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Catalytic Carbon Dioxide Methanation by Alumina-Supported Mono- and Polynuclear Ruthenium Carbonyls

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The catalytic activity and selectivity toward methanation of carbon dioxide using several alumina-supported ruthenium-cluster-derived catalysts have been studied over the temperature range 180–250 °C. The ruthenium clusters used in these investigations include $Ru_3(CO)_{12}$, $KHRu_3(CO)_{11}$, $[PPN][HCO_2Ru_3(CO)_{10}]$, $H_4Ru_4(CO)_{12}$, $KH_3Ru_4(CO)_{12}$, $[PPN][H_3Ru_4(CO)_{12}]$, and $Ru_6C(CO)_{17}$ (PPN = bis(triphenylphosphine)nitrogen(1+)). Comparative studies were made with the mononuclear complexes $RuCl_3$ and $Ru(CO)_5$. The latter species provides a low-valent, organometallic, mononuclear ruthenium source. Catalysts were supported by impregnation over alumina (partially dehydroxylated at 150 °C in vacuo) and activated in hydrogen at 200 °C. Catalyst characterization included diffuse-reflectance infrared spectroscopy, surface area determination, oxygen chemisorption, and electron microscopy. In general, the cluster-derived catalysts were more active than the analogously prepared catalyst obtained from $RuCl_3$; e.g., at 180 °C the catalyst derived from $Ru_6C(CO)_{17}$ was 22 times more active than that derived from $RuCl_3$. The activity of catalysts derived from supported neutral species was observed to increase as the number of ruthenium atoms present in the precursor complex increased; i.e., $Ru(CO)_5 < Ru_3(CO)_{12} < H_4Ru_4(CO)_{12} < Ru_6C(CO)_{17}$. Catalysts derived from supported anionic ruthenium cluster derivatives were less active than their neutral counterparts, displaying a great deal of sensitivity to the nature of the accompanying cation. The diffuse-reflectance FTIR spectra of all the supported, activated catalysts originating from low-valent ruthenium derivatives exhibited the same band pattern in the ν(CO) region, whereas the $RuCl_3$-derived catalyst displayed a quite different ν(CO) infrared spectrum upon addition of carbon monoxide.

Introduction

The interest in applying organometallic chemistry to the study of surface reactions has greatly increased in the past few years.[1] In particular, anchoring metal clusters on inorganic supports (Al_2O_3, SiO_2, etc.) has received considerable attention mainly due to the possibility of obtaining a highly disperse low-valence metal on the supports[2] and the relatively higher activity and selectivity found in the cluster-derived catalysts in comparison with those of the conventionally prepared ones.[3,4]

There is currently much interest in the use of carbon dioxide as a source of chemical carbon.[5] Among the transition metals that catalyze the conversion of CO_2 into methane, ruthenium is perhaps the best methanation catalyst.[6-9] Solymosi and co-workers have reported that the methanation of CO_2 on alumina-supported ruthenium catalysts is faster than that with CO as a source of carbon. The higher selectivity and activity is attributed to the relatively low concentration of "active surface carbon species", which favors methane formation rather than carbon accumulation on the surface with subsequent deactivation of the catalyst. These "surface carbon species" have also been proposed by researchers in studies of CO_2 methanation with ruthenium catalysts supported on silica[8] and molecular sieves.[9]

In these previous studies[6-9] the catalyst precursors have been mononuclear ruthenium complexes (generally $RuCl_3$) anchored by impregnation over the corresponding support. However, Baird and co-workers[4] have recently reported that the use of triruthenium dodecacarbonyl supported on Al_2O_3 in lieu of ruthenium trichloride enhances the conversion of CO_2 to methane and the system operates at a lower reaction temperature (280 vs. 365 °C). Furthermore, the $Ru_3(CO)_{12}$-derived catalyst was found to be more selective toward CH_4 production and had increased longevity as compared with its $RuCl_3$ analogue.

In this paper we wish to report the first of our studies on the methanation of CO_2 using alumina-supported $Ru(CO)_5$ and various ruthenium carbonyl clusters as catalyst precursors. These investigations focus on the diffuse-reflectance infrared spectral analysis and on the catalytic activity and selectivity toward methane production of these supported ruthenium catalysts. Emphasis is placed on noting differences and similarities in spectral properties and catalytic activities based on the nature of the precursor complex. The ruthenium clusters were selected for examination on the basis of variations in cluster nuclearity and overall cluster charge (i.e., 0 or 1−). For the latter anionic species, concomitant assessment of counterion effects was warranted. It is important to point out that the interactions between some of the clusters used in this study ($Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $Ru_6C(CO)_{17}$) and alumina have been previously examined by Bell and co-workers.[10]

Pertinent inquiries involving the use of supported osmium clusters for the methanation of carbon dioxide have recently been reported upon by Jackson and co-workers.[11] Experiments using ^{14}C tracers under steady-state conditions revealed the existence of distinct sites for CO_2 adsorption that were believed to be carbonaceous. Unfortunately, no comparisons were made with osmium catalysts derived from mononuclear complexes. In addition, Moggi and co-workers[12] have described preliminary experiments on the activity of $(\eta^5\text{-}C_5H_5)NiOs_3(CO)_9(\mu\text{-}H)_3$ supported on $\gamma\text{-}Al_2O_3$ for the methanation of carbon oxides. This tetranuclear species was found to be an effective cluster-based

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catalyst for the methanation of CO_2, exhibiting an efficiency much higher than that of catalysts containing only nickel.

Experimental Section

All manipulations were carried out either in an argon drybox or on a double-manifold Schlenk vacuum line under an atmosphere of dry nitrogen. Tetrahydrofuran, hexane, and toluene were dried by refluxing over sodium benzophenone ketyl under nitrogen. Infrared spectra were recorded on an IBM FTIR Model 85 spectrophotometer. Surface area measurements were carried out with a Cahn electrobalance, Model 2000RG, connected to a vacuum line equipped with an oil diffusion pump. For the precise measure of the pressure an MKS Instrument gauge, Model 170M-25B, was used. Transmission electron microscopy experiments were carried out in a Zeiss 10C apparatus at a magnification of 100 000 (underfocused 384 nm). The apparatus used for GC-IR experiments consists of an IBM 85 FTIR spectrometer equipped with a low-volume light pipe and MCT detector that is coupled to a Perkin-Elmer Sigma 3 GC unit.

