In Situ IR Study of the Reactivity of Rh^I(CO)₂/SiO₂ Derived from Rh₆(CO)₁₆ for CO Insertion

Girish Srinivas and Steven S. C. Chuang*

Department of Chemical Engineering, The University of Akron, Akron, Ohio 44325 Received: October 28, 1993; In Final Form: January 4, 1994*

The formation of $Rh^{I}(CO)_{2}$ from $Rh_{6}(CO)_{16}$ impregnated on SiO_{2} and its reactivity toward $C_{2}H_{4}/H_{2}$ have been investigated by *in situ* infrared spectroscopy. Impregnation of $Rh_{6}(CO)_{16}$ on partially dehydroxylated SiO_{2} results in a partially decarbonylated structure exhibiting the terminal and bridging carbonyl bands at 303 K; surface $H_{2}O$ reacts with $Rh_{6}(CO)_{16}$ to form $Rh^{I}(CO)_{2}$ at 373–423 K. The terminal carbonyls show no reactivity toward $C_{2}H_{4}/H_{2}$ at 303 K while they begin to react with $C_{2}H_{4}/H_{2}$ to produce adsorbed acyl and propionaldehyde at 323 K. Under the same condition, the terminal carbonyls are less active for CO insertion than *gem*-dicarbonyl derived from $Rh_{6}(CO)_{16}$ and linear CO on the surface of Rh crystallites. The low reactivity of the terminal carbonyls compared to that of linear CO may be attributed to the lack of neighboring Rh sites for adsorbed alkyl, $C_{2}H_{4}$ and hydrogen. Steady-state ethylene hydroformylation reveals that the Rh is in an oxidized state and that hydrogenation of acyl species is rate limiting at 393 K and 1 MPa. Increasing reaction temperature to 513 K leads to the reduction of oxidized Rh sites, hydrogenation of adsorbed acyl, and an enhancement of propionaldehyde selectivity.

1. Introduction

Comparative studies of metal cluster chemistry and chemistry on metal surfaces have led to the development of the clustersurface analogy.¹⁻¹⁰ The cluster-surface analogy has provided an in-depth understanding of the structure of adsorbed species on supported metal catalysts. In chemisorption of CO on supported metal, the structure of adsorbed CO has been determined on the basis of the analogy in vibrational frequencies between adsorbed CO on the metal surface and CO ligands in metal carbonyls.¹¹⁻²² Although there are similarities in vibrational frequency, bond energy, and coordination between the CO ligands of metal carbonyls and chemisorbed CO on metals, little is known about their similarity and distinction for catalytic reactions. An interesting question that has been raised in cluster-surface analogy is whether the similarity in vibrational frequencies and structure between metal complexes and adsorbed species on the metal surface leads to similar reactivity and catalytic behavior for these metal complexes and adsorbed species.¹

The CO insertion reaction provides an excellent model for studying the analogy in reactivity between adsorbed CO on the Rh surface and the CO ligand of Rh carbonyl because both these CO species can participate in the reaction.^{3-5,21-29} CO insertion is the key step in the formation of higher oxygenates from CO hydrogenation, alcohol carbonylation, and olefin hydroformylation. Rh carbonyls have been used as catalysts for the homogeneous hydroformylation reaction.^{2,4,23-25,29} During reaction, the Rh carbonyls are transformed to mononuclear Rh carbonyl where the migratory insertion of the terminal CO ligand into the alkyl-metal complex takes place. Rh carbonyls have also been anchored to the support surface aimed at combining the advantages of high selectivity of Rh carbonyls with the ease of separation of heterogeneous catalysts.²⁹ However, the lack of stability of the metal carbonyls has limited the use of supported metal carbonyls and complexes as catalysts. The decomposition of metal carbonyls on the oxide support leads to the formation of metal aggregates which have been used as model catalyses for reaction study.8-10 Supported Rh catalysts prepared from decomposition of Rh carbonyls have been found to exhibit higher hydroformylation selectivity than those prepared from Rh salts.^{10,30} Studies of oxide-supported carbonyl systems may also provide useful information in developing the catalytic property

relationships among adsorbed CO on oxide-supported metal, CO ligand of oxide supported carbonyl clusters, and CO ligand of the carbonyl cluster.

The objective of this paper is to study the reactivity of the various forms of adsorbed CO, especially Rh^I(CO)₂, derived from $Rh_6(CO)_{16}$ supported on SiO₂ for CO insertion. The various forms of adsorbed CO were prepared from impregnation of partially dehydroxylated SiO₂ with $Rh_6(CO)_{16}$. $Rh_6(CO)_{16}$ consists of six Rh atoms at the corners of an octahedron; each Rh atom carries two terminal CO groups and the remaining CO groups bridge three Rh atoms.¹⁰ Impregnation of $Rh_6(CO)_{16}$ on partially dehydroxylated SiO₂ results in a partially decarbonylated structure exhibiting the terminal and bridging carbonyl bands at 303 K;^{10,31,32} surface H₂O reacts with $Rh_6(CO)_{16}$ to form Rh^{I} -(CO)₂ at 373-423 K. The reactivity of various forms of adsorbed CO resulting from $Rh_6(CO)_{16}$ was determined from the rate of their consumption during the reaction of adsorbed CO with $C_2H_4/$ H₂. In situ IR spectroscopy is used to monitor the formation of surface Rh carbonyl on SiO_2 and to determine the reactivity of the resulting surface carbonyl with C_2H_4/H_2 . The reactivity of the $Rh_6(CO)_{16}$ -derived carbonyls is compared with those of CO chemisorbed on Rh/SiO₂, RhCl₃/SiO₂, and Rh(NO₃)₃/SiO₂.

2. Experimental Section

 $Rh_{6}(CO)_{16}$ (Strem Chemicals) was dissolved (saturated solution) in CHCl₃ (ACS grade, 99+% purity) in a drybox under a N2 atmosphere. The silica (Strem) disk was prepared by pressing 25 mg of SiO₂ powder (70 μ m) in a stainless steel die at a pressure of 3 MPa. The disk was placed in an IR reactor cell²¹ and partially dehydroxylated at 513 K under flowing nitrogen for 24 h and cooled under N_2 to 303 K. The path length for the IR beam in the cell is slightly less than 0.2 cm, and the net reactor volume is 0.64 cm³. The reactor can be used up to pressures of 6 MPa and in a temperature range of 293-533 K. The infrared spectra of SiO₂ before and after partial dehydroxylation are shown in the inset of Figure 1. The spectrum before partial dehydroxylation shows a very board asymmetric absorption between 2900 and 3750 cm⁻¹ which reduces transmittance to zero. This broad band is attributed to molecular water which is physically adsorbed on the surface. Dehydroxylation at 513 K removed the physisorbed water. This pretreatment process significantly decreased the infrared adsorbance in the region 2100-3750 cm⁻¹ so that any variation in infrared absorbance during impregnation and reaction

[•] Abstract published in Advance ACS Abstracts, February 15, 1994.



