds of the form  $\text{Mo}(\text{CO})_5\text{L}$ , where L is a ligand with little or no  $\pi$ -acid character, are known. Characteristically, they exhibit an absorbance in the vicinity of  $400\text{ nm}$ .<sup>14</sup> A study of  $\text{Mo}(\text{CO})_5$  trapped in the solid state at low temperature revealed an absorbance band at  $411\text{ nm}$ .<sup>15</sup> Thus, the slower process, giving rise to the absorbance at  $410\text{ nm}$ , is ascribed to the loss of CO with formation of  $\text{Mo}(\text{CO})_5(\text{ads})$ , in which the metal is coordinated to a surface oxygen atom. This assignment is also consistent with the time scale in which the IR bands ascribed to  $\text{Mo}(\text{CO})_5(\text{ads})$  are seen to arise.

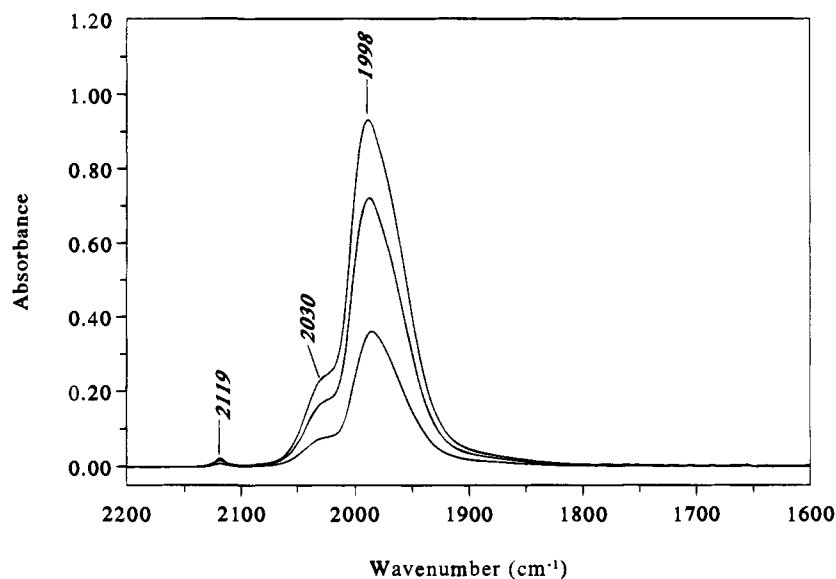
The UV-vis spectra can be analyzed quantitatively in terms of a model of the form of eq 1, in which the species  $\text{Mo}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6(\text{ads})$ , and  $\text{Mo}(\text{CO})_5(\text{ads})$  are in dynamic equilibrium. Under the conditions of the experiment represented by Figure 6, the forward steps are essentially unidirectional. Thus, the kinetics form of the system is  $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ . The absorbance at

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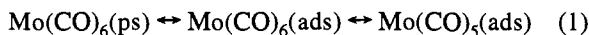


**Figure 6.** UV-vis spectra of  $\text{Mo}(\text{CO})_6$  adsorbed on PDA as a function of time (inset, 410 nm absorbance vs time plot fit to the kinetic expression in eq 3).



**Figure 7.** FTIR spectra, each taken after 1 min following a succession of  $\text{Mo}(\text{CO})_6$  additions to HA.

a convenient wavelength, say 410 nm, contains contributions from both  $\text{Mo}(\text{CO})_6(\text{ads})$ , which we abbreviate as cs, and  $\text{Mo}(\text{CO})_5(\text{ads})$ , which we label dc:



$$A_t = A_{cs} + A_{dc} \quad (2)$$

Using the standard kinetics analysis for an  $A \rightarrow B \rightarrow C$  system,<sup>16</sup> and taking account of the fact that both  $\text{Mo}(\text{CO})_6(\text{ads})$  and  $\text{Mo}(\text{CO})_5(\text{ads})$  absorb at the wavelength of analysis, the expression for the absorbance as a function of time is as shown in eq 3,