Synthesis of the Metal Clusters. $RuCl_3 \cdot xH_2O$ was obtained from Alfa. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals and was used as received. $Ru(CO)_5$,[13] $KHRu_3(CO)_{11}$,[14] $PPNHCO_2Ru_3(CO)_{10}$,[15] $H_4Ru_4(CO)_{12}$,[16] $KH_3Ru_4(CO)_{12}$,[17] $[PPN][H_3Ru_4(CO)_{12}]$[17] (PPN = bis(triphenylphosphine)nitrogen(1+)), and $Ru_6C(CO)_{17}$[18] were prepared and purified according to the previously described methods. Infrared spectroscopy in the carbonyl region was used for identification and characterization of the clusters. Synthesis of the enriched $Ru_3(^{13}CO)_{12}$ was accomplished by employing the method published[19] using a 1:1 THF/methanol mixture as a solvent.

Preparation and Characterization of the Catalysts. The ruthenium carbonyl clusters were supported by mixing a THF solution of a previously weighed amount of cluster (to attain a 1% by weight ruthenium loading) with the corresponding amount of neutral, amorphous alumina (Fisher, partially dehydroxylated by heating in vacuo at 150 °C overnight). For $RuCl_3 \cdot xH_2O$ and $Ru_3(CO)_{12}$, the solvent used for impregnation was acetone and hexane, respectively. This mixture was then vigorously stirred for 2–4 h under nitrogen. Following this treatment, the solvent was removed and the catalyst dried in vacuo overnight. All the supported clusters prepared by this method were stored inside a drybox for manipulation and future use.

Infrared measurements on the supported clusters were carried out with a diffuse-reflectance accessory, "The Collector" (generously supplied by Barnes Analytical), equipped with a controlled-environment chamber. This FT-IR cell allows for the use of powdered samples, which can be loaded inside a drybox, and it is also capable of obtaining spectra at elevated temperatures and reduced or ambient pressures. In a typical experiment, approximately 0.2 g of catalyst (activated or not) was placed inside the previously described cell. This cell was then sealed and transferred to the FT-IR spectrometer. After the spectrum was collected (512 scans), carbon monoxide was allowed to flow through the cell for approximately 20 min. The cell was then evacuated and the spectrum retaken. The reference used for all the IR experiments was pure KBr (Fisher).

In the surface area measurements, the catalyst (approximately 0.1 g) was transferred to a Cahn balance and dried under vacuum (diffusion pump) at 200 °C overnight. After that period, the sample was precisely weighed, cooled with liquid nitrogen, and put in contact with a small amount of nitrogen gas. When the system attained equilibrium, the pressure and the increase in weight was recorded. The last procedure was repeated several times, and after BET calculations a value of approximately 138 m^2/g was found for all the catalysts used in this study.

Transmission electron microscopy was performed by preparing a suspension of the catalyst (activated under hydrogen at 200 °C overnight) in hexane and quickly transferring a drop of the suspension to the microscopy chamber, which was immediately evacuated. Several pictures (three to four) were taken randomly, and approximately 200 particles were measured. The average particle size was determined by averaging of all the particles measured. The results indicated that the *average* particle sizes were ca. 50–100 Å for all the catalysts used in this paper. This is consistent with X-ray measurement, where small particle sizes were indicated (assuming crystalline samples).

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Table I. Relative Reactivities for Methanation of CO_2 Using Alumina-Supported Ruthenium Catalysts[a]

catalyst precursor	180 °C	250 °C
$RuCl_3 \cdot 3H_2O$	1	1[b]
$Ru(CO)_5$	4.7	3.4[c]
$Ru_3(CO)_{12}$	12.6	7.8
$KHRu_3(CO)_{11}$	2.7	2.2
$[PPN][HCO_2Ru_3(CO)_{10}]$	0.1	0.2[c]
$H_4Ru_4(CO)_{12}$	14.6	8.9
$KH_3Ru_4(CO)_{12}$	8.8	4.4
$[PPN][H_3Ru_4(CO)_{12}]$	1.8	1.4
$CRu_6(CO)_{17}$	21.7	9.5

[a] Relative reactivity = moles of CH_4 produced per total moles of ruthenium. Conditions: CO_2:H_2 = 1:2.5; flow rate 0.25 mL/s; glass reactor $^1/_4$ in. thick and 1 ft long, with ca. 2 g of catalyst; products analyzed by GC-IR. [b] CO and ethane were detected by GC-IR. [c] CO was detected by GC-IR.

Oxygen Chemisorption Measurements. The numbers of active sites were determined by oxygen absorption assuming a 2:1 O_2:ruthenium stoichiometry as reported in the literature.[20] In a typical determination, ~0.1 g of a freshly activated ruthenium catalyst was placed in a previously weighed flask (to ±0.1 mg) inside an argon-filled drybox. After the flask was removed from the glovebox, it was accurately reweighed. The flask was connected to a Micromeritics Accusorb apparatus, Model 2100E, and heated under vacuum at 160 °C overnight. Following the determination of the dead volume (using He, Matheson ultrahigh purity), oxygen (Matheson, ultrahigh purity), at a pressure of ~5 torr, was allowed to contact the catalyst at room temperature. When the system reached equilibrium, additional oxygen was admitted to the flask and a new pressure measurement was taken. This process was repeated at least four times. The micromoles of O_2 chemisorbed was calculated by extrapolation to zero of the linear isotherm plots of micromoles of O_2 absorbed per gram of catalyst vs. the equilibrium oxygen pressure for each of the catalysts. Identical runs using only the support indicated that alumina did not chemisorb oxygen at room temperature; hence, no correction was needed. Readsorption experiments were also carried out which demonstrated that no additional oxygen was chemisorbed (extrapolated to zero pressure) on the catalysts.

Catalytic Reactions. The catalytic reactions were carried out by placing ca. 2 g of the supported cluster inside a glass reactor (1 ft long, $^1/_4$ in. thick), followed by passing prepurified (99.995%) hydrogen gas (flow rate >1 mL/s) at 200 °C for at least 8 h (overnight). The metal loading after activation was determined by microanalysis (Galbraith Laboratories, Inc.) to be ca. 1% by weight ruthenium; e.g., the $Ru_3(CO)_{12}$-derived catalyst was analyzed for 0.99% ruthenium metal. After this period, the reactor was cooled, and a CO_2/H_2 mixture (1:2.5 molar ratio, GC analyzed by Air Products, 99.99% instrument grade) was passed through the catalyst bed. The total gaseous effluent was continuously monitored by Fourier-transform infrared spectroscopy after the stationary state was reached at the desired temperature. The reactor bed and adjacent lines were positioned in the oven of the gas chromatograph and thus could be heated to a uniform temperature. The speed, sensitivity, and resolution of the GC-FTIR instrument made possible the definitive identification of the products (methane, ethane, carbon monoxide, water, etc.), and the obtainment of quantitative analysis (by using a calibrated gas tank (Airco) of known composition in reactants and products). This system can also observe moderately fast changes in reaction performances when the oven was not in a stationary state at a given temperature (nonisothermal experiments). The reference for all the GC-IR measurements was taken at 70 °C.