Figure 1. Infrared spectra of injection of $Rh_6(CO)_{16}/CHCl_3$ onto partially dehydroxylated SiO₂. (a) Infrared spectrum of SiO₂ before pretreatment; (b) infrared (background) spectrum of SiO₂ after flowing nitrogen for 24 h at 513 K and cooled to 303 K.

studies can be accurately determined. Spectrum b shown in Figure 1 is used as the background spectrum. A known volume (0.2 cm³) of the solution of $Rh_6(CO)_{16}$ in CHCl₃ was injected at 303 K onto the SiO₂ disk placed in the infrared reactor cell to prepare the $Rh_6(CO)_{16}/SiO_2$ catalysts. Subsequent to injecting the carbonyl solution, the solvent was removed by flushing with N₂ (20 cm³/min) at 303 K.

Transmission infrared spectra were obtained by a fourier transform infrared (FTIR) spectrometer²¹ at a resolution of 4 cm⁻¹. The spectrum of the silica disk before injection of the carbonyl solution was used as the background. Thirty two scans were coadded to increase the signal-to-noise ratio. The batch reaction of C_2H_4/H_2 (1:1) with SiO₂-supported Rh carbonyls at 303 and 323 K and the steady-state hydroformylation reaction (CO:H₂:C₂H₄ = 1:1:1) at 323, 393, and 513 K were carried out in the IR reactor cell. For the batch reaction, the mixture of C_2H_4/H_2 was admitted into the reactor keeping the outlet of the reactor closed. The IR absorbance of the surface species was monitored as a function of time by the FTIR spectrometer. The products of the steady-state reaction were analyzed by an HP 5890A gas chromatograph equipped with an FID.^{21,33}

The Rh content on the SiO₂ disk following the catalytic reaction was determined by a Philips PV 9550 energy-dispersive X-ray fluorescence spectrometer (XRF). Temperature-programmed decomposition (TPDE) in He was undertaken in a hightemperature IR reactor cell³⁴ to determine the quantity of exposed Rh and the IR adsorbance coefficient of the gem-dicarbonyl. In the TPDE study, the solution of $Rh_6(CO)_{16}$ in CHCl₃ was injected into the pretreated SiO₂ disk at 303 K and flushed in He to remove the solvent. Terminal and bridging carbonyls on the catalyst were transformed to gem-dicarbonyl by heating in He to 323 K following by heating in CO to 423 K. The temperature of the IR reactor cell was then increased linearly at 10 K/min in He flow. Infrared spectra of the adsorbed species on the catalyst were obtained as a function of temperature, and the composition of the effluent from the reactor was monitored by a Balzers QMG 112 quadrupole mass spectrometer.³⁴

3. Results

3.1. Injection of $Rh_6(CO)_{16}$ in CHCl₃ onto SiO₂. Figure 1 shows the infrared spectra following the injection of the Rh_{6} -

 $(CO)_{16}$ solution at 303 K onto the silica support and flushing in N₂. The spectra of CO ligands were obtained by subtracting contributions of the SiO₂ background from each sample spectrum. The prominent infrared bands due to chloroform at 3020, 2394. and 1600–1400 cm⁻¹ and that due to H_2O at 1625 cm⁻¹ decreased on flushing with N_2 . Due to the use of partially dehydroxylated SiO_2 , no attempt was made to remove the trace amounts of H_2O from CHCl₃ before impregnation. According to the T_d symmetry of $Rh_6(CO)_{16}$, the prominent IR band at 2081 cm⁻¹ is attributed to terminal carbonyl groups of $Rh_6(CO)_{16}$ on SiO₂, and the weak IR band observed at 1805 cm⁻¹ is due to the bridging carbonyls of the Rh₆(CO)₁₆.³⁵ The band observed at 2045 cm⁻¹ is due to a linear CO species with a lowered symmetry resulting from partial decarbonylation or interaction with the oxide surface. These assignments agree well with those found in literature.^{31,32,35-39} The intensity ratio of the terminal (2081 cm⁻¹) to bridging carbonyl (1805 cm⁻¹) bands does not vary between 1 and 13 h of flushing in N₂. The IR absorbance intensity ratio of the terminal to the bridging carbonyl bands in the spectrum following N₂ flush for 13 h is 7.33, which is higher than 3.33 for $Rh_6(CO)_{16}$ in solution. The high ratio of intensity of the terminal to bridging carbonyl band suggests that 55% of bridging carbonyls in $Rh_6(CO)_{16}$ disintegrate.

Partial decarbonylation of the cluster is known to occur on oxide surfaces such as SiO_2 and Al_2O_3 in the presence of OHand H_2O , according to the following reactions:^{31,32}

$$Rh_{6}(CO)_{16} + nH_{2}O \rightarrow Rh_{6}(CO)_{16-n}H_{2n} + nCO_{2}$$
$$Rh_{6}(CO)_{16} + 6Si-OH \rightarrow 3H_{2} + 6Si-O-Rh^{I}(CO)_{2} + 4CO$$

The former reaction may contribute to the disintegration of the bridging carbonyl following impregnation of the Rh₆(CO)₁₆ onto the partially dehydroxylated SiO₂ at 303 K. The decarbonylation of Rh^I(CO)₂ in the presence of OH⁻, according to the latter reaction, was found to occur above 353 K on the SiO₂ surface and will be discussed later. It has also been proposed that a partially hydrated SiO₂ would promote the formation of three different hydride species, HRhH₂, HRh(CO)₂, and HRh(CO)₁₅^{-,10}

A small shoulder band observed at 1837 cm^{-1} is assigned to bridging CO groups chemisorbed on Rh^o.²¹ Due to vague changes in the 3400–3600-cm⁻¹ region (not shown), where the OHvibration frequencies are exhibited, the involvement of OH-groups in the formation of the supported carbonyls could not be determined. The ratio of intensities of the terminal to bridging carbonyls on SiO₂ did not change under a N₂ atmosphere following 13 h of flushing at 303 K. The IR bands due to CHCl₃ were completely removed, and the decrease in the intensity of the terminal and bridging carbonyl bands leveled off.

