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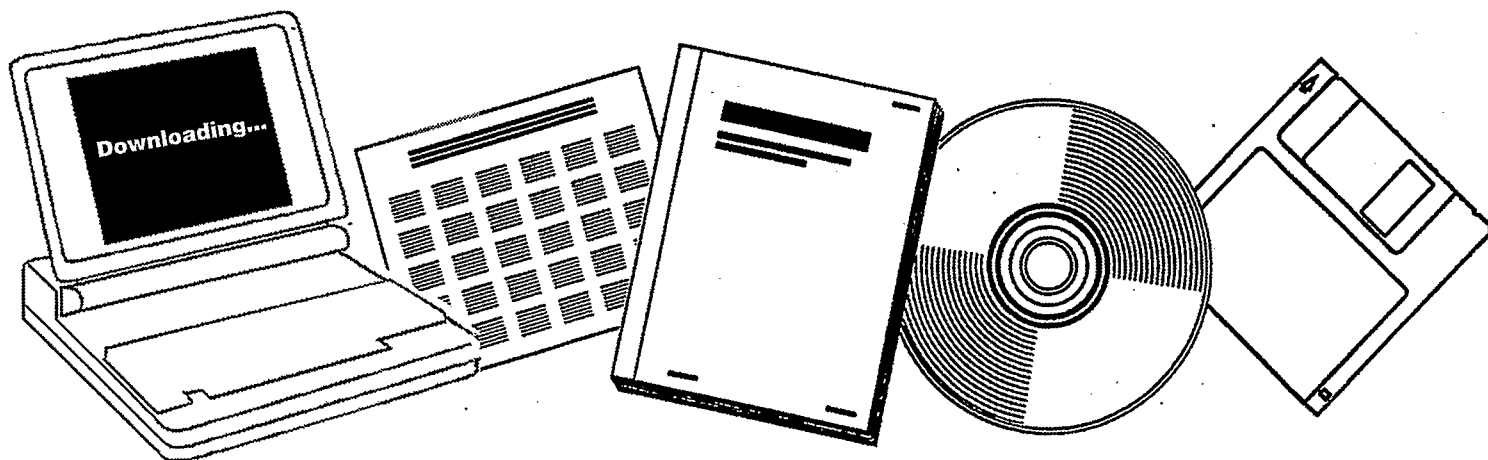
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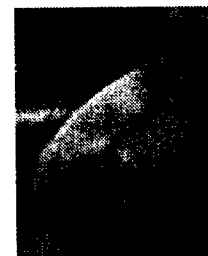
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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

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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 additives 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.

RESULTS TO DATE

During the second quarter of 1991, the nature of active site for CO insertion was investigated by in situ infrared spectroscopic technique. The study found that the Rh^+ is more active than Rh^0 for the CO insertion leading to the formation of higher aldehydes and alcohols.

DISCLAIMER

INTRODUCTION

The insertion of carbon monoxide (CO) into a metal-carbon σ bond is one of the most widely studied reaction in organometallic chemistry [1]. The interest in CO insertion stems from the fact that the reaction provides a pathway for the conversion of olefins or other substrates to high added value chemicals [1,2]. Homogeneous hydroformylation processes have been the largest industrial application of the CO insertion chemistry for more than three decades [3-5]. Although Rh carbonyl complexes are the most active hydroformylation catalysts, mechanistic information about CO insertion has commonly been obtained using metals such as Mn, Ir, or Pt which form unreactive and stable acyl complexes [2]. The use of these organometallic complexes allows close observation of how the migratory CO insertion occurs. Infrared study of the ^{13}CO insertion on the alkyl(pentacarbonyl)manganese has provided direct evidence for the mirgratory insertion of CO into a carbon-metal bond [6]. The rate of the CO insertion on the methyl- (pentacarbonyl)manganese can be further accelerated by the action of a Lewis acid [7].

. It has been suggested that the migratory CO insertion plays a key role in the Fischer-Tropsch (F-T) synthesis [8,9]. Pichler and Schulz first used CO insertion as a model for rationalization of chain growth in the F-T catalysis on surfaces [8]. However, most studies over the past decades have shown that CO insertion is not the major pathway for the chain propagation of adsorbed alkyl [10-15]. The CO insertion step was found to be the chain

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termination step leading to the formation of aldehydes and alcohols [14-21].

