

THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

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SUMMARY

The objective of this research is to elucidate the role of additives on the methanol synthesis over Rh- and Ni-based catalysts. Chemical additives used for this study will include S, P, Ag, Cu, Mn, and Na which have different electronegativities. The effect of additives on the surface state of the catalysts, heat of adsorption of reactant molecules, reaction intermediates, reaction pathways, reaction kinetics, and product distributions is/will be investigated by a series of experimental studies of NO adsorption, reaction probing, steady state rate measurement, and transient kinetic study.

A better understanding of the role of additive on the synthesis reaction may allow us to use chemical additives to manipulate the catalytic properties of Rh- and Ni-based catalysts for producing high yields of ethanol from syngas.

RESULT TO DATE

During the fourth quarter of 1990, the activity of silica-supported $\text{Rh}^+(\text{CO})_2$ catalysts for the CO insertion has been studied by in situ infrared spectroscopy.

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INTRODUCTION

The nature of $\text{Rh}^+(\text{CO})_2$, rhodium gem-dicarbonyl, on the supported Rh catalyst has been extensively studied for more than three decades. Spectroscopic studies of the adsorption of CO on the supported Rh have demonstrated that the gem-dicarbonyl species exhibiting bands in the range of 2116-2090 cm^{-1} and 2048-2022 cm^{-1} are associated with an isolated Rh^+ ion. Generation of $\text{Rh}^+(\text{CO})_2$ on the oxide support can be achieved by (i) adsorption of CO on the oxidized or partially reduced Rh, (ii) exposure of the supported Rh carbonyls to air, and (iii) the reaction of the supported Rh salts such as chlorides and nitrates with CO and H_2O . Most studies on $\text{Rh}^+(\text{CO})_2$ have been confined to the vibrational spectroscopy of the gem-dicarbonyls and characterization of the state of rhodium that associated with the gem-dicarbonyl. Little work has been done on the activity of oxide-supported $\text{Rh}^+(\text{CO})_2$ for catalytic reactions.

In order to gain a better understanding of the catalytic properties of oxide-supported $\text{Rh}^+(\text{CO})_2$, we have examined the reactivity of $\text{Rh}^+(\text{CO})_2/\text{SiO}_2$ with C_2H_4 and H_2 and its activity for catalytic hydroformylation ranging from the condition in which $\text{Rh}^+(\text{CO})_2$ can stay intact to that in which $\text{Rh}^+(\text{CO})_2$ can be decomposed into Rh metal. Hydroformylation was selected as a model reaction for this study because the reaction can be catalyzed by the homogeneous Rh carbonyls, supported Rh carbonyls, and supported Rh metal. An *in situ* infrared method was employed to monitor the change in concentration of $\text{Rh}^+(\text{CO})_2$ and the adsorbed species during the entire course of reaction studies. Gas

chromatography was utilized to determine the product distribution of the reaction.

EXPERIMENTAL

Supported rhodium chloride and nitrate samples were prepared by impregnation of silica (large pore, Strem Chemicals) using aqueous solution of $\text{RhCl}_3 \cdot \text{XH}_2\text{O}$ and $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ (Alfa), respectively. The samples were dried in air at 313 K and then were pressed into self-supporting disks (10 mm. in diameter, 1 mm in thickness, and 25 mg). The disk was placed in an infrared cell which is made of stainless steel and two CaF_2 step windows. The pathlength for the infrared beam in the cell is slightly less than 2 mm and the net reactor volume is 0.2 cm^3 .

$\text{Rh}^+(\text{CO})_2/\text{SiO}_2$ was prepared at 298 K by carbonylation of $\text{RhCl}_3 \cdot \text{XH}_2\text{O}$ and $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ with CO according to the following reaction: $\text{Rh}^{3+} + 3 \text{CO} + \text{H}_2\text{O} \rightarrow \text{Rh}^+(\text{CO})_2 + 2 \text{H}^+ + \text{CO}_2$

The formation of $\text{Rh}^+(\text{CO})_2$ as a function of time and CO pressure was monitored by infrared spectroscopy. Carbonylation led to change in the apparent color of the $\text{RhCl}_3/\text{SiO}_2$ sample from pink to pale orange and the apparent color of $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ from pale yellow to pale orange. The sample was then outgassed for 30 min at 298 K in flowing He to remove gaseous CO.