Results and Discussion

Neutral and anionic ruthenium carbonyls supported on partially dehydrated alumina and activated at 250 °C in hydrogen have been found to be effective catalysts for the hydrogenation of carbon dioxide to methane (eq 1). Table I contains the rates of methanation of carbon dioxide for those low-valent ruthenium species relative to those for $RuCl_3$ at two reaction temperatures. These rates are based on the total ruthenium content and are not corrected here for exposed ruthenium sites (vide infra). The catalytic

$$CO_2 + 4H_2 \xrightarrow{[cat.]} CH_4 + 2H_2O(l) \qquad \Delta H_{298} = -252.9 \text{ kJ/mol} \tag{1}$$

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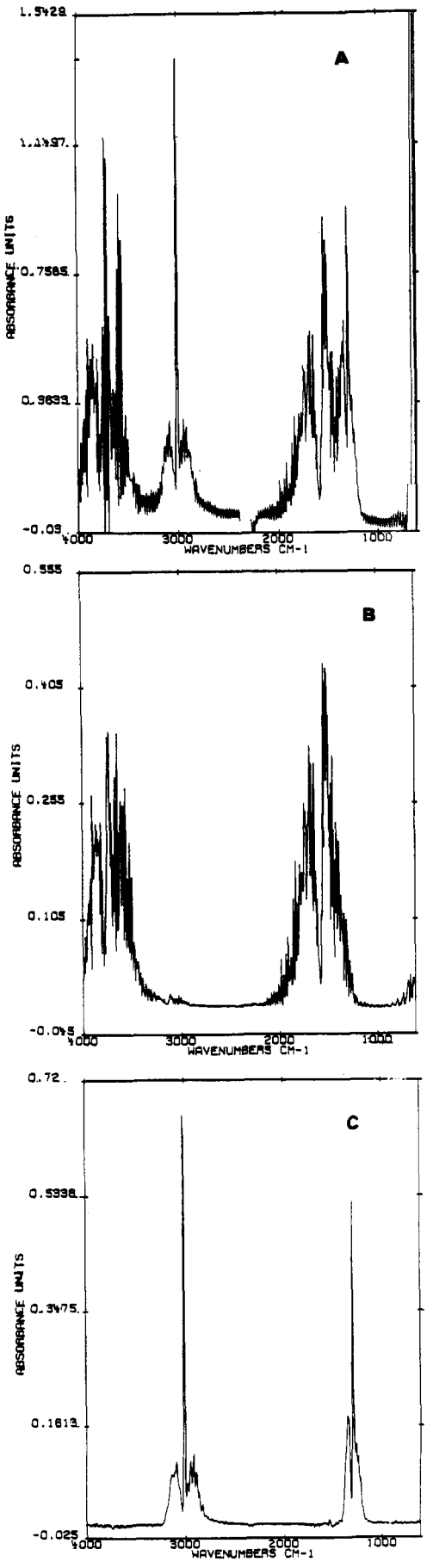

Figure 1. Methanation of CO_2 over supported ruthenium catalysts derived from ruthenium carbonyl clusters: (A) infrared spectrum of products in gas stream of CO_2/H_2 reaction; (B) infrared spectrum of gaseous pure water; (C) infrared spectrum of pure methane.

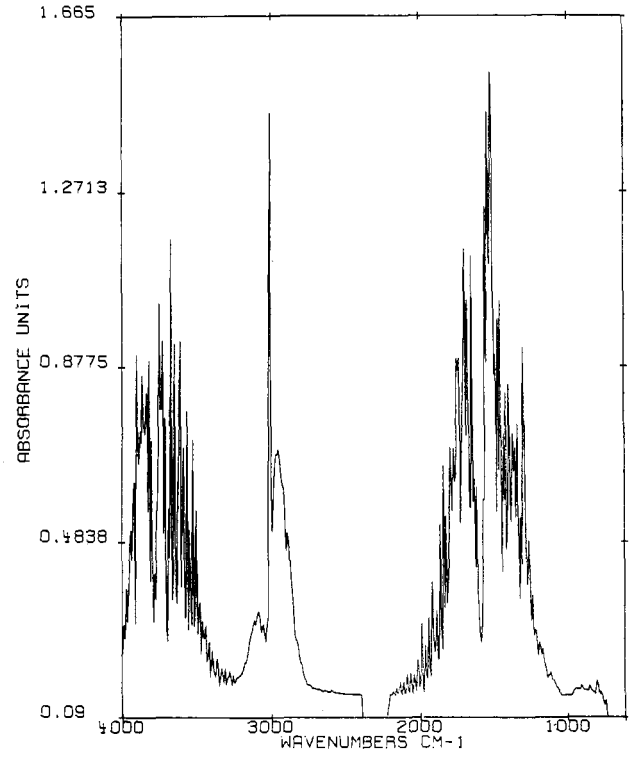

Figure 2. Infrared spectrum of products in gas stream of CO_2/H_2 reaction over supported $RuCl_3$ catalyst.

reactions were carried out in a packed glass column that was heated in the oven of a GC, and the products were monitored by FTIR.[21] The GC-FTIR traces of the products of the methanation reaction can be seen in Figure 1. As is depicted in Figure 1 by direct comparison with authentic samples, water and methane were identified in the gaseous effluent afforded from the reactor.

When ruthenium trichloride was used as catalyst precursor, the infrared spectrum of the gaseous effluents revealed in addition to H_2O and CH_4 (the principal products) an asymmetry in the satellite peaks of the methane at 3086 and 2916 cm^{-1} (see Figure 2). Upon subtraction of the spectrum of an authentic sample of methane from the product infrared trace, a spectrum corresponding to that of ethane remained. Hence, $RuCl_3$-derived catalysts produced not only CH_4 and H_2O but also ethane during the carbon dioxide methanation process.

By monitoring the absorbance of the major infrared peak of methane at 3017 cm^{-1}, it was possible to determine the conversion of CO_2/H_2 to methane as well as the relative reactivities of the various mono- and polynuclear ruthenium catalysts. These results are tabulated, in part, in Table I and are displayed graphically for four different temperatures in Figure 3. As indicated previously, these comparative data are based on total ruthenium content. All Al_2O_3-supported low-valent ruthenium complexes investigated herein provided more active catalysts than $RuCl_3$, with the lone exception of $[PPN][HCO_2Ru_3(CO)_{10}]$.