3.2. Reaction of $Rh_6(CO)_{16}/SiO_2$ with C_2H_4 and H_2 . The supported terminal and bridging carbonyls shown in Figure 1 did not show any reactivity toward C_2H_4/H_2 following exposure for 90 min at 303 K. A fresh SiO₂ disk was impregnated with the same $Rh_6(CO)_{16}$ solution and flushed with N_2 . The IR spectra obtained after flushing the disk with N_2 were similar to those shown in Figure 1. Figure 2 shows the infrared spectra following exposure of the SiO₂-supported Rh carbonyls to 0.1 MPa of $C_2H_4/$ H_2 (1:1) at 323 K. The spectrum obtained before the addition of C_2H_4/H_2 showed the terminal carbonyl band at 2081 cm⁻¹, the shoulder band at 2045 cm⁻¹, the bridging carbonyl band at 1805 cm⁻¹, a bridge CO on Rh° band at 1837 cm⁻¹, and a water band at 1625 cm⁻¹. Admission of C_2H_4/H_2 to the reactor produced bands due to ethylene at 1442 cm⁻¹ (CH₂ deformation), 1888 cm⁻¹ (CH₂ wag), and in the 2800–3000 cm⁻¹ (CH₃ and CH_2 stretch) range. Due to overlapping of the bands, individual contributions of different hydrocarbon species to the bands in the 2800-3000-cm⁻¹ region could not be determined. The band at 3020 cm⁻¹ is due to the CH stretch of a monosubstituted ethylene



Figure 2. Infrared spectra of reaction of C₂H₄/H₂ with adsorbed $Rh_x(CO)_y/SiO_2$ at 323 K.

species, 40 R—CH=CH₂, the R in this case being a CH₃ species. The presence of this distinct band indicates the incorporation of C_2H_4 to C_3H_6 at 323 K. Steady-state $CO/H_2/C_2H_4$ (1:1:1) reaction at 393 K and 0.1 MPa showed that C₃H₆ was produced with a selectivity of 23%. Bands due to ethylene at 1442 and 1888 cm⁻¹ decreased in intensity due to conversion of ethylene to ethane and propionaldehyde.

Decreases in the terminal carbonyl band at 2081 cm⁻¹ and bridging carbonyl bands at 1837 and 1805 cm⁻¹ were accompanied by the appearance and gradual increase in the following: (i) weak bands in 2300-2400-cm⁻¹ region, attributed to gaseous/ adsorbed CO_2 ,⁴¹ (ii) a band at 1685 cm⁻¹ due to adsorbed acyl species, 20,40,42 (iii) a small propionaldehyde shoulder band at 1712 cm⁻¹, and (iv) a linear CO band at 2023 cm⁻¹. The higher rate of decrease in the intensity of the terminal carbonyl band compared to that of the bridging carbonyl bands with the simultaneous increase in the acyl and aldehyde bands suggests that the involvement of the terminal carbonyls in CO insertion is significantly greater than that of the bridging carbonyls. During the entire course of the batch reaction at 323 K, the water band at 1625 cm⁻¹ also increased in intensity. The increase in the H_2O band appears to parallel those of CO₂, suggesting that CO₂ which is produced from CO disproportionation, $2CO \rightarrow CO_2 + C_s$, where C_s is a surface carbon, may undergo the reverse water gas shift reaction to produce H_2O .

The band at 2023 cm⁻¹ formed during the reaction cannot be assigned to the asymmetric stretch of the gem-dicarbonyl since no band corresponding to the symmetric vibration mode of the Rh¹(CO)₂ species was observed. The 2023-cm⁻¹ band can be assigned to a linear CO species. Linear CO on Rh^o is known to exhibit wavenumbers in the 2056-2070-cm⁻¹ range.¹¹⁻²² It is however known that the wavenumber exhibited by linear CO is a function of its coverage;⁴³ lower coverages yield lower wavenumbers. The low wavenumber could also result from a decrease in the dipole-dipole interaction of the linear CO, caused by dilution from adsorbed H, C_xH_y , acyl species, or propionaldehyde on a neighboring Rh atom.⁴³ The specific nature of the dilution cannot be distinguished from the IR spectra. The band at 2023 cm⁻¹ could also be attributed to linear CO with a coadsorbed H atom, a hydrido-carbonyl species.^{14,44} Throughout this work, the species exhibiting the band at 2081 cm⁻¹ is denoted as the terminal carbonyl species and CO species chemisorbed on a Rh^o atom or a Rh⁺ ion and exhibiting band in the 2020–2085 cm⁻¹ are denoted as linear CO species. The infrared spectra did not show any change after 300 min of reaction indicating that the reaction approached equilibrium. Due to the dynamic nature of the terminal carbonyl and the linear CO species during the reaction,





Figure 3. Infrared spectra of steady-state CO/H₂/C₂H₄ reaction at 323 K and 0.1 MPa.

the reactivity of the linear CO species exhibiting the 2023-cm⁻¹ band could not be determined.

Figure 3 shows the IR spectra obtained during steady-state ethylene hydroformylation (CO/H₂/C₂H₄ = 1:1:1) at 323 K and 0.1 MPa following the study shown in Figure 2. Upon admitting the reactants, the spectra showed hydrocarbon bands at 2986, 1888, and 1442 cm⁻¹, gaseous CO bands at 2173 and 2110 cm⁻¹, gem-dicarbonyl bands at 2095 and 2026 cm⁻¹, the water band at 1625 cm⁻¹, the acyl band at 1685 cm⁻¹, and the aldehyde band at 1712 cm⁻¹. Immediate formation of gem-dicarbonyl upon exposure of the catalyst to $CO/H_2/C_2H_4$ suggests that Rh atoms or ions are in a highly dispersed state. Gaseous CO bands were not eliminated by subtraction since no additional information would be obtained by the subtraction. During 60 min of reaction, the gem-dicarbonyl bands grew in intensity and the intensity ratio between the 2095- and 2026-cm⁻¹ bands decreased. The change in the intensity ratio could be due to a decrease in the concentration of a Rh^I(CO) species in the 2085-2102-cm⁻¹ range, 16,45 by conversion to Rh^I(CO)₂. The intensity of the water band at 1625 cm⁻¹ decreased while no apparent change was observed in the aldehyde and acyl bands.

Gas chromatographic analysis of the effluent from the reactor at 323 K showed CH_4 , C_2H_6 , and C_3H_6 as products of the reaction; a trace amount of propionaldehyde was detected as a result of slow hydrogenation of the acyl species and desorption of propionaldehyde at the low reaction temperature. Pulsing propionaldehyde over Rh/SiO₂ catalysts showed that physisorption of propionaldehyde occurred to a significant extent at temperatures below 393 K.⁴⁶ Upon flushing the catalyst with N_2 , the major bands that remain are the gem-dicarbonyl bands at 2095 and 2026 cm⁻¹ and the aldehyde and acyl bands at 1712 and 1685 cm⁻¹, respectively. The inset clearly shows the acyl band at 1685 cm⁻¹ and the aldehyde shoulder band at 1712 cm⁻¹ following flushing the catalyst with N_2 .

The reactivity of the gem-dicarbonyl, formed during the steadystate hydroformylation reaction at 323 K (shown in Figure 3), toward C_2H_4/H_2 was further investigated. Figure 4 shows the IR spectra following the exposure of the gem-dicarbonyl to a mixture of 0.1 MPa of C_2H_4/H_2 (1:1) at 323 K under a batch condition. The spectrum taken before the addition of C_2H_4/H_2 showed intense gem-dicarbonyl bands, water, aldehyde, acyl, and weak hydrocarbon bands.