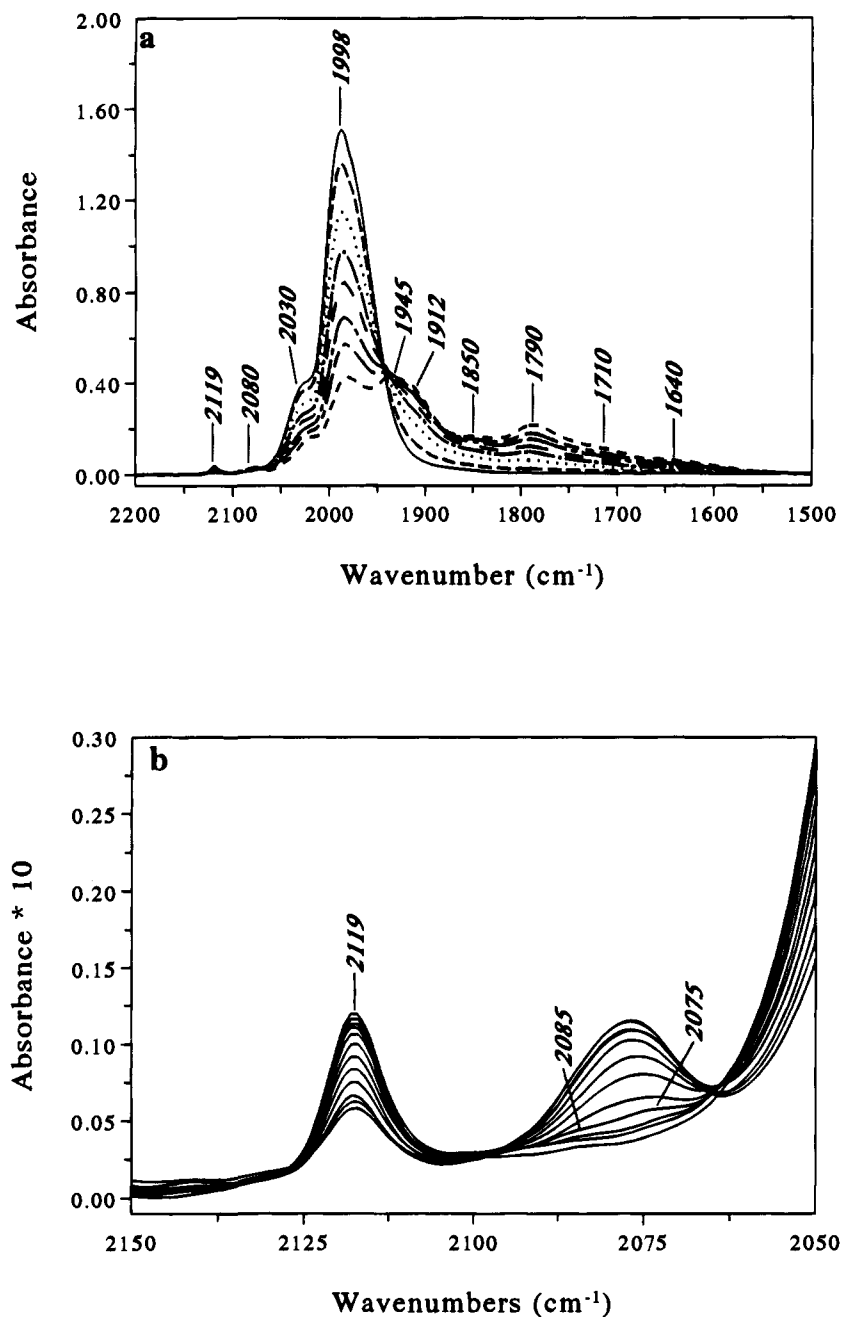
$$C_0 \left\{ \epsilon_c + \left[ \epsilon_b(k_1/(k_2 - k_1)) - \epsilon_c(k_2/(k_2 - k_1)) \right] \exp(-k_1 t) + \left[ \epsilon_c(k_1/(k_2 - k_1)) - \epsilon_b(k_1/(k_2 - k_1)) \right] \exp(-k_2 t) \right\} \quad (3)$$

where  $C_0$  is the total concentration of molybdenum species that go on finally to form  $\text{Mo}(\text{CO})_5(\text{ads})$  and  $\epsilon_i$  are the respective extinction coefficients.