It can be seen in Table I and Figure 3 that the neutral ruthenium-cluster-derived catalysts ($Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$) are more active than their anionic counterparts, $KHRu_3(CO)_{11}$ and $KH_3Ru_4(CO)_{12}$, respectively. Furthermore, the activity of these supported neutral species increases as the number of ruthenium atoms present in the precursor complex increases, i.e., $Ru(CO)_5 < Ru_3(CO)_{12} < H_4Ru_4(CO)_{12} < Ru_6C(CO)_{17}$. A similar observation has been reported for the hydrogenolysis of butane using supported ruthenium clusters[22] and for the dissociative chemisorption of hydrogen using cobalt or niobium clusters.[23] These results strongly suggest that a definitive relationship

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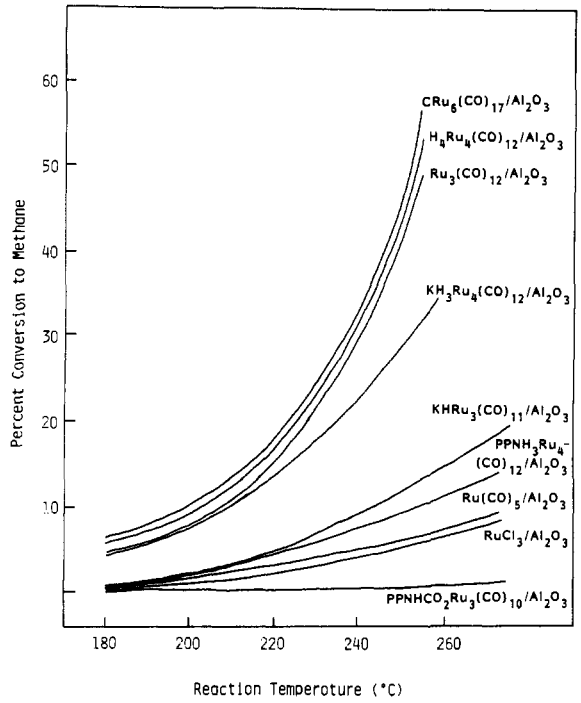

Figure 3. Percent conversion toward methane vs. temperature for various Ru catalysts (catalysts supported over Al_2O_3 (dehydroxylated at 150 °C under vacuum), conversion for 2 g of catalyst (ca. 1% Ru metal), CO_2:H_2 = 1:2.5 mole ratio; F_R = 0.25 mL/s; 1-ft glass reactor; yield determined by GC-IR).

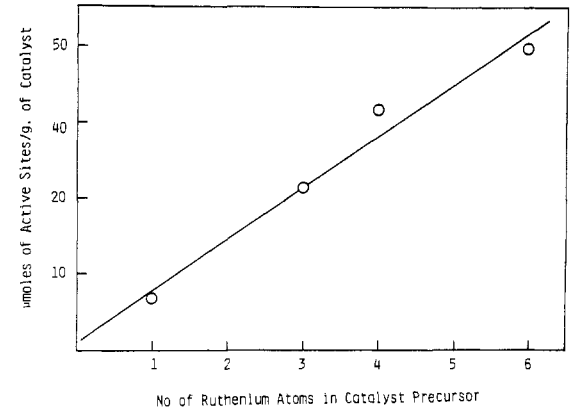

Figure 4. Micromoles of active ruthenium sites per gram of catalyst as a function of number of ruthenium atoms in the neutral, zerovalent catalyst precursor (9.6 μmol of active sites/g of catalyst for $RuCl_3$).

between the structure of the cluster precursor and the nature or dispersion of the metal on the support should exist. In an effort to better understand this phenomenon, we have determined, by means of oxygen chemisorption,[20] the number of micromoles of active ruthenium sites per gram of catalyst, for $RuCl_3$ and these neutral zerovalent ruthenium species ($Ru(CO)_5$, $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $Ru_6C(CO)_{17}$). These measurements clearly demonstrate that the number of active sites (or percent metal dispersion) increases with increasing number of ruthenium atoms in the ruthenium catalyst precursor (Figure 4).

The selectivity toward CH_4 observed with use of either neutral or potassium salts of ruthenium clusters as catalyst precursors was greater than 95% (no other products were detected by GC or GC-IR).[24] The fact that no higher molecule weight hydrocarbons were seen is particularly interesting for the potassium salts because of the known effect of alkali-metal promoters on the hydrogenation of carbon monoxide.[25] There is always the possibility that the ruthenium catalysts used in this study are good cracking catalysts; hence, the higher selectivity observed may be due in part to catalytic cracking of higher molecular weight hydrocarbon products. This was tested by injecting ethane into a previously heated ruthenium-cluster-derived catalyst ($Ru_3(CO)_{12}$) under a stream of pure hydrogen. Methane and unreacted ethane were detected by GC-IR. Hence, the cracking of higher molecular weight hydrocarbons afforded during CO_2 methanation