Figure 5 shows the variation in intensity of the 2093-, 2023-, and 1685-cm⁻¹ bands with time (obtained from Figure 4) upon exposure of the gem-dicarbonyl to C_2H_4/H_2 . Between 0 and 10 min, the intensity of the 2093 cm⁻¹ band decreased, while the intensity of the acyl and aldehyde band remained unchanged,



Figure 4. Infrared spectra of reaction of C_2H_4/H_2 with $Rh^1(CO)_2/SiO_2$ at 323 K.



Figure 5. Absorbance intensity vs temperature during reaction of C_2H_4/H_2 with $Rh^1(CO)_2/SiO_2$ at 323 K.

indicating desorption of the Rh⁺(CO). Between 10 and 60 min, the decrease in the intensities of the 2093- and 2023-cm⁻¹ band was accompanied by an increase in the intensity of the acyl band at 1685 cm⁻¹. Between 60 and 180 min of reaction, the intensity of the 2093 cm⁻¹ band and acyl band increased, while the intensity of the 2023-cm⁻¹ band decreased continuously. The increase in the intensity of the 2093-cm⁻¹ band appears to be due to an increase in the intensity of a shoulder band at 2075 cm⁻¹ which can be assigned to linear CO on reduced Rh sites, Rh^o(CO) (shown in Figure 4). The formation of Rh^o(CO) suggests that a part of the Rh was reduced during the reaction. Following 600 min of the batch reaction, the Rh^o(CO) band decreased in intensity while the *gem*-dicarbonyl bands at 2093 and 2023 cm⁻¹ and the acyl band showed only slight variation in intensity.

Bands at 1589 cm⁻¹ due to carboxylate⁴² and 1553 cm⁻¹ due to carbonate³³ species increased in intensity during the reaction, as shown in Figure 4. Weak bands in the 2300–2400-cm⁻¹ range are due to CO₂. Flushing the catalyst with N₂ resulted in a slight decrease in the intensity of the 2093 cm⁻¹ band. The angle, θ , between the two CO molecules of the *gem*-dicarbonyl can be estimated from the ratio of integrated intensities of the symmetric and asymmetric bands.^{12,14} However, due to overlapping of the linear CO bands with the *gem*-dicarbonyl bands, the effect of reactants and products on the angle between the two CO molecules in the *gem*-dicarbonyl species could not be accurately determined.

The IR spectra corresponding to the steady-state hydroformylation at 1 MPa and 393 and 513 K are shown in Figure 6. Prior to the reaction, the catalyst was flushed with N_2 at 323 and 393



Figure 6. Infrared spectra of steady-state $\rm CO/H_2/C_2H_4$ reaction at 393 and 513 K and 1 MPa.

TABLE 1: Ethylene Hydroformylation on $Rh^{I}(CO)_{2}/SiO_{2}$ Catalyst Derived from $Rh_{6}(CO)_{16}$ at 1 MPa⁴

| product | Product formation g mol/kg of catalyst h | | | | | | | |
|---------------------------------------|--|-------------|---|---|--|--|--|--|
| | 393 K | 513 K | RhCl ₃ /SiO ₂ ^d 513 K | Rh(NO ₃) ₃ /SiO ₂ ^d 513 K | | | | |
| CH ₄ | 0.13 (17.8) | 0.14 (2.4) | 0.06 (0.9) | 0.12 (0.2) | | | | |
| C₂H ₆ | 0.34 (46.5) | 3.97 (69.0) | 4.52 (72.1) | 41.41 (72.4) | | | | |
| C ₃ H ₆ | 0.17 (23.2) | 0.14 (2.4) | 0.01 (0.2) | 0.12 (0.2) | | | | |
| C ₂ H ₃ CHO | 0.09 (12.5) | 1.50 (26.2) | 1.68 (26.8) | 15.55 (27.2) | | | | |
| TOF ^c (min ⁻¹) | 0.12 | 2.03 | 0.53 | 1.31 | | | | |

^a Amount of surface Rh on the catalyst prior to hydroformylation: 12.3 μ mol/g of catalyst. ^b Figures in parentheses indicate product selectivity in mol %. ^c For C₂H₅CHO formation. ^d From ref 34; 1 MPa after 90 min of reaction.

K. The spectra after the N_2 flush at 323 K following the study in Figure 4 showed the gem-dicarbonyl bands at 2093 and 2023 cm^{-1} , the aldehyde and acyl bands at 1712 and 1685 cm^{-1} , the water band at 1625 cm⁻¹, and carboxylate and carbonate bands at 1589 and 1553 cm⁻¹, respectively. Increasing temperature to 393 K during the N_2 flush resulted in a decrease in the aldehyde, acyl, carboxylate, carbonate, and water bands. Exposure of the adsorbed species to a mixture of flowing $CO/H_2/C_2H_4$ (1:1:1; total = $15 \text{ cm}^3/\text{min}$) under steady-state conditions at 393 K and 1 MPa resulted in a slight decrease in the intensity of the gemdicarbonyl bands and an increase in the intensity of the acyl and aldehyde bands. Bands at 2986, 1888, and 1442 cm⁻¹ are due to C_2H_4 , and the 2173- and 2110-cm⁻¹ doublet is due to gaseous CO. Subtraction of the gaseous CO bands was not performed since it would lead to a high noise level in the spectra due to the rotational-vibrational lines at the R branch of gaseous CO around 2110 cm⁻¹ and its high intensity relative to the gem-dicarbonyl band. Table 1 shows the rates of product formation, product selectivity, and TOF (turnover frequency) for propionaldehyde formation corresponding to the IR spectra in Figure 6. The TOF has been calculated using the number of gem-dicarbonyl sites estimated from the TPDE study and the integrated IR absorption coefficient, \bar{A}_{CO_e} , calculated for the gem-dicarbonyl.

Increasing temperature to 513 K resulted in the depletion of the gem-dicarbonyl band at 2023 cm⁻¹ and the disappearance of the acyl band at 1685 cm⁻¹ due to high hydrogenation activity. It is necessary to note that spectral features in the immediate neighborhood of the 1888-cm⁻¹ band are due to incomplete compensation due to the SiO₂ background.³⁵ The aldehyde selectivity was greater at 513 K than at 393 K. The absence of the gem-dicarbonyl band in the IR spectrum at 513 K leads to an uncertainty in the determination of the TOF for propionaldehyde formation. Rates of product formation and TOF for





Figure 7. Infrared spectra of injection of $Rh_6(CO)_{16}/SiO_2$ onto partially dehydroxylated SiO_2 and transformation to $Rh^I(CO)_2/SiO_2$.

propionaldehyde formation for $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2^{34}$ during ethylene hydroformylation are also shown in Table 1 for comparison. XRF analysis of the catalyst following the hydroformylation reaction showed that the catalyst contained 1.9% by weight of Rh.