Figure 6 inset shows the fit of the data to eq 3 for the absorbance data at 410 nm. The fit to two first-order processes is very good, yielding first-order rate constants of  $3.2 \times 10^{-3}$  and  $2.2 \times 10^{-4} \text{ s}^{-1}$ . The larger rate constant represents the binding of  $\text{Mo}(\text{CO})_6$  to the Lewis acid sites. The smaller one represents the decarbonylation of  $\text{Mo}(\text{CO})_6(\text{ads})$  to form  $\text{Mo}(\text{CO})_5(\text{ads})$ . The fact that the data are well-fitted by a single first-order rate constant in each case indicates either that the processes characteristic of the two Lewis acid sites have closely similar rate constants or that the absorbance changes for the more abundant site mask those for the other, or both. The time dependence of the IR spectra suggests that the difference in rates of formation of the two  $\text{Mo}(\text{CO})_6(\text{ads})$  sites is not large. There is no evidence in the IR results for a distinct difference in the rates of decarbonylation from the two sites. However, if the rate of interconversion of  $\text{Mo}(\text{CO})_6(\text{ads})$  between the sites of chemisorption is high, only one effective rate for decarbonylation should be seen.

The issue of whether the surface processes can be modeled as effectively irreversible was addressed by carrying out the kinetics analysis under two widely different conditions of loading. In the experiment illustrated in Figure 6, the maximum initial absorbance due to  $\text{Mo}(\text{CO})_6$  was about 0.25. In another

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**Figure 8.** (a) FTIR spectra for Mo(CO)<sub>6</sub> adsorbed on HA as a function of time. (b) FTIR spectra for Mo(CO)<sub>6</sub> adsorbed on HA in 2150 to 2050 cm<sup>-1</sup> region (absorbance is multiplied by 10).

experiment the loading was increased so that the initial absorbance was about 0.80. Under these conditions, the rate constants obtained were  $4.1 \times 10^{-3}$  and  $2.3 \times 10^{-4} \text{ s}^{-1}$ . The slower process is essentially the same in the two measurements. Given the uncertainties in the analysis, the faster processes also probably have the same rate constants. If there is a difference, a faster process under high loading might arise because of the influence of neighboring adsorbed molecules.

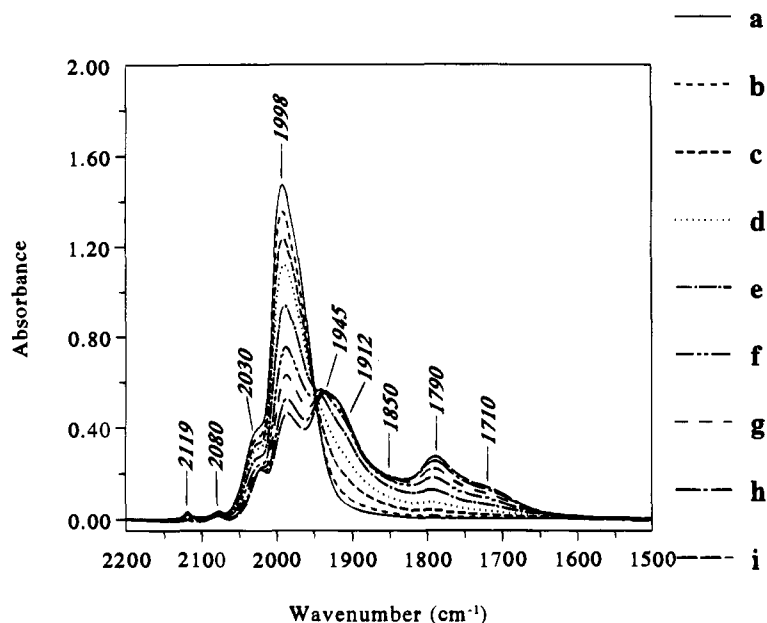
The origin of the kinetic barrier to the formation of Mo(CO)<sub>6</sub>-ads is not clear. The nature of the surface in the present experiments is not well defined. In general, however, the physisorption of Mo(CO)<sub>6</sub> from the gas phase to the surface must involve a substantial free energy decrease, because the surface effectively scavenges all the gas-phase Mo(CO)<sub>6</sub> under the conditions of the experiments. One would not expect to observe a significant barrier to binding of Mo(CO)<sub>6</sub> to the surface Lewis acid site once the Mo(CO)<sub>6</sub> molecule had arrived at the site. The barrier thus probably is characteristic of the migration of physisorbed Mo(CO)<sub>6</sub> on the alumina surface.