While it has been well established that CO insertion occurs via the migration of an alkyl group to a Rh^+-coordinated CO in homogeneous catalysis, much controversy exists concerning active sites for CO insertion in the CO hydrogenation reaction (F-T synthesis). Watson and Somorjai proposed that CO insertion to form C_2^+ oxygenates occurs on Rh^+ sites while CO dissociation take places on Rh^o sites [16,17]. The postulate has been further supported by a number of studies [18-20,22-24]. On the contrary, Katzer et. al. reported from an XPS study that there was no evidence for the existence of Rh^+ on Rh/TiO_2 which was active for the synthesis of C_2 oxygenates [25]. Gysling et. al also found no correlation of C_2^+ oxygenate activity to the amount of Rh^+ present on the $LaRhO_3$ catalyst [26]. They concluded that CO insertion took place on Rh^o rather than any Rh^+ species.

The present study was aimed at identification of the type of adsorbed CO species which participates in the CO insertion step in ethylene hydroformylation. The Rh catalyst system chosen for this study comprises three different forms of Rh: reduced Rh, oxidized Rh, and sulfided Rh. The types of CO adsorbed on these Rh surface are closely related to the surface state of Rh [27-33]. Infrared data for these Rh catalysts under various reaction conditions were obtained to determine the type of adsorbed CO for CO insertion and to shed light on the nature of active sites.

Experimental

Experiments including CO adsorption, $C_2H_4/H_2/CO_{(ads)}$ reaction, and ethylene hydroformylation reaction in this study was carried out in an IR cell. The IR cell consists of four stainless-steel flanges, a gas inlet and outlet, and two step CaF_2 windows as shown in Figure 1. The step windows were used to minimize the reactor volume and to reduce the optical path length between the windows in order to lower the intensity of gas phase species. Infrared spectra were measured by a Nicolet 5XSC FTIR spectrometer with a DTGS detector at a resolution of 4 cm^{-1}.

A 3 wt% Rh sample was prepared by impregnation of SiO_2 (Strem Chemicals, #14-7420, SA: 350 m^2/g) with an aqueous solution of $Rh(NO_3)_3 \cdot 2H_2O$ (Johnson Matthey Chemicals). After impregnation, the sample was dried overnight in air at 301 K and then reduced in flowing hydrogen at 673 K for 16 hr. The reduced Rh/SiO_2 sample was pressed into a self-supported disk (20 mg, 10 mm in diameter, and 1 mm in thickness) and then placed in the IR cell.

The catalyst disk in the IR cell was subject to further one of three treatments, reduction, oxidation, and sulfidation, prior to the experiment. The catalyst disk reduced in H_2 flow at 513 K for 1 hr is designated as the reduced Rh/SiO_2 catalyst; the catalyst disk oxidized in flowing air at 513 K for 1 hr is denoted as the oxidized Rh/SiO_2 catalyst; and the catalyst disk sulfided in H_2S flow (1000 ppm H_2S in H_2) at 513 K for 1 hr is designated as the sulfided Rh/SiO_2 catalyst. It should be noted that the reduction processes did not completely reduce the Rh surface. XPS studies of the same catalyst sample after reduction

at 513 °C shows that the catalyst surface contains approximately 60% of Rh^0 and 40% of Rh^+.

CO adsorption was conducted by exposing the reduced, oxidized, and sulfided catalysts to 1-10 atm CO at 301 K. The infrared spectra of adsorbed CO were recorded as a function of exposure time at 1 atm. Following CO adsorption, N_2 was passed over the catalyst to remove the gaseous CO.

The reactivity of the adsorbed CO was investigated by introducing C_2H_4/H_2 ($C_2H_4:H_2$ molar ratio= 1:1) to the IR cell which served as a batch reactor. The reaction of C_2H_4/H_2 with the preadsorbed CO occurred at 301 K with pressure maintained slightly above 1 atm. The infrared spectra of adsorbed CO and reaction intermediates during the reaction was measured as a function of reaction time.