3.3. Temperature-Programmed Decomposition (TPDE). Temperature-programmed decomposition was undertaken in a hightemperature IR reactor cell³⁴ to determine the integrated IR absorbance coefficient, \bar{A}_{CO_2} , for the gem-dicarbonyl. A fresh SiO₂ disk was partially dehydroxylated as before and impregnated with a saturated solution of $Rh_6(CO)_{16}$ in CHCl₃. Figure 7 shows the IR spectral features upon impregnation of the carbonyl solution and flushing with He. The spectrum taken after impregnation and flushing shows the terminal carbonyl band at 2083 cm⁻¹, the bridging carbonyl band at 1801 cm⁻¹, and a water band at 1625 cm⁻¹. Increasing temperature to 373 K in He resulted in the transformation of the terminal and bridging carbonyls to the gem-dicarbonyl, exhibiting the 2092- and 2035-cm⁻¹ bands and a weakly adsorbed bridged CO on Rh° species exhibiting a 1850cm⁻¹ band. Cooling the IR reactor cell to 323 K did not result in a significant change in the IR spectra. It was found that increasing the temperature of the reactor to 423 K in the presence of 0.1 MPa of gaseous CO resulted in the maximum gemdicarbonyl intensity at 2092 and 2035 cm⁻¹ and a further increase in temperature resulted in the decrease in the intensity of the gem-dicarbonyl. Solymosi and Bansagi¹⁵ have shown that at temperatures above 448 K reductive agglomeration of Rh^I sites occurs, promoting the transformation of Rh¹(CO)₂ species to Rh_x-CO species. The spectrum obtained on cooling the catalyst to 303 K and flushing in He showed the gem-dicarbonyl bands at 2092 and 2035 cm⁻¹, a shoulder band at 2130 cm⁻¹ that is attributed to a linear CO on Rh²⁺ or Rh³⁺,^{14,34} a shoulder band at 1995 cm⁻¹ that can be assigned to a weakly adsorbed linear CO species, a weak bridge CO band at 1865 cm⁻¹, and a shoulder band at 2101 cm⁻¹ due to linear CO on Rh⁺.

There is a difference in the wavenumber of asymmetric vibration of *gem*-dicarbonyl shown in Figures 4 and 7. The slightly upward shift and the high intensity of asymmetric vibration band appear to be resulted from overlapping with the noticeable shoulder band at 1995 cm⁻¹. CO species exhibiting 1995 cm⁻¹ may be adsorbed on the Rh^o surface which is reduced from Rh^I(CO)₂ through a nucleophilic attack by CO or water.⁴⁷ The presence of surface water on the support can also lead to the formation of both Rh¹-(CO)₂ and Rh^{III}(H)(H)(CO) from Rh₆(CO)₁₆/Al₂O₃ through the oxidative additive addition of Al–OH.⁴⁷ The formation of



Figure 8. Infrared spectra during TPDE of chemisorbed CO.

the 2130-cm⁻¹ band may be attributed to the oxidative addition of the Si–OH group to $Rh^{I}(CO)_{2}$ with the formation of Rh^{III}_{-} (H)(H) to which CO coordinates. Careful examination of the whole range of infrared spectra shows a significant decrease in the intensity of surface water band at 1625 cm⁻¹ and little change in the intensity of OH group during the formation of the 2130cm⁻¹ band. The consumption of OH group may be immediately replenished by surface water.

The infrared spectra taken during the temperature-programmed decomposition (10 K/min) of $\text{Rh}^{1}(\text{CO})_{2}$ and adsorbed CO on the catalyst are shown in Figure 8. Increasing the reactor temperature to 453 K resulted in the disappearance of the shoulder bands at 2130 and 1995 cm⁻¹. The intensity of the band at 2092 cm⁻¹ increased initially and decreased slightly, while that of the band at 2035 cm⁻¹ decreased minimally. Increasing temperature to 673 K resulted in desorption of all the *gem*-dicarbonyl species. The reason for the uneven variation in the ratio of intensities of the *gem*-dicarbonyl bands during the TPDE is unknown.

The species monitored during TPDE were CO, CO₂, H₂, H₂O, and CH₄. The only species observed during the TPDE was CO₂. Figure 9A shows the TPDE profile of CO_2 ; the variation in IR absorbance with temperature (from Figure 8) of the gemdicarbonyl bands at 2035 and 2092 cm⁻¹ and the linear CO on Rh^{3+} band at 2130 cm⁻¹ are shown in Figure 9B. CO₂ was observed as the temperature increased to 383 K; the peak temperature for CO_2 was observed at 453 K. The decrease in the intensity of the 2130-cm⁻¹ band at temperatures below 383 K suggests that the species may be converted to the species exhibiting the 2092-cm⁻¹ band or to the gem-dicarbonyl. The linear CO band at 2130 cm⁻¹ decreased in intensity steadily, and the band disappeared completely at 453 K. There was only a slight variation in the intensity of the 2035 cm⁻¹ band between 303 and 453 K, while the 2092-cm⁻¹ band increased in intensity initially and then decreased. Further increase in temperature resulted in the decrease in the gem-dicarbonyl bands at 2092 and 2035 cm⁻¹. The gem-dicarbonyl bands were completely removed at 613 K.

The absence of H₂ during the TPDE suggests that the reaction of surface OH⁻ with CO to form CO₂ and H₂ observed for the formation of CO₂ from adsorbed CO on Rh/SiO₂⁴⁸ did not occur in the present study. CO₂ may be formed by either (i) CO disproportionation $[2CO \rightarrow CO_2 + C]$ or (ii) the reduction of Rh⁺ by oxidation of a CO ligand^{34,44} $[2Rh^{I}(CO)_2 + O^2 \rightarrow 2Rh-$ CO + CO₂ + CO, where O²⁻ is an oxygen of the surface oxide]. The latter path would lead to simultaneous formation of CO and CO₂. The absence of a CO TPDE peak indicates that CO



Figure 9. (A) CO_2 profile during TPDE. (B) Absorbance intensity vs temperature during TPDE.

disproportionation is the only path leading to CO_2 formation. This is consistent with earlier results indicating that CO disproportionation is the major pathway for CO_2 formation during TPDE of oxide-supported metal carbonyls.⁴⁹ During CO disproportionation, each CO_2 molecule is formed from two CO molecules, or one *gem*-dicarbonyl adsorbed on one surface Rh atom. The amount of surface Rh atoms that chemisorb *gem*dicarbonyl is therefore equal to the number of molecules of CO_2 formed from disproportionation of the *gem*-dicarbonyl.