A somewhat analogous time dependence has been noted by Zecchina et al. upon exposure of Na-Y zeolite to Cr(CO)<sub>6</sub> vapor.<sup>17</sup> In that study, the authors ascribed the changes in the spectra to a diffusion-controlled penetration of the carbonyl into the pressed pellet. We have shown that under the conditions of our experiment, the Mo(CO)<sub>6</sub> is essentially entirely adsorbed onto the alumina from the vapor phase. Because the particles from which a disk is pressed are quite large, it is likely that the carbonyl is effectively distributed throughout the disk. The kinetic process observed is thus ascribed to surface migration. In another study of the interaction of Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub> with PDA, we have shown that the barrier for binding to the Lewis acid sites is due to migration of physisorbed species on the alumina surface.<sup>18</sup>

The loss of CO from chemisorbed Mo(CO)<sub>6</sub> is, as expected, considerably faster than dissociative loss of CO from Mo(CO)<sub>6</sub>

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(18) Reddy, K. P.; Brown, T. L. Unpublished results.



**Figure 9.** FTIR spectra for  $\text{Mo}(\text{CO})_6$  adsorbed on HA (deuterated) as a function of time: (a) 3 min; (b) 13 min; (c) 23 min; (d) 33 min; (e) 53 min; (f) 1.23 h; (g) 1.53 h; (h) 2.33 h; (i) 3.13 h.

in hydrocarbon solution. A rate constant on the order of  $10^{-4} \text{ s}^{-1}$  for dissociative CO loss is observed in solution substitution processes only at temperatures on the order of  $100 \text{ }^\circ\text{C}$ .<sup>19</sup> Ozin, Poë, and co-workers have measured rate constants varying from  $10^{-5}$  to  $10^{-3} \text{ s}^{-1}$ , in the temperature range from 45 to  $95 \text{ }^\circ\text{C}$ , for CO loss from  $\text{Mo}(\text{CO})_6$  in Na–Y zeolites.<sup>20</sup> In this system, CO dissociative loss is presumably promoted by coordination of a CO group to the metal ion labilizes the molecule toward CO loss, as compared with the labilization we observe, is consistent with the expectation that the surface sites should be more strongly acidic than  $\text{Na}^+$ .

On the other hand, in the case of HA we notice only the physisorbed  $\text{Mo}(\text{CO})_6$  (Figure 7), characterized by three IR bands in the terminal CO region at 2119, 2030, and  $1998 \text{ cm}^{-1}$  because of the perturbation of octahedral symmetry. Similar IR bands are reported for  $\text{Mo}(\text{CO})_6$  on HA by Laniecki et al.<sup>3e</sup> In addition, no IR bands are present in the low-frequency region at  $1850 \text{ cm}^{-1}$  and below. This is suggestive of the lack of coordination to  $\text{Al}^{3+}$  and indicates that no Lewis acid sites are exposed on the surface of HA activated at  $425 \text{ K}$ .