Steady-state ethylene hydroformylation over the reduced, oxidized, and sulfided Rh/SiO_2 catalysts was carried out at 373-513 K and 1-10 atm. Infrared spectra were recorded as a function of time on stream under the reaction conditions. The effluent of the IR cell was sampled after 40 min at each reaction condition and was analyzed by an on-line HP-5890A gas chromatography with a Porapak PS column and a Porapak QS column.

Results and discussion

CO Adsorption

Figure 2 shows the infrared spectra of CO adsorption on the reduced Rh/SiO_2 at 301 K. Two intensive bands at 2073 and 1898 cm^{-1} are assigned to the linear and bridged CO adsorbed on the reduced Rh crystallite surface, respectively. The small band at

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2104 cm^{-1} and the shoulder at 2037 cm^{-1} are attributed to the symmetrical and asymmetrical C-O stretching of $Rh^+(CO)_2$, the rhodium gem-dicarbonyl. Assignments of these adsorbed CO species are well documented [27-33].

Both linear and bridged CO are the predominant species of which intensity and wavenumber remained about the same with respect to exposure time and variation of CO pressure from 1 to 10 atm. In contrast, the dicarbonyl slowly increased in its intensity without changing its wavenumber as exposure time and CO pressure increased.

The slow development of gem-dicarbonyl may be attributed to the disruption of Rh cluster and the formation of isolated Rh^+ sites. Solymosi and Pasztor [34] proposed the similar effect of CO-induced disruption on different Rh crystallites sizes and reported that the disruption took place to a small extent at higher metal loading or with larger Rh crystallites. EXAFS studies of Rh/Al_2O_3 by Prins et. al. [35] supported the disruption of Rh crystallites via CO adsorption.

Passing N_2 over the catalyst caused a reduction in the intensities of all the three adsorbed CO. The reduction in linear CO and bridged CO led to a downward shift of their wavenumbers. However, the intensity of the dicarbonyl decreased without changing it wavenumber. Coverage-dependent wavenumber shifts are well known for both linear CO and bridged CO and have been attributed to the variation of dipole-dipole coupling with concentration of the linear and bridge CO species [36,37]. The independence of the wavenumber of the gem-dicarbonyl on changing the coverage provides confirmation that dicarbonyl is formed on

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isolated Rh atoms [27,28,30].

Figure 3 shows the infrared spectra of CO adsorption on the oxidized Rh/SiO$_2$ at 301 K. Adsorption of CO on the oxidized catalyst initially formed dicarbonyl (at 2098 and 2025 cm^{-1}) at 1 atm. It is agreed with the fact that dicarbonyl is formed preferentially on oxidized Rh catalysts [27,29,32]. The intensity of the dicarbonyl increased with exposure time and with the pressure of CO. Marked changes in the spectra of adsorbed CO were observed after high-pressure treatment by increasing CO pressure form 1 atm to 10 atm and then decreasing the pressure back to 1 atm. The high-pressure treatment not only increased the intensities of the dicarbonyl but also developed three bands at 2105, 2079, and 1880 cm^{-1}. The intensive band at 2079 cm^{-1} is due to the linear-CO and the 1880-cm^{-1} band is characteristic of the bridged CO. The development of the linear CO and the bridged CO indicates that reduction of the catalyst may occurred at high pressure of CO.

The high-wavenumber band at 2105 cm^{-1} may be assigned to an adsorbed CO on Rh with higher oxidation state [31]. Yang et. al. [27] performed several oxidation experiments on CO adsorption, and found that upon oxidation the liner CO shifted to a higher wavenumber. Study by Gonzalez et. al. showed that exposure of a Rh/SiO$_2$ catalyst to a mixture of CO and O$_2$ gave rise to a band at 2104 cm^{-1} which was assigned to an adsorbed CO on Rh with at least +1 and possibly as high as +3 [39]. Wang and Yates [39] found that tricarbonyl species is formed on oxidized Rh/Al$_2$O$_3$ by IR at 2120, 2078, and 2026 cm^{-1}, however, the present study did not exhibit IR band characteristic of the tricarbonyl species.