A comparison of parts A and B of Figure 9 shows that the initial portion of the CO₂ TPDE peak between 303 and 453 K can be mainly attributed to the desorption of the linear CO species that exhibit the 2130- and 1995-cm⁻¹ bands while the portion of the TPDE profile above 453 K results from the gem-dicarbonyl and the linear CO species displaying the 2102-cm⁻¹ shoulder band. An integrated IR absorbance coefficient, \bar{A}_{CO_8} , for gem-dicarbonyl was determined from the relation⁵⁰

$$\bar{A}_{\rm CO_g} = \frac{1}{\bar{C}_{\rm CO}} \int_{\nu_{\rm l}}^{\nu_{\rm u}} A(\nu) \, \mathrm{d}\nu$$

and the method developed by Rasband and Hecker.⁵¹ \bar{C}_{CO} is the moles of CO chemisorbed/cross-sectional area of the catalyst disk, and v_1 and v_u are the lower and upper wavenumber bounds of the absorption bands. The total amount of CO_2 formed during the TPDE was calculated from the area under the curve in Figure 9A. The amount of CO₂ formed from the disproportionation of the gem-dicarbonyl corresponding to the area under the CO_2 TPDE curve between 453 and 673 K in Figure 9A was found to be 1.55 μ mol of CO₂. The \bar{A}_{CO_3} was calculated from the above relation using the integrated IR absorbance for the gem-dicarbonyl bands, excluding that of the shoulder band at 2102 cm⁻¹ at 453 K in Figure 8 and was found to be 5.01 cm/ μ mol. This value is not far from an earlier estimate for $A_{CO_{e}}$ for gem-dicarbonyl by Cavanagh and Yates.¹³ The absolute error in determination of A_{CO_e} was 10%, due to the error compounded from the measurement of the size of the disk, integrated absorbances, and amount of CO₂ formed. The amount of surface Rh (μ mol/g of catalyst) prior to steady-state hydroformylation was determined from $\bar{A}_{CO_{e}}$ and the integrated absorbance from the gem-dicarbonyl shown in Figure 6. The amount of surface Rh sites was estimated to be 12.3 μ mol of Rh/g of catalyst which was used to estimate the TOFs for propionaldehyde formation in Table 1.

4. Discussion

 $Rh_6(CO)_{16}$ consists of six Rh atoms at the corners of an octahedron; each Rh atom carries two terminal CO groups and the remaining CO groups bridge three Rh atoms.^{10,35} Impregnation of $Rh_6(CO)_{16}$ onto the partially dehydroxylated SiO₂ disk in this study led to initial rapid decarbonylation, as seen by a reduction in the ratio of the intensity of the bridging to terminal carbonyls. Flushing the reactor with N₂ resulted in no further decarbonylation and the ratio of the intensities of the bridging to terminal carbonyls remained constant. The absence of gemdicarbonyl species following impregnation suggests that the Rh atoms may form stable aggregates. The rates of decarbonylation are dependent on conditions of pretreatment of the support.³² It is also known that the surface species formed by impregnating $Rh_6(CO)_{16}$ onto SiO₂ are stable under a CO atmosphere and undergo slow decomposition in the presence of dry air at 323 K.52 It has been shown that the $Rh_6(CO)_{16}$ cluster reacts only weakly at 298 K with Al₂O₃ pretreated at 773 K and retains the Rh₆ framework.^{8,47} In the presence of trace amounts of water, however, the cluster is known to disintegrate at 298 K to form Rh^I(CO)₂ species.

The stability of the partially decarbonylated $Rh_x(CO)_y/SiO_2$ framework was investigated by heating the catalyst in He to 373 K. The terminal and bridging carbonyls resulting from a partial decarbonylation of the $Rh_6(CO)_{16}$ were converted to the gemdicarbonyl at 373 K. The formation of the gem-dicarbonyl is due to the reaction of the terminal and bridging carbonyls with H₂O on the SiO₂ support. IR spectral features in the 3300–3600-cm⁻¹ region showed that the concentration of the surface H₂O decreased while the concentration of Rh¹(CO)₂ increased upon introduction of gaseous CO at 323–423 K in Figure 7. This is consistent with our earlier observations that H₂O plays a dominant role in the formation of the gem-dicarbonyl on RhCl₃ 0.7H₂O/SiO₂.⁵³ The most favorable temperature for the formation of gem-dicarbonyl was found to be 423 K; linear CO and bridge CO on Rh crystallite emerged at temperatures above 423 K.

A comparison of the TPDE profiles of adsorbed CO and Rh^I-(CO)₂ prepared from Rh₆(CO)₁₆ in this study and RhCl₃/SiO₂ and Rh(NO₃)₃/SiO₂ in our earlier work³⁴ shows that the only product during the TPDE in this study is CO₂ with a peak temperature at 453 K, whereas CO and CO₂ with peak temperatures at 453 and 565 K on RhCl₃/SiO₂ and 335 and 393 K on Rh(NO₃)₃/SiO₂ were observed. These results suggest that the adsorbed CO and gem-dicarbonyl formed from Rh₆(CO)₁₆ is more reactive for CO₂ formation than those formed from RhCl₃ and Rh(NO₃)₃. The lower reactivity of RhCl₃/SiO₂ and Rh-(NO₃)₃/SiO₂ toward CO₂ formation could be due to the presence of Cl or NO₃ species on the catalyst.

Reactivity of the supported terminal and bridging carbonyls toward C_2H_4/H_2 was investigated by in situ FTIR spectroscopy to determine the CO insertion activity of the cluster derived catalyst. Table 2 summarizes the chemisorbed species detected by FTIR spectroscopy under different experimental conditions in this study. Exposure of terminal and bridging carbonyls to C_2H_4/H_2 at 323 K resulted in the transformation to a linear CO species and the formation of acyl and aldehyde species. Reaction of gem-dicarbonyl species obtained from $Rh_6(CO)_{16}$ with $C_2H_4/$ H_2 also resulted in the formation of aldehyde and acyl species on the catalyst. A comparison of the reactivity between the terminal and gem-dicarbonyls toward C_2H_4/H_2 , shown in Figures 2 and 4, shows that the gem-dicarbonyls are more active toward CO insertion than the terminal CO at 323 K. The higher activity of the gem-dicarbonyls could be due to their coordination with a Rh⁺ site, which has been found to be more active than the Rh^o site for CO insertion.^{21,45}

While the terminal carbonyls show no reactivity for CO insertion at 303 K, its heterogeneous counterpart, linear CO on the reduced crystallite surface, has been found to actively

TABLE 2: Chemisorbed Species Observed during Development and Reaction of Surface Carbonyls^a

| conditions | terminal/ bridging carbonyls | O C mmm | O C Thinks | | aldehyde | acyl | acetate | carbonate |
|---|------------------------------------|---------------|------------------|-----|----------|------|---------|-----------|
| 1. Rh ₆ (CO) ₁₆ impregnation onto SiO ₂ (303 K, 0.1 MPa) | s/w | | w | | | | | |
| 2. C ₂ H ₄ /H ₂ , batch (323 K), 0.1 MPa | - | S | | | sh | 8 | | |
| 3. CO/H ₂ /C ₂ H ₄ steady-state (323 K, 0.1 MPa) | | w | | s | sh | S | | |
| 4. C ₂ H ₄ /H ₂ , batch (323 K) 0.1 MPa | | w | | S . | sh | S | w | sh |
| 5. CO/H ₂ /C ₂ H ₄ steady-state (393 K, 1.0 MPa) | | | | S | sh | S | | |
| 6. CO/H ₂ /C ₂ H ₄ steady-state (513 K, 1.0 MPa) | | | | | S | | | |

" Legend: s: strong; w: weak; sh: shoulder; blank: not observed.

participate in CO insertion at 303 K^{21} Temperatures higher than 323 K are required to activate CO insertion of the terminal carbonyls. The difference in the reactivity of the linear CO on Rh^o and terminal carbonyl species toward CO insertion may be explained by the state of these CO species during reaction.