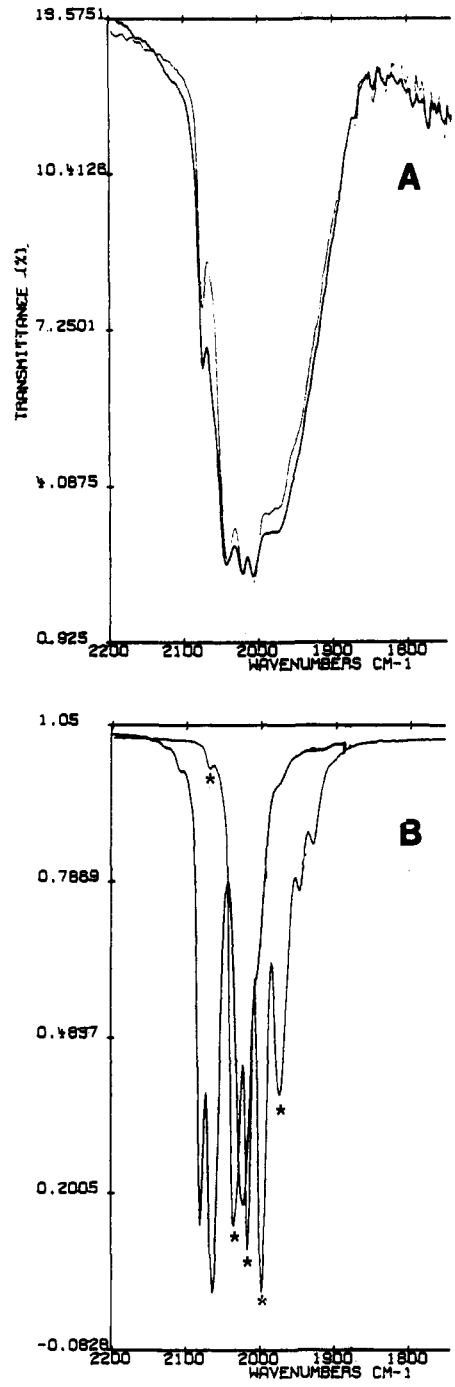

Figure 5. (A) Diffuse internal reflectance infrared spectra of $H_4Ru_4(CO)_{12}$ (dark trace) and $KH_3Ru_4(CO)_{12}$ (light trace), both supported on Al_2O_3, prior to activation. (B) Solution infrared spectra in THF in ν(CO) region of $H_4Ru_4(CO)_{12}$ (dark trace) and $KH_3Ru_4(CO)_{12}$ (light trace, peaks indicated with asterisks).

(24) When $Ru(CO)_5$ or PPN^+ salts of the tetra- and triruthenium clusters were employed as catalyst precursors, CO was produced during the methanation reaction, indicating a selectivity toward methane not higher than 90%. The presence of CO with $Ru(CO)_5$ as catalyst precursor is a good indication that a cluster is needed in order to achieve higher selectivity toward methane production.

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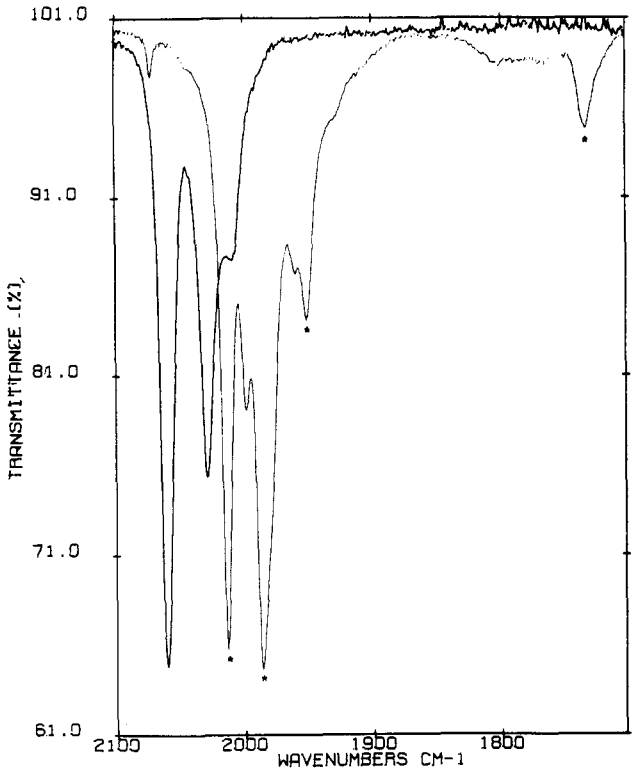
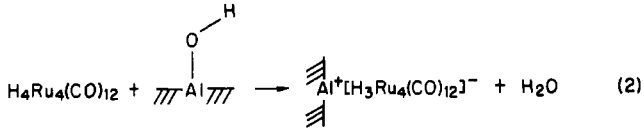


Figure 6. Solution infrared spectra in THF in ν(CO) region of $Ru_3(CO)_{12}$ (dark trace) and $KHRu_3(CO)_{11}$ (light trace, peaks indicated with asterisks).

cannot be overlooked. Indeed, Simpson and Whyman have reported that the activity toward hydrogenolysis of straight-chain aliphatic hydrocarbons to methane superficially correlates with the smaller metal crystallite sizes (15–20 Å) reproducibly obtainable when $Ru_3(CO)_{12}$ was used as catalyst precursor.[3]

By way of contrast, the ruthenium chloride derived catalyst afforded ethane as a product in addition to CO at temperatures higher than 220 °C. For these reasons the selectivity to methane production for this catalyst was found to be between 80 and 85%.

The mode of interaction of $H_4Ru_4(CO)_{12}$ with the support is via the surface –OH groups of alumina (eq 2). This is clearly



$$H_4Ru_4(CO)_{12} + \text{(surface)} \rightarrow \text{(surface)}\ Al^+[H_3Ru_4(CO)_{12}]^- + H_2O \qquad (2)$$

demonstrated when one compares the infrared spectrum in the ν(CO) region of a freshly prepared catalyst of $H_4Ru_4(CO)_{12}/Al_2O_3$ with that of $KH_3Ru_4(CO)_{12}/Al_2O_3$ prior to their activation in hydrogen (Figure 5). An examination of the solution spectra in the ν(CO) region of these two ruthenium carbonyl clusters vividly points out the similarities of the spectrum of the $H_3Ru_4(CO)_{12}^-$ anion with that obtained initially from either $H_4Ru_4(CO)_{12}$ or $KH_3Ru_4(CO)_{12}$ on Al_2O_3. Further inspection of the ν(CO) infrared spectrum of the $[PPN][H_3Ru_4(CO)_{12}]$ salt supported on Al_2O_3 reveals a slight shifting of the identical band pattern to lower frequencies ($\sim$4 cm^{-1} on the average) introduced by the PPN^+ cation. All three tetraruthenium species afforded identical ν(CO) band patterns and frequencies upon activation by heating under hydrogen (vide infra). At this point in our studies we attribute differences observed in the reactivity toward CO_2 hydrogenation to methane to PPN^+ and K^+ counterion deactivation effects.[26,27] For example, Okuhara and co-workers[27b] have

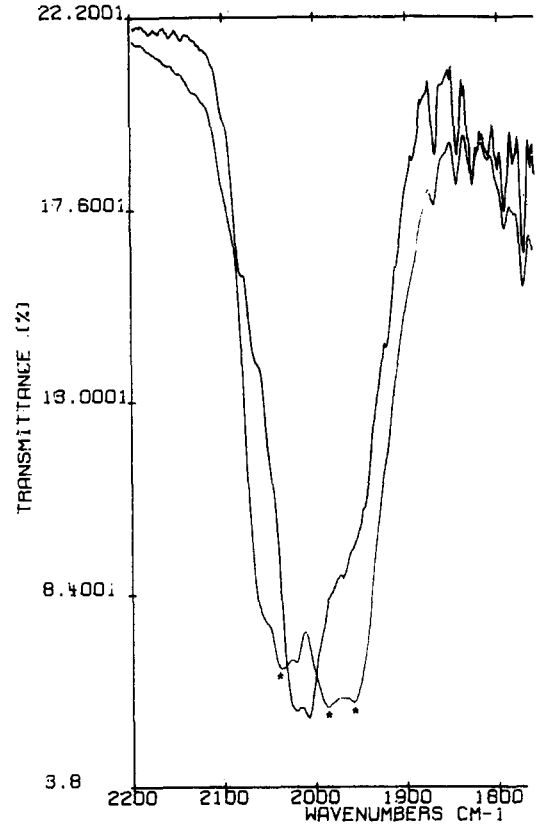


Figure 7. Diffuse internal reflectance infrared spectra of $Ru_3(CO)_{12}$ (dark trace) and $KHRu_3(CO)_{11}$ (light trace, peaks indicated with asterisks), both supported on Al_2O_3, prior to activation.

