natural mordenites, whereas our samples were synthetic mordenites. Tentatively it may be denoted that the difference in crystallization times for synthetic mordenites versus natural ones (short and long, respectively) does not allow the Al atoms to reach the energetically most favored positions for synthetic mordenites.

Additionally conflicting evidence has been put forward by the very recent solid-state NMR of Bodart et al.,<sup>23</sup> since their experimental data have also been obtained on synthetic mordenite samples. The dealumination mechanism of the mordenite lattice has been studied by these researchers<sup>23</sup> by <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectroscopy and by IR spectroscopy of the OH stretching vibration region. Regrettably the adsorption properties of their samples have not been investigated. In complete agreement with this work, the authors conclude that during dealumination Al is extracted from the 4-rings in the framework. However, from the Si(nAl) areas (n = 0, 1, 2) in their <sup>29</sup>Si NMR spectra, they conclude that the Al atoms are sited exclusively on  $T_{3,4}$  positions, each 4-ring containing two or zero Al atoms. We doubt, however, if the intrinsic accuracy of their and our <sup>29</sup>Si NMR results on mordenites, based on an area deconvolution of three different strongly overlapping regions, could be performed with a precision of better than 5%. Thus in our opinion the discrimination between the six models for Al siting<sup>23</sup> with mutually subtle differences (cf. Figure 10 of ref 23) is a nontrivial task; moreover, the parameters involved are obtained after applying additional corrections. The Si/Al ratio of the framework, e.g., is obtained from elemental analysis data and must be corrected for extra-framework Al derived from quantitative  ${}^{27}$ Al NMR data, while the Si(nAl) areas have been obtained by deconvolution of the <sup>29</sup>Si NMR spectra, followed by a correction of the SiOH content.

In our opinion the propagation of even small errors may lead, during the evaluation of the experimental <sup>29</sup>Si NMR areas, to errors in the final values too large to allow for model discrimination.

## Conclusions

It has been shown by <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectroscopy, by IR spectroscopy, and by benzene adsorption that the transformation of SP to LP mordenite is due to dealumination of the zeolite framework. The transition is complete at about 20% dealumination. SP mordenite contains only tetrahedral Al, whereas LP mordenite contains at least ca. 20% octahedral Al. The octahedral Al is present in a neutral form that does not contain hydrated cations, for instance, as  $Al_2O_3$ . The bands at 620 and 710-730 cm<sup>-1</sup> in the IR spectrum of

mordenite must be assigned to Al-O vibrations in single 4-rings. It was concluded from the IR spectra of the samples that by the dealuminating treatment Al<sup>IV</sup> is removed from the 4-rings only and that  $Al^{IV}$  was randomly distributed over 4- and 5-rings in the starting SP mordenite.

These results confirm the conclusion of Raatz et al.<sup>3</sup> that the pore blocking of SP mordenite is caused by structural defects. The structure is made accessible by removal of aluminum from the 4-rings forming the walls of the main channels. In this way connections with a large aperture are created, and a two-dimensional pore system is obtained.

Acknowledgment. We thank P. H. van Oeffelt and F. H. A. M. J. Vandenbooren (DSM) for carrying out the benzene adsorption measurements and preparing the samples, respectively. For technical assistance at the Dutch National 500-MHz HF NMR facility at Nijmegen (The Netherlands) we acknowledge P. A. W. van Dael, W. Guijt, and C. A. G. Haasnoot.

Registry No. Benzene, 71-43-2.

# Catalytic Oxidation of CO on Rh/SiO<sub>2</sub>: A Rapid-Response Fourier Transform Infrared Transient Study

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The catalytic oxidation of CO has been studied over Rh/SiO<sub>2</sub> by using a rapid transient response FTIR-mass spectrometric technique. The reactivity of linearly adsorbed CO was found to be considerably greater than that of the dicarbonyl species at both 85 and 200 °C. The frequency of linearly adsorbed CO was observed to undergo a continuous red shift during the duration of the transient, suggesting the formation of a mixed CO-oxygen adlayer. Induction times required for the formation of gas-phase CO<sub>2</sub> were found to be nearly 2 orders of magnitude lower than those observed for Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>. Self-sustained CO- $O_2$  oscillations reinforce the greater reactivity of linearly adsorbed CO.  $H_2$ -CO- $O_2$  transient studies also suggest the formation of mixed hydrogen-CO adlayers. Hydrogen was observed to react with the dicarbonyl species to form a hydridocarbonyl species. The CO which is displaced by hydrogen reacts rapidly with chemisorbed oxygen to form CO<sub>2</sub>.

### Introduction

A major problem in the use of infrared spectroscopy to probe the structure of intermediates adsorbed on surfaces under reaction conditions has been to distinguish adsorbed spectator molecules from true reaction intermediates of catalytic significance. There are many examples in the catalytic literature in which strongly adsorbed molecules have been identified by using infrared spectroscopy only to discover that these species are formed on an active metal site and later migrate to the support. Important examples of this type of behavior include the formation of isocyanate during the NO-CO<sup>1-3</sup> reaction on supported metals, the formation of

methoxy and surface acetate species in the oxidation of ethanol,<sup>4,5</sup> and growing hydrocarbon chains during the Fischer-Tropsch synthesis.<sup>6</sup> In all of these cases, considerable efforts were made to untangle true reactive intermediates from spectator molecules.