The decrease in the concentration of linear CO on Rh° during CO insertion resulted in a lowering of the intensity and wavenumber of the linear CO band from 2070 to 2035 cm^{-1,21} The decrease in the wavenumber is due to a decline in the dipoledipole coupling of CO brought about by a decrease in the CO coverage, or, due to dilution by adsorbed H or $C_x H_y$ on neighboring atoms.43 This result suggests that the linear CO which participates in CO insertion chemisorbs on the surface of Rh crystallites which also provide sites for other adsorbed CO and adsorbed alkyl species, C₂H₄, and hydrogen. The decrease in the concentration of terminal carbonyl during CO insertion at 323 K, shown in Figure 2, resulted in a decrease in the intensity of the band at 2081 cm⁻¹ without a significant decrease in the wavenumber. Absence of the variation in the wavenumber of CO suggests that the terminal carbonyls locate on isolated Rh sites in the absence of CO dipoledipole interactions between neighboring CO molecules. The isolation of the terminal CO site and the lack of neighboring Rh sites that are required to chemisorb $C_x H_y$ or H may be one of the reasons for the lower CO insertion reactivity of the terminal carbonyls.

Although zeolite-supported Rh carbonyls provide potential to anchoring metal carbonyls, terminal carbonyl and gem-dicarbonyls resulting from Rh₆(CO)₁₆ have shown no activity for CO insertion toward adsorbed alkyl species at 393 K and total pressure of 3.0-9.0 kPa.³⁹ It should be noted that the rate of a reaction depends on not only the rate constant but also the reactant concentration. The absence of CO insertion may be related to the low concentration of reactant used. In situ IR study suggests that the gem-dicarbonyl, terminal, and bridging carbonyls on RhNaX and RhNaY zeolites may not actively participate in propylene hydroformylation at 423 K.³⁸

The reactivity of adsorbed CO appears to depend on its chemical environment. The present study and our previous studies^{21,22,34,45} show that the terminal CO on the partially decarbonylated Rh₆-(CO)₁₆ on SiO₂, linear CO on the Rh⁺ and Rh^o sites, and gemdicarbonyl can participate in CO insertion at different rates, while bridge CO and bridging carbonyl are essentially inactive for the reaction. The fact that various forms of adsorbed CO on single Rh sites can participate in CO insertion is analogous to CO insertion in homogeneous hydroformylation. CO insertion has long been known to take place on the mononuclear metal carbonyl in homogeneous hydroformylation.^{2-5,23-29}

Ethylene hydroformylation on Rh/SiO₂ at 513 K has shown that a pressure of 0.7 MPa is required to generate enough acyl species to be detected by FTIR spectroscopy.²⁰ The appearance of the acyl band at 1685 cm⁻¹ on the Rh¹(CO)₂/SiO₂ catalyst derived from Rh₆(CO)₁₆ in this study suggests that hydrogenation of the acyl species could be rate limiting at 323–393 K and 0.1 MPa. Under the same conditions, a surface carbonate species was also detected at 1553 cm⁻¹, which could be a spectator during the formation of acyl or aldehyde species. We have been able to identify a similar carbonate species as a spectator by steadystate isotopic transient analysis and *in situ* IR spectroscopy on a Ce–Rh/SiO₂ catalyst during ethylene hydroformylation at 453 K and 0.1 MPa.³³

The presence of Rh gem-dicarbonyl during the steady-state ethylene hydroformylation at 393 K and 1 MPa indicates that most of the Rh surface is in the oxidized state. Increasing temperature to 513 K resulted in a reduction of the Rh+ sites and an improvement in the aldehyde selectivity. The increased aldehyde selectivity could be due to an enhancement in the hydrogenation of acyl species. The TOF for aldehyde formation has been calculated using the number of surface Rh atoms estimated from the TPDE experiment. A comparison of the TOF for aldehyde formation at 513 K and 1 MPa after 60 min of reaction between the Rh₆ cluster-derived catalyst, RhCl₃/SiO₂ and $Rh(NO_3)_3/SiO_2$ in our earlier study³⁴ shown in Table 1 reveals that the TOF for propionaldehyde formation is higher on the Rh₆ cluster-derived catalyst than those on RhCl₃/SiO₂ and Rh(NO₃)₃/ SiO₂. The percentage of CO converted and the CO insertion activity during the CO-H₂-C₂H₄ reaction on Rh₄(CO)₁₂- and $Rh_6(CO)_{16}$ -derived catalysts have also been found to be higher than those on catalysts prepared from RhCl₃·3H₂O.³⁰ The origin of the difference in activity between these catalysts remains to be investigated.

5. Conclusions

Impregnation of $Rh_6(CO)_{16}$ onto partially dehydroxylated SiO₂ resulted in partial decarbonylation and the formation of terminal and bridging carbonyls on the SiO_2 at 303 K. The terminal and bridging carbonyls were converted to gem-dicarbonyl at 373 K in the presence of He. The formation of gem-dicarbonyl can be enhanced at 423 K in the presence of 0.1 MPa CO. In situ FTIR investigation revealed that the terminal and the gem-dicarbonyls derived from $Rh_6(CO)_{16}$ were both active for CO insertion at 323 K; the gem-dicarbonyls were more active than the terminal carbonyls. Under steady-state ethylene hydroformylation conditions at 393 K and 1 MPa, the surface Rh in an oxidized state showed low rate of hydrogenation of the acyl species resulting in low TOF for aldehyde formation. At 513 K, the surface Rh atoms in a reduced crystallite state exhibited a higher TOF for propionaldehyde formation than that at 393 K. The TOF for propionaldehyde formation at 513 K was higher than those on RhCl₃/SiO₂ and Rh(NO₃)₃/SiO₂ catalysts. The site requirements for CO insertion observed in this study are consistent with those reported in homogeneous hydroformylation and our previous studies.

Acknowledgment. We gratefully acknowledge the partial support of this research by the Faculty Research Grant of the University of Akron.

References and Notes

- Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer,
 W. R. Chem. Rev. 1979, 79, 91.
- (2) Masters, C. Homogeneous Transition-Metal Catalysis—A Gentle Art; Chapman and Hall: New York, 1981.
 - (3) Ugo, R.; Psaro, R. J. Mol. Catal. 1983, 20, 53.