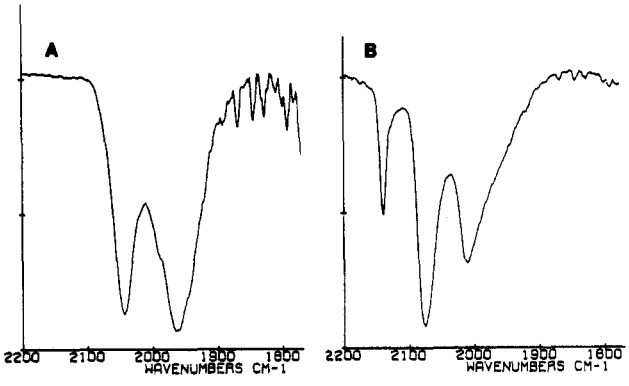
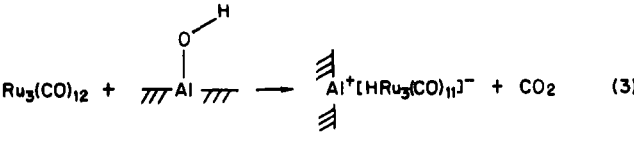


Figure 8. Diffuse internal reflectance infrared spectra: (A) $Ru_3(CO)_{12}$ on alumina (dehydroxylated at 150 °C in vacuo for 24 h) activated at 200 °C under H_2; (B) $RuCl_3$ on alumina (dehydroxylated at 150 °C in vacuo for 24 h) activated at 200 °C under H_2 followed by CO addition at ambient temperature and evacuation.

suggested in studies of CO hydrogenation catalyzed by supported ruthenium clusters that the addition of potassium reduces the activation of H_2.

Analogous considerations account for the differences observed in the catalyst systems involving triruthenium cluster derivatives. The case for the formation of $HRu_3(CO)_{11}^-$ from the reaction between alumina and $Ru_3(CO)_{12}$ (eq 3) seems rather clear



$$Ru_3(CO)_{12} + \text{(surface)} \rightarrow \text{(surface)}\ Al^+[HRu_3(CO)_{11}]^- + CO_2 \qquad (3)$$

(26) Most of the phosphorus present in the PPN^+ salt remains on the supported catalyst after activation. Elemental analysis of the activated catalyst derived from $[PPN][HRu_3(CO)_{11}]$ revealed 0.24% P (expected on the basis of preparation, 0.21%), whereas that derived from $[PPN][H_3Ru_4(CO)_{12}]$ had 0.094% P (calculated, 0.154%).

(27) (a) Okuhara, T.; Enomoto, T.; Tamura, H.; Misono, M. *Chem. Lett.* **1984**, 1491. (b) Okuhara, T.; Kobayashi, K.; Kimura, T.; Misono, M.; Yoneda, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 1114.

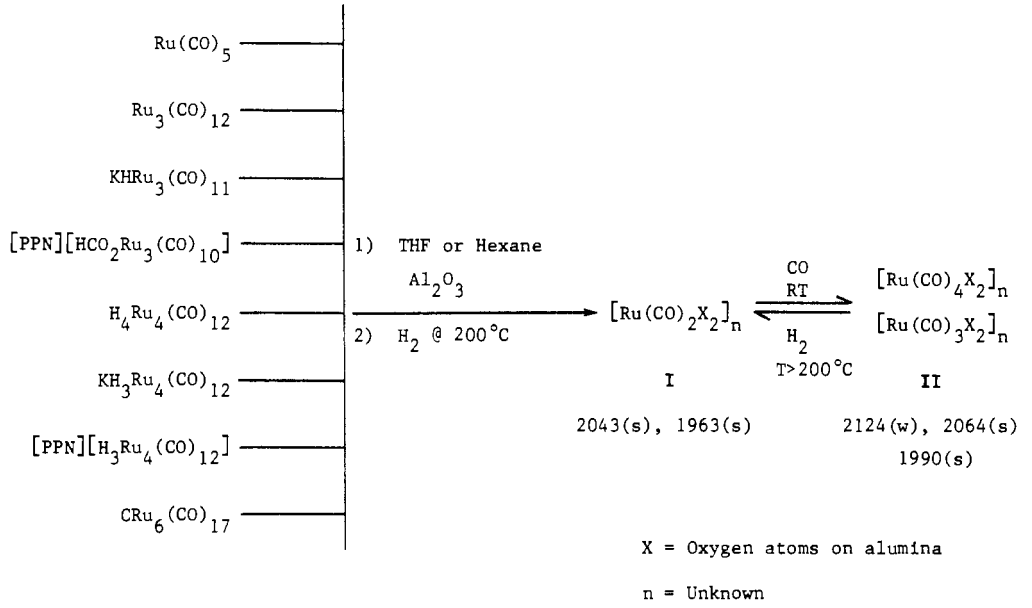


Figure 9. Species obtained for the activated-alumina-supported zero valent ruthenium catalyst precursors.