Figure 8 shows IR spectra taken at increasing time. The IR bands due to the physisorbed species decline in intensity while new bands grow in their place at 2085, 2075, 1945, 1912, 1850, 1790, 1710, and  $1640 \text{ cm}^{-1}$ . In contrast, Laniecki et al.<sup>3e</sup> reported that no new IR bands were observed even after 15 min. In order to ascertain whether the band at  $1640 \text{ cm}^{-1}$  is due to surface hydroxyl groups or the newly formed subcarbonyl species, experiments were repeated under analogous conditions with deuterated alumina; the IR spectra obtained as a function of time are shown in Figure 9. These spectra are characterized by the conspicuous absence of the band at  $1640 \text{ cm}^{-1}$ , which can thus be assigned to surface hydroxyl groups.

The interaction of  $\text{Mo}(\text{CO})_6$  with the surface can be understood in terms of the nucleophilicity of hydroxyl groups on the alumina surface<sup>21</sup> and the feasibility of nucleophilic attack at the carbon center of metal carbonyls.<sup>22</sup> It has been argued that there exist five different types of hydroxyl groups on the

$\gamma$ -alumina surface.<sup>21</sup> It is entirely plausible that two of these are basic enough to attack the carbon center of a carbonyl group. Some of the new IR bands that arise in place of the physisorbed species can thus be deconvoluted as a pair of triplets (Table 1). We interpret these sets as due to  $\text{Mo}(\text{CO})_5(\text{L})$ , where L represents the two different types of surface hydroxyl groups that are capable of attacking the carbon center of a metal carbonyl. The loss of CO from  $\text{Mo}(\text{CO})_6$  coordinated to hydroxyl groups on the surface is not surprising since it is well established that base attack on  $\text{Mo}(\text{CO})_6$  promotes *cis*-labilization.<sup>12a,d</sup> The vacant coordination site formed by the loss of CO is then occupied by the neighboring hydroxyl group on the surface with concomitant rupture of the interaction between the carbonyl and hydroxyl group, leading to the formation of  $\text{Mo}(\text{CO})_5(\text{L})$ . The formation of  $\text{Mo}(\text{CO})_5(\text{L})$  is further supported by the appearance of a new band at  $410 \text{ nm}$  in the UV–vis spectra obtained as a function of time (Figure 10b). Several examples of compounds of the form  $\text{Mo}(\text{CO})_5\text{L}$ , where L is a ligand with little or no  $\pi$ -acid character, are known; they exhibit an absorbance in the vicinity of  $400 \text{ nm}$ .<sup>14</sup> Howe<sup>2k</sup> interpreted the IR spectra of  $\text{Mo}(\text{CO})_6$  on HA as due to the presence of  $\text{Mo}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_5(\text{L})$ , and a lower subcarbonyl species. He assigned the IR bands at 2075, 1950, and  $1910 \text{ cm}^{-1}$  to  $\text{Mo}(\text{CO})_5(\text{L})$ . The bands at 2030, 1935, 1790, and  $1725 \text{ cm}^{-1}$  were ascribed to a mixture of stable lower subcarbonyls of unknown composition. In our experiments we notice also that in addition to  $\text{Mo}(\text{CO})_5\text{L}$ , a lower subcarbonyl is formed in small quantities in the initial stages. It is the only species remaining when the sample is placed under dynamic vacuum. A careful look at spectra c and d in Figure 10a shows that while there is no change in intensity of the bands at 1945 and  $1912 \text{ cm}^{-1}$ , the band at  $1790 \text{ cm}^{-1}$  increases. The corresponding UV–vis spectra show a decline in intensity of the band at  $410 \text{ nm}$ . This may be due to the conversion of  $\text{Mo}(\text{CO})_5(\text{L})$  to a lower subcarbonyl while only a small amount of the  $\text{Mo}(\text{CO})_5(\text{L})$  is being produced from  $\text{Mo}(\text{CO})_6$ . Placing the sample under vacuum for 2 min results