Figure 4 shows the infrared spectra of CO adsorption on the sulfided Rh/SiO$_2$ catalyst at 310 K. Initial CO adsorption produced a linear-CO band at 2090 cm^{-1}. Exposure of CO for 60 min resulted in an increase in the intensity of the linear-CO band and a formation of two bands at 2029 and 2005 cm^{-1}. The species displaying these two bands appears to be weakly adsorbed on the sulfided Rh surface as indicated by the easy of elimination of these species by flowing N$_2$.
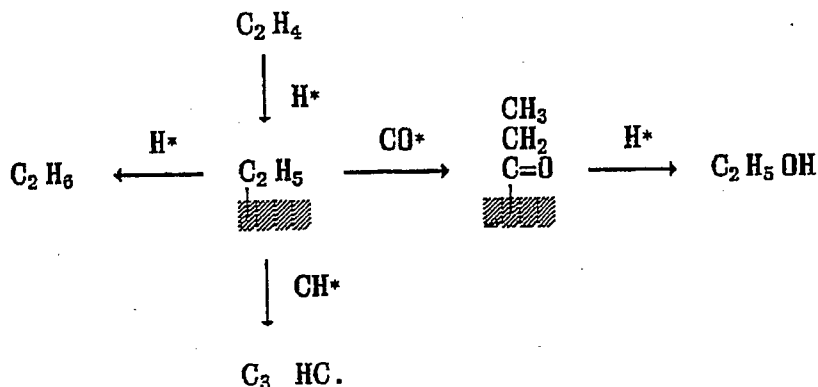
Comparison of infrared spectra of CO adsorption on reduced and sulfided catalysts (Figures 2 and 4) shows that the bridged CO and dicarbonyl were suppressed by the presence of sulfur and that the linear-CO band presented at a higher wavenumber over the sulfided catalyst. Sachtler et. al. conducted CO chemisorbed on Rh/SiO$_2$ as a function of sulfur coverage and showed that the intensities of the bridged CO and dicarbonyl species were decreased by increasing the surface coverage of sulfur [40]. The adsorbed sulfur has been found to disrupt the adjacent pairs of Rh metal atoms and blocks the sites for the formation of the bridged CO [41-44]. The increase in the wavenumber of the linear-CO band has been explained as an electronic effect of the presence of sulfur [44]. The electronic effect induced by sulfur, an electron accepter, results in strengthening the C-O bond by withdrawing electron from the anti-bonding of CO [44].

Ethylene Hydroformylation

The reaction rate and infrared data for the steady-state ethylene hydroformylation were collected simultaneously by gas chromatograph and infrared spectrometer, respectively. Infrared

spectra for the reaction are shown in figures 5-7. The rate of product formation corresponding to infrared spectra taken under the same reaction condition are presented in Table 1. Figure 5 shows the infrared spectra under the reaction conditions of the ethylene hydroformylation. Gaseous CO was observed at 2170 and 2115 cm^{-1}; gaseous ethylene was observed at the bands at 3124, 3077, 3009, and 2968 cm^{-1} as well as a sharp peak at 1888 cm^{-1} superimposed with a bridge-CO band. A close examination of infrared spectra for adsorbed species in figure 5 and rate data for the reduced Rh in Table 1 shows that the dominated species on the reduced Rh surface were linear CO at 2053-2042 cm^{-1} and bridged CO at 1880-1871 cm^{-}; the major reaction product was ethane at 373 K, 1 atm. As the reaction temperature increased from 373 to 513 K, the intensities of the linear-CO and bridged-CO bands decreased and the wavenumbers of these bands shifted downward. The intensity of hydrocarbon bands and the rate of hydrocarbon formation also increased. The rate of formation of oxygenated products such as acetaldehyde and propionaldehyde increased under this reaction condition. Subsequent increases in reaction presure from 1 atm to 10 atm resulted in increases in the formation rate and the selectivity of propionaldehyde. The infrared spectra showed a continuous growth of the propionaldehyde band (1730 cm^{-1}), however, the intensities of both linear- and bridge-CO bands decreased. The decreases in the intensities of the linear CO and bridged CO might be due to a competitive adsorption between H_2, C_2H_4, and CO over the catalyst surface and due to high reactivity of the adsorbed CO at the high temperature and pressure conditions.