The reaction of $\text{Rh}^+(\text{CO})_2/\text{SiO}_2$ with C_2H_4 and H_2 was performed by exposure of the catalyst sample to C_2H_4 and H_2 in a closed system where the IR cell was used as a batch reactor. Steady-state ethylene hydroformylation ($\text{CO}:\text{H}_2:\text{C}_2\text{H}_4=1:1:1$) was carried out in the same IR cell under various temperatures and

pressures. H_2 (UHP, 99.999%), CO (CP, 99.0%), He (UHP, 99.999%), C_2H_4 (CP, 99.5%) were purified by passing through a trap of liquid nitrogen before use. The reaction products were analyzed by by a HP-5890A gas chromatograph. IR spectra were recorded by a Nicolet 5SXC Fouier transform infrared spectrometer at a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Figure 1 shows the spectral development for $\text{Rh}^+(\text{CO})_2$ following exposure of $\text{RhCl}_3/\text{SiO}_2$ to 1 MPa CO at 298 K. High CO pressure is used to facilitate the carbonylation of $\text{RhCl}_3/\text{SiO}_2$ to $\text{Rh}^+(\text{CO})_2/\text{SiO}_2$. The spectra taken at 0.1 MPa and 298 K following exposure of 1 MPa CO exhibits bands at 2172, 2158, 2108, 2077 and 2041 cm^{-1} . These bands are results of overlapping with gaseous CO . Passing a He flow over the catalyst removed gaseous CO and resulted in emergence of the bands at 2146, 2105, and 2041 cm^{-1} . These IR bands closely matched those produced form exposure of $\text{RhCl}_3/\text{SiO}_2$ to 0.1 MPa CO at 323 K for 1 hr. The bands at 2105 and 2041 cm^{-1} have been assigned to gem-dicarbonyls based on the analogy with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. Comparative studies of infrared spectra of $[\text{Rh}(\text{CO})_2\text{Cl}]_2/\text{SiO}_2$ and CO adsorbed on the $\text{RhCl}_3/\text{SiO}_2$ suggested that carbonlyation of $\text{RhCl}_3/\text{SiO}_2$ by CO adsorption resulted in the formation of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ that physiorbed on SiO_2 . The highest frequency band at 2146 cm^{-1} has been attributed to the linear CO on Rh^{+3} ; the intensity of the band appears to depend upon details of treatment.

Analogous experiments involving the formation of $\text{Rh}^+(\text{CO})_2$ were performed on $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$. Figure 2 shows the spectra for $\text{Rh}^+(\text{CO})_2$ following the adsorption of CO on $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$. The behavior of CO adsorption and $\text{Rh}^+(\text{CO})_2$ formation on the $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ is similar to that observed for the $\text{RhCl}_3/\text{SiO}_2$ in Figure 1. The Rh gem-dicarbonyl on the $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ showed peaks at 2091 and 2033 cm^{-1} . The shoulder at 2106 cm^{-1} has been suggested to arise from vibrational coupling between the carbonyl bands across the Rh-Rh bond of the dimer. By analogy with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ on $\text{RhCl}_3/\text{SiO}_2$ and oxybridged dimers like $[\text{Rh}(\text{CO})_2\text{OSiPh}_3]_2$, the Rh gem-dicarbonyl on the $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ has been proposed in the form of $[\text{Rh}(\text{CO})_2\text{O}_s]_2$, where O_s is a surface oxide. The slight difference in the wavenumber of the gem-dicarbonyl on RhCl_3 and $\text{Rh}(\text{NO}_3)_3$ appears to be due to the use of different precursors. Keyes and Watters reported that $\text{Rh}^+(\text{CO})_2/\text{SiO}_2$ prepared from $\text{RhCl}_3/\text{SiO}_2$ at 323 K and 600 Torr CO displayed higher wavenumber bands than those prepared from $\text{Rh}(\text{NO}_3)_3$.