In the absence of adsorption on the support, a second problem that sometimes confronts the catalyst researcher is to decide which

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Figure 1. Block diagram of the infrared cell reactor together with the associated flow-system components.

of several chemisorbed species is the most reactive for a given catalytic reaction. One of the most powerful methods that can be used to obtain the reactivity of adsorbed intermediates is the use of the transient response method (ref 7 and references cited therein). In this method, the surface is saturated with one of the reactants. The reactivity of the species present on the surface is then studied by either pulsing or flowing the second reactant over the catalyst while simultaneously monitoring the reaction products by using infrared spectroscopy or some other appropriate spectroscopic technique.

In order to ensure that the requirements of a transient response be met, an infrared cell reactor should, as a minimum, conform to the following: (1) the residence time in the infrared cell reactor should be less than the time required for scanning the spectrum; (2) the reactant gases should preferably be forced through the sample disk with little or no leakage around the edges; (3) the outlet from the infrared cell reactor should be interfaced with a gas-phase measuring device, such as a quadrupole mass spectrometer; and (4) the cell should be constructed to handle adequate heating schedules. Nagai et al.<sup>8</sup> have recently described an infrared cell reactor design that meets these criteria. Because the dead-space volume within the reactor was less than 1.5 mL, residence times of about 1 s were achieved at reactant flow rates of 100 mL/min. With a scan rate of 0.25 scans/s, four interferograms could be co-added to yield data points that met the transient response study requirements.

As a model reaction, we selected the catalytic oxidation of CO over  $Rh/SiO_2$ . This choice was made for the following reasons: (1) the nature of the CO species chemisorbed on Rh is reasonably well understood, (2) some controversy exists regarding the reactivity of different adsorbed CO species with  $O_2$ ,<sup>9-11</sup> and (3) self-sustained CO-O2 oscillations are easily obtained on Rh/SiO2.12

# **Experimental Section**

Infrared Cell Reactor. For the unidirectional transient studies, a small single-pass differential reactor with a net volume of 1.5 mL was used. Details concerning the reactor design have been published elsewhere.<sup>5</sup> For the self-sustained oscillation studies, a larger single-pass differential reactor having a volume of 56 mL was employed. This reactor is similar in design to the smaller reactor. Details regarding its design have been published by Sharma et al.13

Flow System. A block diagram of the associated components used in the flow system is outlined in Figure 1. The reactor was placed in the sample chamber of an FTIR (FTS 40, Digilab) spectrometer. The gas-phase composition in the reactor was monitored by a quadrupole mass spectrometer (QMG 112, Balzers). A synchronizer was designed in our laboratory to coordinate the scanning of the FTIR and the QMG. The infrared

data were processed with a 3240-SPC Data Station (Digilab) and could be transferred to a personal computer (IBM-AT). The mass spectral data were collected and analyzed in the IBM-AT. The temperature of the reactor was controlled by a temperature programmer (Model PC 6011, Valley Forge Instruments Inc.). The temperature gradient between the inside and the outside of the reactor was observed to vary between 10 and 50 °C depending upon reactor temperature. All of the temperatures reported were gas-phase temperatures measured inside the reactor.

Materials. The silica-supported Rh catalysts were prepared by wet impregnation. Initially, the appropriate weight of Rh-Cl<sub>3</sub>·3H<sub>2</sub>O (Strem Chemical) was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the support. The solutions were mixed with Cab-O-Sil, grade M-5 (Cabot Corp., Boston, MA), until a slurry having the consistency of a thin paste was formed. The surface area and the average pore size of Cab-O-Sil, as reported by the manufacturer, are 200  $m^2/g$  and 14.0 nm, respectively. The slurry was dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The metal loading was 3 wt%. The dried catalyst was then ground into a fine powder, less than 45  $\mu$ m, and pressed into self-supporting disks with an optical density of approximately 80 mg/cm<sup>2</sup>. For the self-sustained oscillatory studies, an optical density of about 90 mg/cm<sup>2</sup> was used.

The gases used in this study were subjected to the following purification treatment: H<sub>2</sub> (ultrahigh purity: Linox Co., Chicago, IL) was further purified by passing it through a deoxo unit to convert  $O_2$  impurities to  $H_2O$ , which was then removed by a molecular sieve maintained at 77 K by means of a dry ice-acetone trap. It was then passed through an MnO trap which had been activated in flowing H<sub>2</sub> at 673 K. It was found convenient to use  $O_2$  and CO premixed with He to give the following compositions: 5% CO in He and 5% O<sub>2</sub> in He. Both gases were of research grade or better and were obtained from Spectra Gases Inc., Newark, NJ.