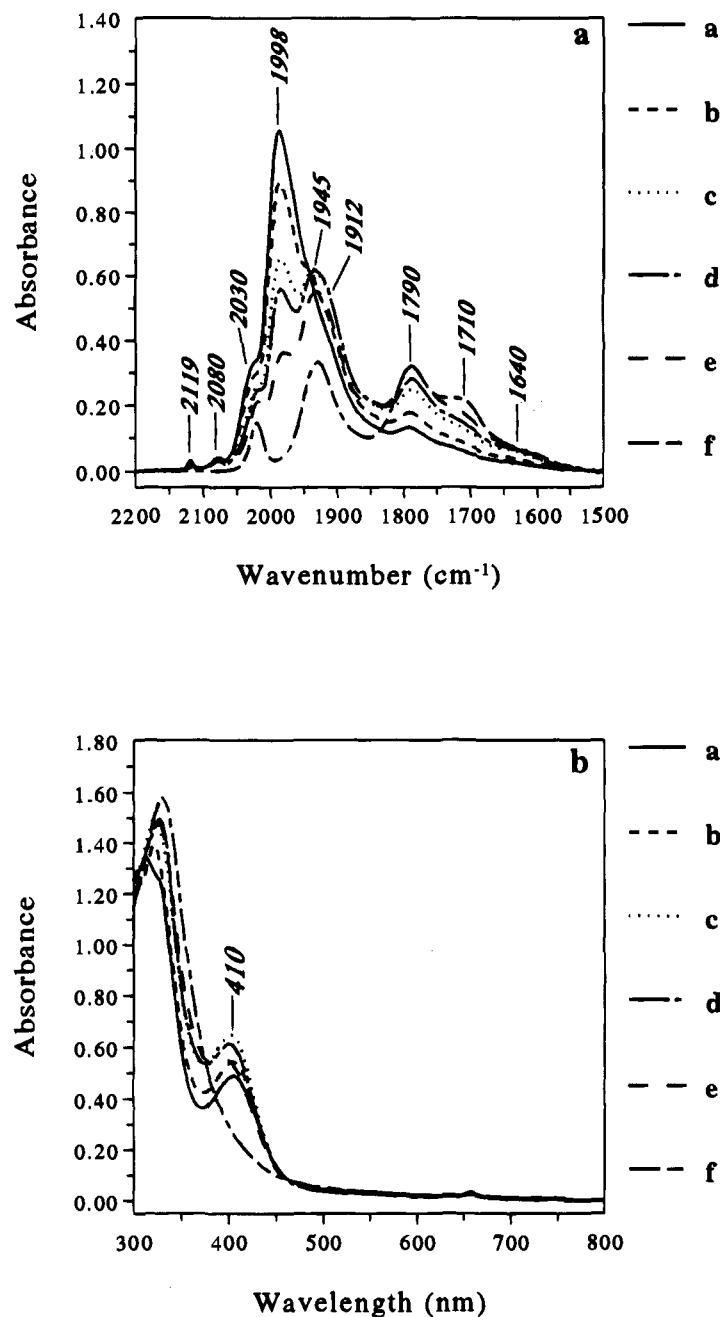
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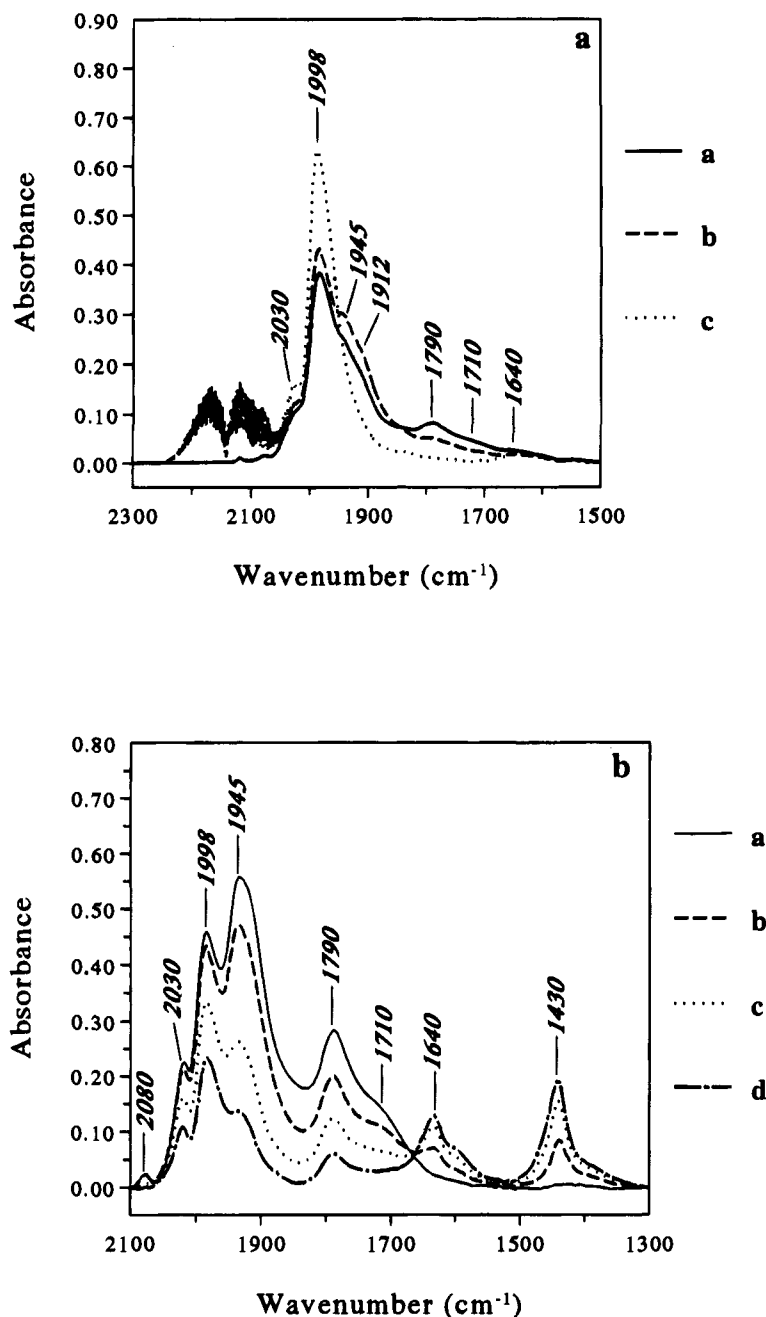