The infrared spectra taken during temperature programmed decomposition of $\text{Rh}^+(\text{CO})_2$ on $\text{RhCl}_3/\text{SiO}_2$ and $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ are shown in Figure 3 and 4, respectively. There was no shift in the wavenumber of the bands at 2099 and 2034 cm^{-1} during the decomposition. A growth in the peak for carbon dioxide at the vicinity of 2350 cm^{-1} occurred with increasing temperature. The formation of CO_2 in the decomposition of the $\text{Rh}^+(\text{CO})_2$ was also confirmed by the analysis of the effluent of the IR cell. Our

recent study has also shown that CO_2 is the major product in temperature programmed desorption/decomposition of $\text{Rh}^+(\text{CO})_2$ on the oxidized Rh/SiO_2 catalyst. The CO associated with the gem-dicarbonyl on $\text{RhCl}_3/\text{SiO}_2$ desorbed completely at 473 K while the CO for the gem-dicarbonyl on the $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ persisted even at temperature above 513 K and no shift in their wavenumber was observed. Higher decomposition temperature for the $\text{Rh}^+(\text{CO})_2$ on the $\text{Rh}(\text{NO}_3)_3$ compared with those for the RhCl_3 indicates that the $\text{Rh}^+(\text{CO})_2$ prepared from $\text{Rh}(\text{NO}_3)_3$ is more strongly bonded to the catalyst surface than that prepared from RhCl_3 . Keyes and Watters have shown that $\text{Rh}^+(\text{CO})_2$ prepared from the carbonylation of RhCl_3 is in the form of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ that physisorbs on the surface of the $\text{RhCl}_3/\text{SiO}_2$; the species can readily be extracted from the surface by pentane. In contrast, the $\text{Rh}^+(\text{CO})_2$ prepared from the $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ may directly interact with the surface oxide present on the $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ to form silanato bridge complexes which cannot be easily removed from the surface.

The absence of a shift in the wave number of the $\text{Rh}^+(\text{CO})_2$ during the TPD reflects the lack of interaction such as dipole-dipole coupling between the CO. The observed invariance of the wavenumbers of the $\text{Rh}^+(\text{CO})_2$ with their intensities (concentration) is consistent with those reported for rhodium gem-dicarbonyl. It has led to the conclusion that the binding site for the gem-dicarbonyl is an isolated or an edge Rh atom.

In order to clarify the role of the $\text{Rh}^+(\text{CO})_2$ species in hydroformylation, the gem-dicarbonyls produced from both $\text{RhCl}_3/\text{SiO}_2$ and $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ were exposed to a 1:1 mixture of C_2H_4

and H_2 . Figure 5 shows the IR spectra for the reaction of $\text{Rh}^+(\text{CO})_2/\text{SiO}_2$ (prepared from $\text{RhCl}_3/\text{SiO}_2$) with C_2H_4 and H_2 at 298 K and 0.1 MPa. The initial spectrum prior to the admission of C_2H_4 and H_2 to the IR cell exhibited the band for CO adsorbed on Rh (III) at 2146 cm^{-1} and the gem-dicarbonyl bands at 2105 and 2041 cm^{-1} for symmetric and asymmetric C-O stretching. It is important to note that the high frequency (2104 cm^{-1}) band of gem-dicarbonyl is significantly more intense than that for the low frequency (2039 cm^{-1}) band. Repeated runs on carbonylation of the $\text{RhCl}_3/\text{SiO}_2$ showed that the intensity of the high frequency band is dependent on the condition of pretreatment. One possible interpretation for the high intensity ratio of the symmetric to the asymmetric band is the presence of an additional adsorbed CO that exhibit the IR band overlapping with the symmetric band.