(4) Henrici-Olive, G.; Olive, S. The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide; Springer-Verlag: New York, 1984.
(5) Sachtler, W. M. H. In Proceedings of 8th International Congress on

- Catalysis; Ertl, G., Ed.; DECHEMA: Frankfurt am Main, 1984; Vol. 1, p 151
- (6) Brenner, A. In Metal Clusters; Moskovits, M., Ed.; John Wiley and Sons: New York, 1986; pp 249-281.
- (7) Bradley, J. S. Metal Clusters; Moskovits, M., Ed.; John Wiley and Sons: New York, 1986; pp 105-130.
- (8) Lamb, H. H.; Gates, B. C.; Knozinger, H. Angew. Chem., Int. Ed. Engl. 1988, 27, 1127.
- (9) Basset, J. M.; Candy, J. P.; Choplin, A.; Leconte, M.; Theolier, A. In Aspects of Homogeneous Catalysis; Ugo, R., Ed.; Kulwer: The Netherlands, 1990; Vol. 7, p 85.
- (10) Ichikawa, M. In Advances in Catalysis; Academic Press: New York, 1992; Vol. 38, pp 283-400.
- (11) Yang, A. C.; Garland, C. W. J. Phys. Chem. 1957, 61, 1504.
 (12) Yates, J. T., Jr.; Duncan, T. M.; Worley, S. D.; Vaughan, R. W. J.
 Chem. Phys. 1979, 70, 1219.
- (13) Cavanagh, R. R.; Yates, J. T., Jr. J. Chem. Phys. 1981, 74(7), 4150.
- (14) Rice, C. A.; Worley, S. D.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. J. Chem. Phys. 1981, 74, 6487.
 - (15) Solymosi, F.; Bansagi, T. J. Phys. Chem. 1993, 97, 10133. (16) Konishi, Y.; Ichikawa, M.; Sachtler, W. M. H. J. Phys. Chem. 1987,
- 91, 6286. (17) Vannice, M. A. In Catalysis-Science and Technology; Anderson, R
- Boudart, M., Eds.; Springer-Verlag: New York, 1984; Vol 3, pp 140–197. (18) Underwood, R. P.; Bell, A. T. J. Catal. 1988, 111, 325.
 - (19) Li, Y. E.; Gonzales, R. D. J. Phys. Chem. 1988, 92, 1529.
 (19) Li, Y. E.; Gonzales, R. D. J. Phys. Chem. 1988, 92, 1589.
 (20) Chuang, S. S. C.; Pien, S. I. J. Mol. Catal. 1989, 55, 12.
 (21) Chuang, S. S. C.; Pien, S. I. J. Catal. 1992, 135, 618.
 (22) Chuang, S. S. C.; Pien, S. I. J. Catal. 1992, 138, 536.

 - (23) Calderazzo, F. Angew. Chem., Int. Ed. Engl. 1977, 16, 299.
- (24) Pino, P.; Piacenti, F.; Bianchi, M. In Organic Syntheis via Metal
- Carbonyls; Wender, I., Pino, P., Ed.; Wiley: New York, 1977; Vol. 2, p 43. (25) Parshall, G. W. Homogeneous Catalysis—The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes; Wiley: New
- York, 1981; p 85. Schler, W. M. H.; Ichikawa, M. J. Phys. Chem. 1986, 90, 4752.
 Marko, L.; Vizi-Orosz, A. In Metal Clusters in Catalysis; Gates, B.
- (21) Marias, E., Vizi-Olszi, A. III Metal Clusters in Calabysis; Gates, B.
 C., Guczi, L., Knozinger, H., Eds.; Studies in Surface Science and Catalysis; Elsevier: New York, 1986; Vol. 29, pp 89–120.
 (28) Correa, F.; Nakamura, R.; Stimson, R. E.; Burwell, R. L., Jr.; Shriver, D. F. J. Am. Chem. Soc. 1980, 101, 5864.

(29) Cornils, B. In New Syntheses with Carbon Monoxide; Falbe, J., Ed.; Springer-Verlag: New York, 1980.

- (30) Ichikawa, M. J. Catal. 1979, 59, 67.
- (31) van't Blick, J. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. J. Am. Chem. Soc. 1985, 107, 3139.
- (32) Bilhou, J. L.; Bilhou-Bougnol, V.; Graydon, W. F.; Basset, J. M.; Smith, A. K.; Zanderighi, G. M.; Ugo, R. J. Organomet. Chem. 1978, 153,
- 73. (33) Srinivas, G.; Chuang, S. S. C.; Balakos, M. W. AIChE J. 1993,
- 39(3), 530. (34) Chuang, S. S. C.; Srinivas, G.; Mukherjee, A. J. Catal. 1993, 139, 490.
- (35) Conrad, J.; Ertl, G.; Knozinger, H.; Kuppers, J.; Latta, E. E. Chem. Phys. Lett. 1976, 42(1), 115.
- (36) Iwatate, K.; Dasgupta, S. R.; Schneider, R. L.; Smith, G. C.; Watters, K. L. Inorg. Chim. Acta 1975, 15, 91.
- (37) Theolier, A.; Smith, A. K.; Leconte, M.; Basset, J. M.; Zanderighi, G. M.; Psaro, R.; Ugo, R. J. Organomet. Chem. 1980, 191, 415
- (38) Rode, E. J.; Davis, M. E.; Hanson, B. E. J. Catal. 1985, 96, 574. (39) Takahashi, N.; Mijin, A.; Suematsu, H.; Shinohara, S.; Matsuoka,
- H. J. Catal. 1989, 117, 348. (40) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. Introduction to Infrared
- and Raman Spectroscopy; Academic Press: New York, 1990.
 - (41) Solymosi, F.; Knozinger, H. J. Catal. 1990, 122, 166. (42) Arakawa, H.; Fukushima, T.; Ichikawa, M. Appl. Spectrosc. 1986,
- 40, 884.
 - (43) Stoop, F.; Toolenar, F. J. C.; Ponec, V. J. Catal. 1982, 73, 50.
 - (44) Solymosi, F.; Paztor, M. J. Phys. Chem. 1986, 90, 5312.
 - (45) Srinivas, G.; Chuang, S. S. C. J. Catal. 1993, 144, 131.
- (46) Balakos, M. In Ph.D. Dissertation, preliminary data, University of Akron, 1993.
- (47) Basset, J. M.; Besson, B.; Choplin, A.; Theolier, A. Philos. Tans. R. Soc. London, A 1982, 308, 115
- (48) Koerts, T.; Welters, W. J. J.; van Wolput, J. H. C.; van Santen, R. A. Catal. Lett. 1992, 16, 287.
- (49) Knozinger, H. In Metal Clusters in Catalysis; Gates, B. C., Guczi, L., Knozinger, H., Eds.; Elsevier: New York, 1986; p 259.

 - (50) Winslow, P.; Bell, A. T. J. Catal. 1984, 86, 158.
 - (51) Rasband, P. B.; Hecker, W. C. J. Catal. 1993, 139, 551.
- (52) Smith, G. C.; Chojnacki, T. P.; Dasgupta, S. R.; Iwatate, K.; Watters, K. L. Inorg. Chem. 1975, 14(6), 1419.
 - (53) Chuang, S. S. C.; Debnath, S. J. Mol. Catal. 1993, 79, 323.