**Figure 10.** (a) FTIR spectra for  $\text{Mo}(\text{CO})_6$  adsorbed on HA: (a) 1.30 h after addition; (b) 2.30 h after addition; (c) 6.10 h after addition; (d) 7.10 h after addition; (e) 2 min after placing sample d under vacuum; (f)  $\sim 13$  h after placing sample e under vacuum. (b) UV-vis spectra for  $\text{Mo}(\text{CO})_6$  adsorbed on HA: (a) 1.30 h after addition; (b) 2.30 h after addition; (c) 6.10 h after addition; (d) 7.10 h after addition; (e) 2 min after placing sample d under vacuum; (f)  $\sim 13$  h after placing sample e under vacuum.

in further loss in intensity of the 410 nm band (spectrum e, Figure 10b). This is further supported by the decline of IR bands at 1945 and 1912  $\text{cm}^{-1}$  while those at 1790 and 1710  $\text{cm}^{-1}$  grow. This is indicative of the partial removal of physisorbed  $\text{Mo}(\text{CO})_6$  and CO which in turn promotes the conversion of  $\text{Mo}(\text{CO})_5(\text{L})$  to a lower subcarbonyl. When the sample at this stage is placed under vacuum overnight ( $\sim 13$  h), all  $\text{Mo}(\text{CO})_6$  is removed, while the  $\text{Mo}(\text{CO})_5(\text{L})$  is converted totally to the more stable lower subcarbonyl with IR bands at 2030, 1945, 1790, and 1710  $\text{cm}^{-1}$ . A shift of the IR bands to lower frequency is consistent with binding to additional hydroxy groups on the surface following the loss of CO groups from  $\text{Mo}(\text{CO})_5(\text{L})$ . An interesting feature in the IR spectrum f, Figure 10a, is that there is no change in intensity of the band at 1790  $\text{cm}^{-1}$ , while the band at 1710  $\text{cm}^{-1}$  increases sharply. This could mean that the loss in intensity of the band at 1790  $\text{cm}^{-1}$ , due to  $\text{Mo}(\text{CO})_5(\text{L})$ , is compensated for by formation of the