Gas flow rates were controlled by using Tylan (Model FC260) electronic flow controllers. The flow controllers were calibrated by the manufacturer using gas mixtures that were identical with those used in this study. The calibration was rechecked in our laboratory by means of a bubble flow meter and a gas chromatograph.

Chemisorption measurements were performed by using the dynamic pluse method.<sup>14</sup> Metal dispersions were calculated on the basis of a CO/Rh(s) adsorption ratio of 1 and found to be 43%. The CO/Rh(s) ratio of 1 is only valid when the surface concentration of the CO dicarbonyl species is small, as is the case for well-reduced  $Rh/SiO_2$ . For the case of  $Rh/Al_2O_3$  or for very highly dispersed Rh catalysts this assumption is not valid.<sup>15</sup>

Procedure. Prior to a transient study, the freshly pressed sample disks were reduced according to the following schedule: The catalyst was exposed to flowing He (100 mL/min) at 50 °C. The temperature was then increased at a linear rate of 10 °C/min to 150 °C in flowing He and maintained at 150 °C for 0.5 h. The He flow was switched to  $H_2$  (100 mL/min) at 150.°C, and the temperature was then increased at 10 °C/min to 455 °C. The catalyst was reduced in flowing H<sub>2</sub> for 3 h at 455 °C followed by treatment in flowing He for 0.5 h at the same temperature. The temperature was then reduced to 50 °C in flowing He.

The procedure for the  $CO-O_2$  transient study was as follows: the surface was initially saturated with oxygen by flowing 5%  $O_2$ (100 mL/min) over it for about 40 min. The transient was initiated by switching the gas to 5% CO while the infrared and the mass spectral response were recorded continuously. Following the conclusion of the transient (about 5 min), the 5% CO flow over the catalyst was continued for an additional 40 min in order to allow a sufficient time to process the data. The gas flow was then switched to 5%  $O_2$  in He (100 mL/min), and the reverse

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TABLE I: Infrared Frequency Assignments for CO on Rhodium Species (cm<sup>-1</sup>)

surface	Rh <sup>0</sup> (CO)	Rh <sup>I-III</sup> (CO) <sup>a</sup>	Rh(CO) <sub>2</sub>	Rh <sup>0</sup> <sub>2</sub> (CO)	Rh <sup>I</sup> <sub>2</sub> (CO)	Rh(CO)(H)	ref	
Rh/SiO <sub>2</sub>	2040-2050	2205-2112	2098, 2040	1898-1928		2040-2063	this work	
$Rh/SiO_2$	2040-2060		2080, 1990–2020	1890-1900			22	
$Rh/Al_2O_3$	2040-2076	2060-2100	2096–2102, 2022–2032	1845-1875	2000-2020		23	
$Rh/Al_2O_3$	2058-2070		2101, 2031			2048	24	

2395

<sup>a</sup> The oxidation states between I and III.

transient was studied in the same manner.

The procedure for the  $H_2$ -CO-O<sub>2</sub> transient study was as follows: the transient was initiated by exposing a saturated layer of adsorbed CO to a gas flow of  $O_2$  for 40 min. The gas flow was then switched to pure  $H_2$  (100 mL/min) at the temperature of the transient. The infrared spectra and the mass spectral response were recorded continuously for about 5 min. However, the  $H_2$ flow was continued for an additional 40 min before the CO transient was carried out. The CO transient was initiated by switching the gas flow from  $H_2$  to 5% CO(He) and the infrared and mass spectral signals were recorded. The 5% CO(He) was continued for an additional period of 40 minutes before it was replaced by 5%  $O_2(He)$ . Transient response studies were performed at 85 and 200 °C. About three transient studies were performed at each temperature.

### Results

Infrared Band Assignments. The infrared absorption bands for CO adsorbed on  $Rh/SiO_2$  are in good agreement with as-signments proposed in the literature.<sup>15-23</sup> The intense infrared band absorbing at 2072 cm<sup>-1</sup> is undoubtedly due to CO linearly adsorbed on Rh(0) sites.<sup>11,22,23</sup> The pressure dependence of the CO bands absorbing at 2044 and 2098 cm<sup>-1</sup> suggests that both of these infrared bands should be assigned to the same CO chemisorbed species. There is ample documentation in the literature which suggests that they should be assigned to the symmetric and antisymmetric stretching modes of a Rh dicarbonyl species. A certain amount of controversy has arisen in the literature regarding the nature of the Rh surface sites giving rise to the dicarbonyl species. The most common assignment is that the dicarbonyl species are adsorbed primarily on Rh(I) sites. However, several workers have assigned the dicarbonyl species to small isolated Rh particles. Because small Rh particles are generally more difficult to reduce than large Rh particles, this assignment remains somewhat ambiguous. However, the CO/ Rh(s) stoichiometry of CO adsorbed on highly dispersed Rh adds validity to this argument. We prefer the assignment that places the dicarbonyl species on partially oxidized Rh surface sites but remain open minded on this controversy. The observation that the adsorption of the dicarbonyl species is inhibited on highly reduced Rh/SiO<sub>2</sub> reinforces our argument.<sup>11</sup>