(Figures 6 and 7). However, unlike the case for the supported $H_4Ru_4(CO)_{12}/KH_3Ru_4(CO)_{12}$ catalysts, the initial ν(CO) infrared spectrum of $Ru_3(CO)_{12}/Al_2O_3$ is somewhat different from that of $KHRu_3(CO)_{11}$ supported on Al_2O_3 (Figure 7). On the basis of solution infrared spectral measurements on $KHRu_3(CO)_{11}$ we would not expect this dissimilarity to be due simply to contact-ion pairing between the cluster anion and potassium.[28,29] Hence, the nuclearity of the alumina-supported ruthenium clusters prior to catalyst activation is the same as the homogeneous precursors as shown herein and as shown previously by Bell and co-workers.[10] Our infrared spectral results on the nature of the initially supported $Ru(CO)_5$ species were inconclusive, although it was clear that trinuclear or tetranuclear species were not formed. It is assumed to remain mononuclear upon being supported as was shown for the $Fe(CO)_5$ analogue.[1h]

The diffuse-reflectance FTIR spectrum of the thermally activated $Ru_3(CO)_{12}/Al_2O$ catalyst is depicted in Figure 8A. Analogous infrared spectra for all the other alumina-supported ruthenium clusters employed in this study, as well as that of the $Ru(CO)_5$-derived catalyst, exhibit quite similar ν(CO) band patterns with only slight variation in frequencies (no more than 1 cm^{-1}). The observed infrared bands at 2043 (s) and 1963 (s) cm^{-1} are in agreement with those reported by Bell and co-workers[10] using wafered supported ruthenium clusters that were thermally activated in the manner similar to that reported herein.

A comparison of the bands found in the literature for other homogeneous and heterogeneous compounds is shown in Table II.[30] As can be seen in Figure 9, a general formulation of $[Ru(CO)_2X_2]_n$ (where X = oxygen atom on the alumina) can be proposed for all the activated-alumina-supported zerovalent ruthenium catalysts.[31] The value of n in the proposed surface-bound complex is unknown; that is, the extent to which the cluster aggregation occurs is not defined. In accordance with the results reported by Bell and co-workers,[10] the reaction of species I with CO gave species II, which exhibited a totally different behavior toward CO_2 methanation. When II is used as a catalyst, H_2O, CO, ethane, and methane are found in the reaction effluents during the first 0.5 h of the reaction. After the reaction reached stationary state at the desired temperature (approximately 1 h), only CH_4 and H_2O were detected and species I was regenerated. Hence, the *additional* CO adsorption sites that become evident upon exposure of species I to carbon monoxide exhibit hydrogenation behavior much like the CO sites in the catalyst derived from $RuCl_3$.

The ruthenium chloride derived supported catalyst evinced, after a brief exposure to carbon monoxide followed by evacuation, a ν(CO) infrared spectrum totally different from that observed for the activated supported metal cluster catalysts (Figure 8B). These infrared bands are consistent (see Table II) with the formulation depicted in Figure 10 for species III and IV. Hence, there appears to be a definite interaction between ruthenium and Cl^- in the $RuCl_3$-derived catalyst.[20,32] This would account for the lower

Table II. Selected ν(CO) Values for Homogeneous and Heterogeneous Ru Complexes

compd	ν(CO), cm^{-1}	ref
$[Ru(CO)_2Cl_2]_n$	2066 (s), 1988 (s)	30
$[Ru(CO)_2Br_2]_n$	2059 (s), 1990 (s)	30
$[Ru(CO)_2I_2]_n$	2053 (s), 1995 (s)	30
$[Ru(CO)_2(SPh_2)_2]_n$	2105 (w), 2042 (s), 1985 (s), 1945	30
$[Ru(CO)_2X_2]_n/Al_2O_3$	2045–2050 (s), 1965–1970 (s)	10
cluster-derived catalyst[a]	2043–2044 (s), 1962–1964 (s)	this work
$Ru_2(CO)_6Cl_4$	2143 (s), 2075 (s), 2015 (m)	30
$Ru_3(CO)_{12}Cl_6$	2138 (m), 2068 (s), 2007 (m)	30
$RuCl_3$-derived catalyst[b]	2140 (m), 2075 (s), 2013 (m)	this work

[a] Activated under hydrogen at 200 °C overnight. [b] Exposed to 1 atm of CO at room temperature.

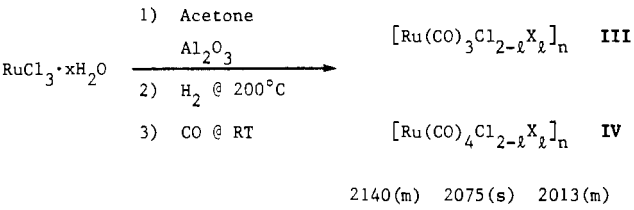


Figure 10. Species obtained for the activated-alumina-supported $RuCl_3$ catalyst after addition of CO.

The temperature at which $RuCl_3$ decomposes is about 500 °C.[20] The catalyst used in this study was heated at 200 °C.

(28) Schick, K. P.; Jones, N. L.; Sekula, P.; Boag, N. M.; Labinger, J. A.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 2204.
(29) Darensbourg, M. Y. *Prog. Inrog. Chem.* **1985**, *33*, 221.
(30) Johnson, B. F.; Johnston, R. D.; Josty, P. L.; Lewis, J.; Williams, G. *Nature (London)* **1967**, *213*, 901.
(31) EXAFS studies of the surface structure of $Ru_3(CO)_{12}/\gamma$-Al_2O indicated the presence of monoatomically dispersed ruthenium atoms. No Ru–Ru interaction was found in the region 2–4 Å with the coordination sphere around ruthenium containing two CO ligands and two supporting oxygen atoms with a Ru–O distance of 2.17 Å. The two ν(CO) absorptions were reported, however, at significantly higher frequencies than for species I, i.e., at 2080 and 2030 cm^{-1} (Asakura, K.; Yamada, M.; Iwasawa, Y.; Kuroda, H. *Chem. Lett.* **1985**, 511).

Table III. Carbonyl Frequencies for Ruthenium Catalysts

catalyst[a]	ν(CO), cm^{-1}
$Ru_3(CO)_{12}/Al_2O_3$	2043 (s), 1963 (s)
$Ru_3(^{13}CO)_{12}/Al_2O_3$	1993 (s), 1923 (s)
$RuCl_3/Al_2O_3$[b]	2140 (m), 2075 (s), 2013 (m)
$RuCl_3/Al_2O_3$[c]	2089 (m), 2028 (s), 1968 (m)

[a] Activated under hydrogen at 200 °C overnight. [b] Exposed to 1 atm of CO at room temperature. [c] Exposed to 1 atm of ^{13}CO at room temperature.

catalytic activity for CO_2 hydrogenation observed for this catalyst as is proposed for other systems in which chloride acts as a poison.[2,33,34] In addition, species III and IV were found to give higher molecular weight products during the methanation of carbon dioxide, a fact consistent with ruthenium acting as a Fischer–Tropsch catalyst.[25]

The alumina-supported ^{13}C-labeled ruthenium carbonyl species were prepared and activated from $Ru_3(^{13}CO)_{12}$ or $RuCl_3$ followed by the introduction of ^{13}CO. The infrared bands for these ^{13}CO surface species display the expected frequency shifts to lower energies and are tabulated in Table III. The carbon dioxide methanation reactions carried out with these ^{13}CO-labeled catalysts showed quite interesting results. When $Ru_3(^{13}CO)_{12}$ was employed as the catalyst precursor, only $^{12}CH_4$ (3017 cm^{-1}, ν(CH)) was found in the reaction effluents. No trace of $^{13}CH_4$ or ^{13}CO was detected by GC-FTIR at any stage of the reaction. Furthermore, the infrared spectrum of the catalyst after methanation was terminated showed the presence of the ^{13}CO-labeled catalyst with only a small quantity of bound ^{12}CO (presumably resulting from the water-gas shift reaction). The results indicate that the ruthenium carbonyl sites as defined in species I are not involved in the CO_2 methanation reaction and, further, that the CO sites in species I do not undergo exchange with the added CO sites exhibited in species II.