more stable subcarbonyl. Further evidence for the total conversion of  $\text{Mo}(\text{CO})_5(\text{L})$  to lower subcarbonyls is provided by loss of the band at 410 nm (spectrum f, Figure 10b).

The loss of CO on HA is reversible at room temperature. An IR spectrum (Figure 11a) obtained 1 min following addition of CO shows that the bands at 1790 and 1725  $\text{cm}^{-1}$  decrease in intensity at a rapid rate, with the simultaneous growth of bands due to  $\text{Mo}(\text{CO})_5(\text{L})$  at 1945 and 1912  $\text{cm}^{-1}$ . Over an extended period these are replaced by the bands at 1998 and 2028  $\text{cm}^{-1}$ , ascribed to physisorbed  $\text{Mo}(\text{CO})_6$ . Finally, the addition of  $\text{CO}_2$  to the subcarbonyl species on deuterated HA results in formation of a bicarbonate with displacement of the subcarbonyls. Although we do not have any direct evidence on this point, the subcarbonyls are presumably recombining with CO as the  $\text{CO}_2$  occupies the active surface sites. The bands at 1640 and 1470  $\text{cm}^{-1}$  can be assigned to the symmetric and asymmetric stretching modes of  $\text{DCO}_3^-$  respectively, formed following the



**Figure 11.** (a) FTIR spectra of  $\text{Mo}(\text{CO})_6$  on HA, followed by addition of CO: (a) 2.30 h after addition of  $\text{Mo}(\text{CO})_6$  to HA; (b) 1 min after addition of CO to a; (c)  $\sim 2$  h after b was obtained. (b) FTIR spectra of  $\text{Mo}(\text{CO})_6$  on deuterated HA, followed by addition of  $\text{CO}_2$ : (a)  $\sim 3.30$  h after addition of  $\text{Mo}(\text{CO})_6$ ; (b) 1 min after addition of  $\text{CO}_2$  to a; (c) 2 min after b was collected; (d) 8 min after c was obtained.

coordination of  $\text{CO}_2$  to OD on the surface (Figure 11b).<sup>8c,23</sup> Deuterated alumina was employed in this experiment with  $\text{CO}_2$  so as not to confuse the  $\text{CO}_2$  symmetric stretch band at  $1640\text{ cm}^{-1}$  with that of hydroxyl on the surface.

In summary, the experimental work reported here provides the first clear evidence for migration of an initially-physisorbed  $\text{Mo}(\text{CO})_6$  species to Lewis acid sites on the surface of PDA. Second, we have established clearly the presence of a heretofore elusive  $\text{Mo}(\text{CO})_5(\text{ads})$  intermediate in the sequence of decarbonylation processes that culminates in formation of  $\text{Mo}(\text{CO})_3(\text{ads})$ . We have presented the first UV-vis spectra associated with the adsorption and decarbonylation of  $\text{Mo}(\text{CO})_6$  and have employed them to obtain quantitative kinetic results related to

binding to acid sites and for the decarbonylation process  $\text{Mo}(\text{CO})_6(\text{ads}) \rightarrow \text{Mo}(\text{CO})_5(\text{ads}) + \text{CO}$  on PDA. In addition, we have shown through the use of IR and UV-vis spectral data the formation of  $\text{Mo}(\text{CO})_5(\text{L})$  and a stable lower subcarbonyl on HA. Finally, we have shown that the decarbonylation processes are reversible at room temperature for both PDA and HA following the addition of CO and also displacement of the subcarbonyls in the case of HA when  $\text{CO}_2$  is added.

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