In addition to these major infrared absorption bands, small infrared absorption bands are observed at 2112 and 2210 cm<sup>-1</sup>. Because these infrared bands are frequently observed following treatment in oxygen at high temperatures, we suggest that they are most likely due to the adsorption of CO on more highly oxidized Rh surface sites which could be oxidic in nature.<sup>24</sup> Kiss

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Figure 2. FTIR transient response for  $O_2$  reacted with a monolayer of CO at 85 °C on Rh/SiO<sub>2</sub> (5% O<sub>2</sub> in He; flow rate = 100 mL/min).

and Gonzalez<sup>11</sup> have previously noted that the CO species giving rise to these infrared bands are only slightly reactive during CO oxidation. The small broad band centered at 1902 cm<sup>-1</sup> is assigned to CO coordinated to two Rh surface atoms (i.e., bridge-bonded CO). All six infrared bands are shown in Figure 2 (time = 1 s). The infrared assignments for CO adsorbed on Rh, together with the appropriate references, are summarized in Table I.

Unfortunately, the frequencies of the CO (gas) absorbance band and the surface CO absorbance band overlap and result in a convoluted peak. These infrared bands were mathematically separated by a method that has been previously described.<sup>13</sup> In addition to the infrared bands assigned to the CO chemisorbed species throughout the transient study, the rate of evolution of CO<sub>2</sub> was followed by monitoring the R-branch of the gas-phase  $CO_2$  band centered at 2361 cm<sup>-1</sup>. This provides for a qualitative independent check of the mass spectral response data. The induction period was taken as the time elapsed between CO entry into the reactor and the time at which the evolution of gas-phase CO<sub>2</sub> was first detected by the quadrupole mass spectrometer.<sup>25</sup> Induction periods were corrected for the dead-space volume corresponding to the stainless steel tubing located upstream of the reactor, by means of a dead-space-time calibration.

Low-Temperature Studies. The transient FTIR response study for the reaction of  $O_2$  (gas) with the various species of CO adsorbed on  $Rh/SiO_2$  is shown in Figure 2. A very high rate of reaction was observed for the CO linearly adsorbed on the Rh(0) surface sites. The rate of disappearance of the infrared band at 1912 cm<sup>-1</sup> assigned to bridge-bonded CO nearly paralleled that due to linearly adsorbed CO. The frequency of the infrared band assigned to linearly adsorbed CO was observed to decrease steadily from 2072 to 2055  $cm^{-1}$  prior to its disappearance after 4 s. The induction time for the appearance of CO<sub>2</sub> in the gas phase was about 7 s. This induction time is about 2 orders of magnitude lower than that observed for similar transient response studies obtained over Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>.<sup>26</sup> The infrared bands at

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Figure 3. FTIR transient response for CO reacted with a monolayer of oxygen at 85 °C on Rh/SiO<sub>2</sub> (5% CO in He; flow rate = 100 mL/min).

2098 and 2041 cm<sup>-1</sup> assigned to the CO dicarbonyl species were observed to react very slowly with O<sub>2</sub> (gas). The infrared spectrum of CO obtained following an 87-s exposure to O<sub>2</sub> (gas) at 85 °C shows that the features that are characteristic of the adsorbed dicarbonyl species still persist on the surface.

The most important feature arising from this study is the observation that the frequency of the  $2072 \cdot \text{cm}^{-1}$  band is observed to shift continuously throughout the duration of the transient response study. This is in sharp contrast to the invariance in the position of the infrared absorption band assigned to linearly adsorbed CO on both Pt/SiO<sub>2</sub><sup>25,26</sup> and Pd/SiO<sub>2</sub>,<sup>25</sup> throughout the duration of the CO-O<sub>2</sub> transient. This suggests that CO dipole-dipole coupling persists on both Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>. On Rh/SiO<sub>2</sub>, a decrease in dipole-dipole coupling suggests the presence of a mixed oxygen-CO adlayer. The adsorbed dicarbonyl species do not give rise to dipole-dipole coupling, and for this reason their position is invariant to changes in CO surface coverage. The reactivity of the CO species adsorbed on the higher oxidation states of Rh is low and essentially parallels those due to the dicarbonyl species.