In addition, ruthenium cluster catalysts were able to produce CH_4 using H_2 as the carrier gas at a temperature <200 °C after more than 2 h of continuous CO_2 methanation followed by flushing with hydrogen at ambient temperature for 20 min. Therefore, a species carbonaceous in character is believed to be chemisorbed on the catalysts and to be responsible for the methane production. Water was detected as well, indicating that some oxygenated species were also present on the catalysts after the CO_2 methanation reactions.

By way of contrast, with use of a catalyst derived from the reaction of alumina-supported $RuCl_3$ and ^{13}CO, $^{13}CH_4$ (3009 cm^{-1}, ν(CH)) as well as ^{13}CO were produced in the early stages of the reaction.[35] This same product distribution was obtained when an activated $Ru_3(CO)_{12}/Al_2O_3$ catalyst was pretreated with ^{13}CO prior to exposure to CO_2/H_2 at 200 °C. These results confirm previous observations regarding the activity of ruthenium as a carbon monoxide hydrogenation catalyst and are consistent with the $Ru_3(^{13}CO)_{12}$-derived catalytic results described above. It is important to reiterate here that this pretreatment of the $Ru_3(CO)_{12}/Al_2O_3$ catalyst with ^{13}C does not effect facile carbonyl ligand exchange between the existing Ru–^{12}CO species and the incoming ^{13}CO ligand.

Summary

These investigations have demonstrated that ruthenium clusters, supported on partially dehydroxylated alumina and activated in hydrogen at 200 °C, are very effective catalysts for the selective production of methane from carbon dioxide and hydrogen. In general, these cluster-derived catalysts were more active than the analogously prepared catalyst obtained from $RuCl_3$. There was some attenuation of this enhanced activity exhibited by cluster-derived catalysts with increasing reaction temperature (Table I). The activity of these supported neutral species was observed to increase as the number of ruthenium atoms present in the precursor complex increased; i.e., $Ru(CO)_5 < Ru_3(CO)_{12} < H_4Ru_4(CO)_{12} < Ru_6C(CO)_{17}$. Catalysts derived from supported anionic ruthenium cluster derivatives were less active than their neutral counterparts, displaying a great deal of sensitivity to the nature of the accompanying cation.[36]

The diffuse-reflectance FTIR spectra of all the supported, activated catalysts originating from low-valent ruthenium derivatives exhibit the same band pattern in the ν(CO) stretching region. In addition to these strongly absorbed CO species (I) there are other ruthenium sites in these activated catalysts for less effective binding of CO; i.e., the CO groups are more easily removed and possess a higher average value of ν(CO). It has been shown with the aid of ^{13}C-labeled CO that it is these sites (II), and not the strongly bonded CO sites (I), that are involved in the catalytic hydrogenation of the oxides of carbon. Differences in the reactivity of these various low-valent, organometallic ruthenium complexes are attributed to differences in the dispersion of the metal and/or counterions. Concomitantly, the metal dispersion should be related to the extent of aggregation of the surface-bound complex. The smaller crystallite size and concomitant better metal dispersion throughout the catalyst surface has been suggested by others in their studies of supported metal cluster catalysis.[3,25,37,38]

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated. The GC/IR interface equipment was purchased with a grant from the Texas A&M University Center for Energy and Mineral Resources. Special thanks are due to Dr. R. G. Anthony and Dr. Ben Zu Wan for their help with the oxygen titration experiments.

Registry No. $RuCl_3$, 10049-08-8; $Ru(CO)_5$, 16406-48-7; $Ru_3(CO)_{12}$, 15243-33-1; $KHRu_3(CO)_{11}$, 80662-65-3; $[PPN][HCO_2Ru_3(CO)_{10}]$, 86528-72-5; $H_4Ru_4(CO)_{12}$, 34438-91-0; $KH_3Ru_4(CO)_{12}$, 67269-70-9; $[PPN][H_3Ru_4(CO)_{12}]$, 70073-19-7; $Ru_6C(CO)_{17}$, 27475-39-4; CO_2, 124-38-9; H_2, 1333-74-0; O_2, 7782-44-7.

Supplementary Material Available: Tables of data points for the information provided graphically in Figure 3 and of percent metal dispersion as determined by oxygen chemisorption, along with the graphical representation of one such measurement for the catalyst derived from $Ru(CO)_5$ (3 pages). Ordering information is given on any current masthead page.

(33) Somorjai, G. A. *Chemistry on Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981; p 397.
(34) In this connection we have recently observed that $Ru(NO)(NO_3)_3$ supported on alumina and activated at 200 °C in hydrogen is a much more active catalyst for CO_2 methanation than supported $RuCl_3$ treated similarly, displaying an activity approaching that of $Ru_3(CO)_{12}$.
(35) These reactions were carried out under nonisothermal conditions (see Experimental Section) with a rate of heating at 23 °C/min. The first appearance of methane (labeled or unlabeled) was observed at ~140 °C for the $RuCl_3/Al_2O_3$ catalyst and at ~130 °C for the cluster-derived catalyst.
(36) The rates of methanation of carbon monoxide for silica-supported catalysts derived from $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ have been found to be quite similar and much higher than the corresponding rates for catalysts derived from anionic ruthenium carbonyl derivatives: Kaesz, H. D., personal communication. Mafrana, B. A. Ph.D. Dissertation, Department of Chemistry, University of California at Los Angeles, 1982.
(37) Commereuic, D.; Chavin, Y.; Hugues, F.; Basset, J. M.; Obier, D. *J. Chem. Soc., Chem. Commun.* **1980**, 154.
(38) Brenner, A. *J. Chem. Soc., Chem. Commun.* **1979**, 251.