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Formation of propionaldehyde in ethylene hydroformylation has been suggested to follow an insertion of CO into C_2H_x which is produced from ethylene adsorption followed by hydrogenation as shown in the following reaction pathway.

$$C_2H_6 \xleftarrow{\;H*\;} \underset{\displaystyle \text{(surface)}}{C_2H_5} \xleftarrow[\;\;]{\;H*\;} C_2H_4$$

with C_2H_5 leading via $CO*$ to $\underset{\text{(surface)}}{\overset{CH_3\;CH_2\;C=O}{\;}}$ then via $H*$ to C_2H_5OH; and C_2H_5 via $CH*$ to $C_3\;HC.$

Because the formation of propionaldehyde, ethane, and C_{3+} hydrocarbons involves a common intermediate, C_2H_x, a higher rate ratio of C_2H_5CHO to C_2H_6 and to C_{3+} HC represents a higher CO insertion selectivity. Increase in the ratio of C_2H_5CHO/C_2H_6 and C_2H_5CHO/C_{3+} HC with increasing temperatures and pressures (see Table 1) indicated that CO insertion competed favorably with hydrogenation and chain growth at higher reaction temperatures and pressures.

Figure 6 shows a series of infrared spectra as a function of time in the ethylene hydroformylation reaction at 373 K and 1 atm. We have limited the reaction temperature to 373 K because the oxide Rh tends to be reduced at high reaction temperature in the presence of H_2. The infrared spectra demonstrated a linear-CO band at 2033-2025 cm^{-1}, a bridge-CO band at 1881-1866 cm^{-1}, and a 20830-cm^{-1} band characteristic of the symmetrical gem-dicarbonyl. The asymmetrical gem-dicarbonyl band was

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overlapped by the linear-CO band. Carbon dioxide was produced and was observed at 2360 and 2340 cm^{-1}. Hydrocarbon products were observed in the C-H stretching range (2890-2988 cm^{-1}). The product of propionaldehyde was observed at 1733 cm^{-1}. A close examination of the spectra shows that the intensities of linear CO and dicarbonyl were oscillating during the reaction; the intensity of the bridged CO remained unchanged; and the bands of hydrocarbons and propionaldehyde were developed in the first 5 min and then attenuated as the reaction time elapsed. The products at this reaction condition consisted of methane, ethane, and propionaldehyde (see Table 1).

A reduction process of the catalyst was observed under this reaction condition. Presence of intensive linear-CO and bridge-CO bands on the catalyst indicates a formation of reduced Rh metal sites. Formation of CO_2 during the reaction also reveals that oxygen on the oxidized catalyst might interact with the adsorbed CO to form CO_2.

Figure 8 shows the influences of reaction pressures and temperatures on the infrared spectrum of ethylene hydroformylation on the sulfided Rh/SiO_2. At 373, 1 atm, the only adsorbed CO species is the linear CO displaying the band at 2090 cm^{-1}. Methane and ethane were identified to be the major products while no oxygenates were observed under this reaction condition. As the temperature increased from 373 to 513 K, the linear CO shifted form 2090 to 2049 cm^{-1} and its intensity increased; a small amount of propionaldehyde was produced. As reaction pressure increased from 1 to 10 atm, the rate of product formation increased in the order of $CH_4 < C_2H_6 < C_2H_5CHO$. The

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infrared spectra showed a decrease in the intensity of the linear
CO and increases in the intensities of hydrocarbon products and
propionaldehyde.

This ethylene hydroformylation study reveals that the
reduced, oxidized, and sulfided Rh/SiO_2 are active for
propionaldehyde synthesis. Comparison of the product
distribution between the oxidized catalyst, the sulfided catalyst
and the reduced catalyst shows that the oxidized catalyst
exhibited higher activity and selectivity toward propionaldehyde
than the reduced catalyst at 373 K and 1 atm while the sulfided
catalyst did not produce propionaldehyde at this condition.
However, the sulfided Rh/SiO_2 catalyst had a higher selectivity
of propionaldehyde than the reduced catalyst at 513 K.

Somorjai and coworkers [16] have found that Rh oxide is more
active than Rh metal for oxygenate synthesis. Suppression of CO
dissociation by oxidized Rh catalysts [45] may also enhance the
formation of propionaldehyde. On the other hand, the presence of
sulfur is known to poison catalytic reaction, particularly
involving H_2 and CO [41,44]. In the present study, the sulfided
catalyst showed suppression of the ethane formation more than
propionaldehyde formation and enhanced the selectivity of
propionaldehyde. Similar observation has been reported in
literature [40,43]

The in situ infrared spectra show that linear CO and bridged
CO were formed on the reduced Rh/SiO_2; linear CO, bridged CO, and
dicarbonyl were formed on the oxidized Rh/SiO_2; and only linear
CO was observed on the sulfided Rh/SiO_2 under the steady-state
reaction conditions. However, no obvious relation between

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infrared spectra of the adsorbed CO and the activity for CO insertion can be discerned.