Following the conclusion of the above  $CO-O_2$  transient, 5% O<sub>2</sub>(He) was continuously passed over the catalyst at 85 °C for 40 min. Even after this relatively long exposure to  $O_2$ , the infrared bands assigned to the dicarbonyl species were observed to persist in the infrared spectrum of CO. The O2-CO transient study was initiated by switching the gas flow from  $5\% O_2(He)$  to 5% CO(He)while maintaining the temperature at 85 °C. The results of the  $O_2$ -CO transient response study are shown in Figure 3. Both the mass spectral and FTIR transient responses showed that CO<sub>2</sub> was observed in the gas phase immediately following the initiation of the transient study. The induction time was, therefore, less than 1 s. The results of this study show that initially there is a sharp increase in the absorbance of the infrared bands assigned to the dicarbonyl species. The absorbance of the infrared band assigned to linearly adsorbed CO was observed to increase to a maximum after 6 s had elapsed. The infrared band centered at 1902 cm<sup>-1</sup> assigned to bridge-bonded CO increased monotonically throughout the duration of the transient. This result is in complete agreement with the concept that the most reactive CO surface species in the oxidation of CO is linearly adsorbed CO. Initially, the relatively unreactive dicarbonyl species adsorbs on Rh surface sites vacated as the result of the CO-oxygen reaction. After 3 s  $CO_2$  is no longer observed in the gas-phase spectrum, indicating the conclusion of the rapid portion of the transient. Following the conclusion of the reaction, the absorbance of the linearly adsorbed CO rapidly increases to its maximum value. It is also noteworth that, unlike the CO-O<sub>2</sub> transient, the position of the infrared band assigned to linearly adsorbed CO remains constant at 2075 cm<sup>-1</sup> throughout the duration of the transient. This



Figure 4. FTIR transient response for  $H_2$  reacted with a mixed layer of CO and oxygen at 85 °C on Rh/SiO<sub>2</sub> (H<sub>2</sub>; flow rate = 100 mL/min).

suggests the presence of strong CO dipole-dipole coupling, inferring the formation of adsorbed CO phases on the surface. The slightly higher frequency observed for the dicarbonyl species is in all likelihood due to a slightly higher oxidation state of Rh, induced by the relatively long exposure of the catalyst to gas-phase oxygen.<sup>11</sup>

In order to obtain a better understanding regarding the stability of the various adsorbed CO species in a more reducing environment,  $H_2$  (gas) was added to an oxidized Rh surface on which only the dicarbonyl species was present. This was easily obtained by exposing a surface containing the various adsorbed CO species to  $O_2$  (gas) at 85 °C. Under these conditions only the dicarbonyl species, in addition to traces of other CO species adsorbed on the higher oxidation states of Rh, were retained on the surface.

Following exposure to O<sub>2</sub> (gas) at 85 °C, the gas flow was switched to  $H_2$  and the transient response was started. The results of this study are shown in Figure 4. The products obtained included both H<sub>2</sub>O and CO<sub>2</sub> which were verified by using the quadrupole mass spectrometer. Following the initiation of the transient response study, a decrease in the absorbance of the high-frequency infrared band due to the dicarbonyl species was observed. Concomitant with this decrease, and following the appearance of both the CO<sub>2</sub> and H<sub>2</sub>O in the gas phase, the absorbance of both linearly adsorbed and bridge-bonded CO was observed to increase continuously. After 127 s, only trace amounts of the dicarbonyl species remained on the surface. The absorbance of the low-frequency component of the dicarbonyl doublet appears larger due to the convoluted effect of linearly adsorbed CO. We interpret these results to mean that the CO adsorbed in the dicarbonyl configuration is displaced by chemisorbed hydrogen. This displaced CO reacts rapidly with adsorbed oxygen to form CO<sub>2</sub>. The dominant CO surface species following the conclusion of the transient is most likely a hydridocarbonyl species, similar to that proposed by Solymosi et al.<sup>21</sup>

The reaction of the dicarbonyl species with  $H_2(gas)$  outlined in the transient study shown in Figure 4 suggests the following reaction pathway: Initially, hydrogen displaces a CO ligand corresponding to the dicarbonyl species, thus converting the dicarbonyl species to a hydridocarbonyl species which absorbs at 2062 cm<sup>-1</sup>. The displaced CO molecules react rapidly with chemisorbed oxygen to form CO<sub>2</sub>, while H<sub>2</sub>O is formed as the result of the reaction between chemisorbed oxygen and hydrogen. The reaction may be summarized as follows:

$$H_2(g) \to 2H(s) \tag{1}$$

$$2H(s) + 2Rh(CO)_2 \rightarrow 2Rh(CO)(H) + 2CO(g)$$
(2)

$$2CO(g) + 2RhO \rightarrow 2CO_2(g) + 2Rh(s)$$
(3)

$$RhO + 2H(s) \rightarrow H_2O + Rh(s)$$
 (4)

The transient response obtained when  $H_2$  flowing over reduced Rh was switched to 5% CO(He) is shown in Figure 5. It is

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Figure 5. FTIR transient response for CO reacted with a monolayer of hydrogen at 85 °C on  $Rh/SiO_2$  (5% CO in He; flow rate = 100 mL/min).



Figure 6. FTIR transient response for  $O_2$  reacted with the hydridocarbonyl species on Rh/SiO<sub>2</sub> at 85 °C (5% O<sub>2</sub> in He; flow rate = 100 mL/min).

apparent that the presence of chemisorbed hydrogen completely inhibits the formation of the dicarbonyl species.<sup>21</sup> The dominant CO species on the surface at the conclusion of the transient is most likely the hydridocarbonyl species. The position of the infrared absorption band due to linearly adsorbed CO is strongly dependent on surface coverage. This suggests that a mixed hydrogen-CO adlayer is formed and reinforces the idea of a hydridocarbonyl complex on the surface. The formation of separate CO and hydrogen phases on the surface would result if strong dipole-dipole coupling were to occur. This would, in turn, lead to a CO infrared band that is invariant with surface coverage.