Exposure of $\text{Rh}^+(\text{CO})_2/\text{SiO}_2$ to 0.1 MPa $\text{C}_2\text{H}_4/\text{H}_2$ mixture at 298 K led to a rapid decrease in the intensity of the band at 2105 cm^{-1} , a gradual decrease in the intensity of the band at 2041 cm^{-1} , and a slow increase in the intensity of propionaldehyde band at 1722 cm^{-1} at the first 5 min of the reaction. Both C_2H_4 and H_2 did not cause any shift in the wave number of the band at 2041; however, they shifted the band at 2105 slightly downward. The difference in rate of intensity change for the bands at 2105 and 2041 cm^{-1} suggested that the band at 2105 cm^{-1} is due to combination of the band for the symmetric stretching of $\text{Rh}^+(\text{CO})_2$ with a band displayed by a highly reactive CO species. CO adsorption on positive metal ions have been known to give rise to bands at higher frequency than CO on zerovalent metal atoms. Ichikawa et

al. have suggested from their studies on sulfided Rh/SiO₂ that the highly intense band at 2090 cm⁻¹ on the rhodium is due to the combination of linear CO adsorbed on positive rhodium ions and the symmetrical vibration of the gem-dicarbonyl. They observed that the intensity of the high frequency band increases with increasing coverage of sulfur on the Rh/SiO₂ suggesting that the electronegative sulfur atoms leave adjacent Rh atoms with a net positive charge. Rice et. al. have also assigned the band at 2080 - 2010 cm⁻¹ on the oxidized Rh/Al₂O₃ to the linear CO adsorbed on the Rh⁺. Therefore, it is possible in our study that a linear CO is present on the Rh⁺ which rapidly reacted with the C₂H₄/H₂ to form propionaldehyde.

A slow decrease in the intensity of both symmetric and asymmetric bands for Rh⁺(CO)₂ accompanied by a slow growth of propionaldehyde band after the first 5 min of reaction suggests that CO in the Rh gem-dicarbonyl may involve in CO insertion to produce propionaldehyde; however, it appears to be less reactive than the linear CO on the Rh(I).

The adsorbed CO on Rh(III) exhibited the band at 2146 cm⁻¹ which changed slightly during the entire course of reaction. The species appears to be a spectator species which was not involved in the reaction. Other bands at the 1400-1500 cm⁻¹ and 1800-1900 cm⁻¹ range can be ascribed to the adsorbed C₂H₄; bands at 2900-3500 cm⁻¹ are assigned to adsorbed hydrocarbons which are produced from ethylene hydrogenolysis and hydrogenation. It is important to note that RhCl₃ is active for ethylene hydrogenolysis and hydrogenation. The presence of the hydrogenation product

suggests that a part of the RhCl_3 which did not form $\text{Rh}^+(\text{CO})_2$ could be responsible for the ethylene hydrogenation.

Fig. 6 shows the IR spectra for the reaction of C_2H_4 and H_2 with $\text{Rh}^+(\text{CO})_2$ prepared from $\text{Rh}(\text{NO}_3)_3/\text{SiO}_2$ at 298 K. The initial spectrum prior to the onset of the reaction consisted of the bands at 2106, 2092 and 2033 cm^{-1} . The intensity of the bands at 2093 and 2034 cm^{-1} showed a initial decrease and remained constant with reaction time while the intensity of propionaldehyde band at 1722 cm^{-1} increased slowly with reaction time. Comparison of the rate of the decrease in the intensity of the CO bands in Figure 5 and 6 revealed that the $\text{Rh}^+(\text{CO})_2$ prepared from $\text{Rh}(\text{NO}_3)_3$ is less reactive with $\text{C}_2\text{H}_4/\text{H}_2$ than those prepared from $\text{RhCl}_3/\text{SiO}_2$ at 298 K and 0.1 MPa. The reactivity of $\text{Rh}^+(\text{CO})_2$ generally depends on its chemical environment. $\text{Rh}^+(\text{CO})_2$ formed on the Rh-zeolite Y has been shown to exhibit little activity for the reaction with $\text{C}_2\text{H}_4/\text{H}_2$ to produce propionaldehyde. Other studies on the reaction of $\text{Rh}^+(\text{CO})_2$ with CH_3I have also demonstrated that CO insertion can occur on $\text{RhCl}_3/\text{SiO}_2$, but did not take place on the RhCl_3/MgO .

CONCLUSIONS

The linear CO that adsorbes possibly on the Rh(I) has been demonstrated to be most active CO for the insertion into adsorbed ethylene species to produce propionaldehyde. The results clearly shows the important role of linear CO and Rh^+ for the CO insertion that is the key step for the formation of higher alcohols in CO hydrogenation.

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