The results discussed above reveal the catalyst activity and selectivity for propionaldehyde synthesis and the presence of adsorbed CO on the catalyst surface under the reaction conditions. However, the steady-state results did not tell the intermediates involving in the CO insertion reaction. The following reaction of C_2H_4/H_2 with the preadsorbed CO was used to determine which type of adsorbed CO is the really reactive intermediate for CO insertion. It should be noted that the formation of the presorbed CO on reduced, oxidized, and sulfided catalysts has been discussed in the previous CO adsorption studies.

Reaction of Adsorbed CO with C_2H_4 and H_2

Figure 8 shows the infrared spectra taken during the reaction of C_2H_4/H_2 with the preadsorbed CO on the reduced Rh/SiO_2 catalyst at 301 K. The infrared spectrum prior to admission of C_2H_4/H_2 exhibited linear CO at 2070 cm^{-1}, bridged CO at 1891 cm^{-1}, and gem-dicarbonyl at 2104 and 2040 cm^{-1}. An obvious ethylene band was observed 2-min after the introduction of C_2H_4/H_2, and then a growing propionaldehyde band at 1724 cm^{-1} was observed, paralleling with an attenuation of the linear-CO band, while the intensity of the bridged CO and dicarbonyl were not changed. The correlation of the intensity of the propionaldehyde band with the intensity of the linear-CO band indicates that linear CO is the major adsorbed CO participating in CO insertion leading to the formation of propionaldehyde.

Following the reaction time after 13 min, the ethylene band
slowly eliminated. The intensity of the adsorbed CO also
decreased: linear CO shifted downward to 2035 cm^{-1}; bridged CO
shifted to 1867 cm^{-1}; symmetrical dicarbonyl was observed at 2100
cm^{-1}. The intensity of the propionaldehyde increased to a
certain extend and then decreased while the hydrocarbon species
were continuously developed. The observation indicates that the
liner CO tended to form propionaldehyde faster than hydrocarbons.

Figure 9 shows the reaction of C_2H_4/H_2 with the preadsorbed
CO on the oxidized Rh/SiO_2 catalyst at 301 K. The spectra prior
to reacting with C_2H_4 and H_2 showed linear-CO band at 2078 cm^{-1};
bridge-CO band at 1885 cm^{-1}; gem-dicarbonyl doublet at 2096 and
2040 cm^{-1}; and the 2105-cm^{-1} band characteristic of a linearly
adsorbed CO at Rh with higher oxidized states (Rh^{n+}). Exposure
of the adsorbed CO to C_2H_4/H_2 for 2 min caused (i) a downward
shift of linear-CO band to 2033 cm^{-1}, (ii) a growth of an
intensive bridge-CO band, (iii) a decrease of the intensity of
the dicarbonyl and the 2105-cm^{-1} bands, and (iv) a formation of a
small propionaldehyde band at 1723 cm^{-1}.

An obvious growth of the propionaldehyde band with respect
to time was observed after 2-min of reaction. In order to
clearly discern the species involved in the formation of
propionaldehyde, sequential difference spectra was taken as shown
in Figure 10. The sequential difference spectra demonstrate the
increment or the decrement of each species with respect to time.
The intensities of all the adsorbed CO bands were observed to
increase suddenly between 2 and 3 min. The results of subsequent
changes in intensity show that the linear-CO band (2033 cm^{-1}) at

Rh^0 sites and the gem-dicarbonyl bands (2096 and 2040 cm^{-1}) were increased first and then were decreased; the band (2105 cm^{-1}) of linearly adsorbed CO at Rh^{n+} sites decreased continuously and much faster than the linear-CO band at Rh^0 sites; and the bridge-CO band (1890 cm^{-1}) and the 2084-cm^{-1} band increased continuously. The propionaldehyde band observed at 1723 cm^{-1} grew simultaneously. The result suggests that linearly adsorbed CO on higher oxidized Rh^{n+} sites was responsible for the formation of propionaldehyde via a CO insertion reaction.