The hydridocarbonyl species shown in Figure 5 reacts rapidly with  $O_2$  (gas) to form  $CO_2$  (gas) and  $H_2O$  (gas). The results of this transient study are shown in Figure 6. The mass spectral responses of the data shown in Figure 6 suggest that both  $H_2O$ and  $CO_2$  are formed at comparable rates.

High-Temperature Studies. The transient response studies shown in Figures 2–6 were repeated at 200 °C. At higher temperatures the more weakly bonded dicarbonyl species in addition to CO species adsorbed on the higher oxidation states of Rh were not observed. As a result, only two infrared bands which are assigned to linearly adsorbed and bridge-bonded CO are observed in the infrared spectrum of CO. The position of the infrared absorption band due to linearly adsorbed CO is red shifted by 5 cm<sup>-1</sup>, as compared to that at 85 °C. This is in all probability due to the lower CO surface coverage at 200 °C, which results in weaker dipole–dipole coupling. The effect of surface temperature on the position of the infrared band assigned to linearly adsorbed CO is shown in Table II.

The results of the CO- $O_2$  transient response study at 200 °C are shown in Figure 7, and the  $O_2$ -CO transient study is shown in Figure 8. The important features shown in Figures 2 and 3 are essentially duplicated at 200 °C. However, the resulting







Figure 8. FTIR transient response for CO reacted with a monolayer of oxygen at 200 °C on Rh/SiO<sub>2</sub> (5% CO in He; flow rate = 100 mL/min).

TABLE II: Frequency of Adsorbed CO at Monolayer Coverage on  $Rh/SiO_2$  as a Function of Temperature

temp, °C	freq, cm <sup>-1</sup>		
200	2060		
144	2068		
85	2075		

spectra are considerably simplified due to the absence of the dicarbonyl species. The  $CO-O_2$  transient shown in Figure 7 clearly shows the decrease in the absorption frequency of CO throughout the duration of the transient, suggesting a mixed  $CO-O_2$  adlayer. The reaction between adsorbed  $O_2$  and gas-phase CO clearly shows the invariance in the position of the CO absorption band with surface coverage. It is apparent from this result that, during this portion of the transient, CO adsorbs in a highly coupled island configuration.

Even though the difference in induction times for the formation of CO<sub>2</sub> at 85 and 200 °C for the O<sub>2</sub>-CO transients is small ( $\sim 7$ s), the duration of the 200 °C transient is considerably longer. This is undoubtedly due to the competitive nature of the O<sub>2</sub>-CO adsorption. At 200 °C the rate of CO desorption increases sharply. This results in a longer period of time required to saturate the surface with a monolayer of CO.

The results of the H<sub>2</sub>-CO transient at 200 °C is shown in Figure 9, and the transient reaction between the hydridocarbonyl species and  $O_2$  is shown in Figure 10. The results are entirely self-consistent with the 85 °C transient studies, suggesting a completely mixed hydrogen-CO adlayer.

The induction times at different temperatures are summarized in Table III. A comparison is made with similar transient studies performed on  $Pt/SiO_2$  and  $Pd/SiO_2$ .

Self-Sustained Oscillations. In order to observe the reactivity of the various adsorbed CO species under non-steady-state oscillatory conditions, self-sustained oscillations were performed at 75 °C. The procedure used to initiate oscillatory reaction con-



Figure 9. FTIR transient response for CO reacted with a monolayer of hydrogen at 200 °C on  $Rh/SiO_2$  (5% CO in He; flow rate = 100 mL/min).



Figure 10. FTIR transient response for  $O_2$  reacted with hydridocarbonyl species on Rh/SiO<sub>2</sub> at 200 °C (5% O<sub>2</sub> in He; flow rate = 100 mL/min).

TA	BLE	III:	Induction	Time vs	Tem	perature
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temp, °C	Pd/SiO <sub>2</sub> , <sup><i>a</i></sup> s	temp, °C	Pt/SiO <sub>2</sub> , <sup>b</sup> s	temp, °C	Rh/SiO <sub>2</sub> , <sup>c</sup> s		
200	$1 \pm 0.1$	195	$4 \pm 0.2$	200	0		
168	$9 \pm 0.5$	162	12 ± 1.6				
132	$25 \pm 1.7$	132	$27 \pm 2.3$	144	$1 \pm 0.3$		
114	$38 \pm 0.5$	117	39 ± 1.9				
80	98 ± 0.4	80	109 ± 8.6	85	$7 \pm 0.5$		

<sup>a</sup>Pd/SiO<sub>2</sub>: 1% loading, 14.7% dispersion. <sup>b</sup>Pt/SiO<sub>2</sub>: 1% loading, 22.4% dispersion. <sup>c</sup>Rh/SiO<sub>2</sub>: 3% loading, 43% dispersion.

ditions has been extensively described by Sharma et al.<sup>13</sup> and by Kaul and Wolf.<sup>27</sup> Briefly, the reaction temperature is ramped from 50 °C to the ignition temperature ( $\sim 200$  °C). The temperature programmer is then turned off, and the reactor is allowed to cool in a constant flow of CO and O<sub>2</sub>. When the infrared bands reappear and begin to show unstable behavior, the reaction conditions are set and self-sustained oscillations are followed. In this study a CO/O<sub>2</sub> partial pressure ratio of 1.8 was used.

The self-sustained oscillations are shown in Figure 11. The amplitude of the oscillations is enormous although somewhat chaotic in behavior (Figure 11B). Figure 11A clearly shows that only the infrared band assigned to linearly adsorbed CO exhibits oscillatory behavior. The dicarbonyl species appear as small shoulder bands superimposed on the larger infrared absorption bands assigned to linearly adsorbed CO. The absorbances of these shoulder bands remained constant throughout the oscillatory





Figure 11. (A) Spectra of  $CO/O_2$  oscillations on  $Rh/SiO_2$  at 75 °C ( $CO/O_2 = 1.8$ ; He flow rate = 40 mL/min; total flow rate = 100 mL/min). (B) Spectragram of  $CO/O_2$  oscillations shown in (A).

period. The frequency of the infrared absorbance band assigned to linearly adsorbed CO was observed to shift from a minimum of 2069 cm<sup>-1</sup> to a maximum of 2073 cm<sup>-1</sup> over the duration of the period. These data again reinforce the enhanced reactivity of linearly adsorbed CO in CO oxidation and also suggest the formation of mixed CO–O<sub>2</sub> adlayers. This is in marked contrast to self-sustained oscillations obtained under similar conditions over Pt/SiO<sub>2</sub>.<sup>26</sup>

#### Discussion

The enhanced reactivity for CO oxidation of the linearly adsorbed CO on well-reduced Rh(0) sites is clearly shown in the transient studies exhibited in Figures 2 and 3. In sharp contrast to similar transient studies performed on  $Pt/SiO_2$ ,<sup>25</sup> the induction time required for the initial formation of product  $CO_2$  molecules at 85 °C is 2 orders of magnitude lower on Rh/SiO<sub>2</sub>. The reactivity of bridge-bonded CO appears to parallel that of linearly adsorbed CO while the dicarbonyl species is nearly unreactive. The infrared spectrum of the dicarbonyl species persists in flowing O<sub>2</sub> at 85 °C even after 40 min. We conclude from these results that the dicarbonyl species act as spectator molecules and are not catalytically important in the oxidation of CO. These results are in conflict with two other published studies regarding the reactivity of adsorbed CO with oxygen. Zhong<sup>9</sup> and Dais and Worley<sup>10</sup> concluded on the basis of static infrared CO oxidation experiments that the dicarbonyl species reacts with oxygen in preference to the linearly adsorbed CO species. However, these differences can be reconciled by considering the thermal stability of the two adsorbed CO species.<sup>24</sup> Dais and Worley<sup>10</sup> exposed a reduced Rh catalyst to a  $CO/O_2$  gas mixture having a partial pressure ratio of 2 at room temperature. This was followed by heating the reaction mixture statically and by continuously scanning the infrared spectrum of the adsorbed CO species. Because the infrared

<sup>(27)</sup> Kaul, D. J.; Wolf, E. J. Catal. 1985, 91, 216.

absorption band assigned to the dicarbonyl species disappeared first, they concluded that it was more reactive than the linearly adsorbed CO species. However, it is well documented that the thermal stability of the linear species is considerably greater than that of the dicarbonyl species.<sup>24</sup> What may have occurred under their experimental conditions was that the dicarbonyl species underwent thermal desorption followed by readsorption as the linearly adsorbed CO species. This is in good agreement with our results at 200 °C which show only linear and bridge-bonded CO adsorbed on the surface. The higher reactivity of the linearly adsorbed CO is also clearly demonstrated during the self-sustained oscillatory reaction shown in Figure 11 A. Even though the gas-phase temperature was only 75 °C, previous studies have shown that the actual support temperature may oscillate by as much as 60 °C during the period of the oscillations.<sup>13,27</sup> For this reason the linearly adsorbed CO is the predominant species on the surface and is also the only species that is observed to undergo self-sustained oscillations. The dicarbonyl species appear as unreactive shoulders during the period of the oscillations. It is not clear from Zhong's published data9 exactly how the reactivity study was performed.

The above discussion emphasizes the importance of the transient technique. These experiments can be performed under more realistic catalytic conditions which in turn may lead to a completely different set of conclusions.

A second important conclusion that may be derived from this transient study concerns the structure of the reactive adlayer. The CO-O<sub>2</sub> transient studies at 85 °C (Figure 2) and 200 °C (Figure 7) clearly show that the oxygen and CO surface phases are mixed. This is in marked contrast to similar transient and steady-state CO oxidation studies performed on Pt/SiO<sub>2</sub><sup>25,26</sup> and Pd/SiO.<sup>25</sup> On Rh/SiO<sub>2</sub> there is a distinct shift in frequency of the linearly adsorbed CO species throughout the duration of the transient while on  $Pt/SiO_2$  and  $Pd/SiO_2$  it is invariant. This implies that the structure of CO on both Pt and Pd is highly segregated and that the reaction occurs at the reactive boundaries of these so-called islands of reactivity. The invariance in the CO absorption frequency in an island configuration occurs as the result of strong dipole-dipole coupling. Eischens and Pliskin<sup>28</sup> and Ponec et al.<sup>2</sup> have convincingly shown that dipole-dipole coupling is the primary mode that leads to shifts in the infrared absorption frequency with increasing surface coverage. On Rh/SiO<sub>2</sub> the rather large shift in the absorption frequency throughout the duration of the transient implies a mixed CO-O2 adlayer. Results similar to those obtained on  $Rh/SiO_2$  have been reported by Saymeh and Gonzalez on Ir/SiO<sub>2</sub>.30

The formation of CO islands of reactivity has been implicated as a possible requirement for the existence of self-sustained oscillations.<sup>31,32</sup> The formation and collapse of these CO islands of reactivity together with the adsorbate phase changes that they may generate could lead to inhibitory and autocatalytic reaction pathways capable of sustaining oscillatory behavior. However, this study clearly shows that self-sustained oscillations can also occur with completely mixed CO-adsorbed oxygen adlayers. This is also likely for the case of  $H_2-O_2$ , CO-NO,  $NH_3-O_2$ ,  $C_2H_4-O_2$ ,  $CH_3OH-O_2$ ,  $NO-O_2$ , and  $C_6H_{12}-O_2$  reactions which also exhibits strong self-sustained oscillations (ref 34 and references cited therein).

The very low induction time observed at 85 °C for the CO– $O_2$  transient suggests that  $O_2$  adsorption onto a surface saturated with CO is easier than on Pt/SiO<sub>2</sub> or Pd/SiO<sub>2</sub>. This implies either that the CO desorption rate is very slow or that the dissociative sticking coefficient for  $O_2$  on Rh is very high. From this study we cannot unequivocally conclude which of these two factors is the most important. Fisher has recently measured the dissociative sticking coefficient of  $O_2$  on Rh(100) as a function of CO surface coverage and has found it to be nearly 2 orders of magnitude greater than that on Pt(111).<sup>34</sup> This result is in excellent agreement with the decrease in the induction time by 2 orders of magnitude on Rh/SiO<sub>2</sub> compared to that observed over Pt/SiO<sub>2</sub>.

Because of the nature of the frequency shifts for linearly adsorbed CO observed during the  $H_2$ -CO transient experiments (Figures 5 and 9), we must also conclude that the hydrogen-CO adsorbate phases are completely mixed. However, the apparent invariance in the frequency of linearly adsorbed CO during the duration of the O<sub>2</sub>-CO transient study (Figures 3 and 8) suggests that when CO (gas) reacts with adsorbed oxygen, islands of CO are immediately formed on the surface.

#### Conclusions

The following important conclusions emerge from the results of this study: (1) Linearly adsorbed CO is the most reactive surface species in CO oxidation over Rh/SiO<sub>2</sub>. (2) The oxidation of CO over Rh/SiO<sub>2</sub> proceeds through a mixed oxygen-CO adlayer. (3) Hydrogen and CO form a mixed adlayer on Rh/SiO<sub>2</sub>. (4) A mechanism is suggested for H<sub>2</sub> reacting with the dicarbonyl species: Hydrogen reacts with the dicarbonyl species to form a hydrido surface carbonyl species. The CO which is displaced by hydrogen reacts rapidly with chemisorbed oxygen to form CO<sub>2</sub>. (5) Induction times for the CO-O<sub>2</sub> transient are much shorter than those observed over Pt/SiO<sub>2</sub> and Pd/SiO<sub>2</sub>. This could be attributed to the much higher oxygen dissociative sticking coefficient for O<sub>2</sub> over Rh/SiO<sub>2</sub> than either Pt/SiO<sub>2</sub> or Pd/SiO<sub>2</sub>.

Acknowledgment. We acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, for this research. We also thank Lambert Lucietto of the Byron-Lambert Co., Franklin Park, IL, for his much-needed input in overcoming numerous technical problems associated with the infrared cell reactor design. Y.-E.L thanks the University of Illinois for a University Fellowship. Finally, we are grateful to the U.S. Department of Energy (Grant DOE FG02-86ER-13531), which supplied funds for the purchase of a large portion of the equipment used in this research.

Registry No. CO, 630-08-0; H<sub>2</sub>, 1333-74-0; Rh, 7440-16-6.

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