Figure 11 shows the changes of infrared spectra taken during the interaction of C_2H_4 and H_2 with adsorbed CO on the sulfided Rh/SiO$_2$ catalyst at 301 K. The intensity of the linear CO at 2901 cm^{-1} decreased following the addition of C_2H_4 and H_2. No detectable propionaldehyde was observed during the entire period of the study. The previous ethylene hydroformylation study has shown that ethylene hydroformylation occurred on sulfided Rh/SiO$_2$ at 1 atm and 513 K. Recent study has also demonstrated that propionaldehyde was formed at reaction temperature above 343 K on sulfided Rh/SiO$_2$ [46].

Previous investigators have reported conflicting data on the active sites for CO insertion. Somorjai and coworkers [16], conducting CO hydrogenation over hydrated and anhydrous rhodium oxides, found that the anhydrous rhodium oxide reduced to metallic rhodium rapidly while the hydrated rhodium oxide was quite stable under the reaction condition. This stable hydrated rhodium oxide showed catalytic activity for CO insertion in CO hydrogenation leading to the formation of acetaldehyde. We observe that the oxidized Rh/SiO$_2$ catalyst produced

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propionaldehyde in a reaction of C_2H_4/H_2 with the preadsorbed CO at 310 K; furthermore, we find that the linearly adsorbed CO on the Rh^{n+} sites was active for CO insertion producing propionaldehyde. The ethylene hydroformylation study on the oxidized Rh/SiO_2 catalyst also showed higher propionaldehyde selectivity than on the reduced Rh/SiO_2 catalyst at 373 K, but the oxidized catalyst tended to be reduced in the reaction. On the other hand, Rh-based catalysts without the presence of Rh^{n+} have also shown CO insertion activity at temperature above 573 k [25,26]. In our present study, the reduced Rh/SiO_2 exhibited high activity in ethylene hydroformylation to produce propionaldehyde. Moreover, the linear-CO at Rh^o sties on the reduced Rh/SiO_2 catalyst was shown to participate in CO insertion.

A partial poisoning effect of sulfur in ethylene hydroformylation was also presented in this study. The sulfided Rh/SiO_2 catalyst suppressed bridged CO and dicarbonyl but enhanced the selectivity of propionaldehyde. Similar observation has been observed on promoted Rh catalysts which promote the formation of oxygenated products. These chemical additives, such as Zn and Fe, not only stabilize the Rh^+ sites but also block the sites for bridged CO and force the adsorbed CO into linear CO [47-49].

The above observations and discussions indicate that both linearly adsorbed CO on the reduced Rh sites (Rh^o) and the Rh ion sites (Rh^{n+}) are active for CO insertion to form oxygenated products. However, it is suggested that addition of promoter is necessary to stabilize the metal oxide for CO insertion.

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LIST OF TABLES AND FIGURES

Table 1. Rates of Products of Ethylene Hydroformylation over Reduced, Oxidized, and Sulfided Rh/SiO_2 Catalysts [a]

Product	Reduced			Oxidized	Sulfided		
	373 K	513 K		373 K	373 K	513 K	
	1 atm	1 atm	10 atm	1 atm	1 atm	1 atm	10 atm
CH_4	0.025	0.037	0.17	0.012	0.013	0.023	0.094
C_2H_6	0.14	8.27	66.4	0.075	0.001	2.5	48.9
C_{3+} HC.	-	0.098	0.094	-	-	-	0.092
CH_3CHO	-	0.097	0.075	-	-	-	-
C_2H_5CHO	0.016 (8.8)	1.4 (14.1)	24.5 (26.8)	0.025 (22.3)	-	(14.6)	27.0 (35.5)[b]
$\dfrac{C_2H_5CHO^c}{C_2H_6}$	0.11	0.17	0.37	0.33	0	0.17	0.55

a: The rates of product formation (mole/Kg-hr) corresponding with the infrared spectra were taken 40-min after the reaction was started.

b: Selectivity of propionaldehyde.

c: Ratio of the formation rate

flange

fluid
in

O-ring

CaF$_2$
window

nut

fluid
out

Side view

Front view
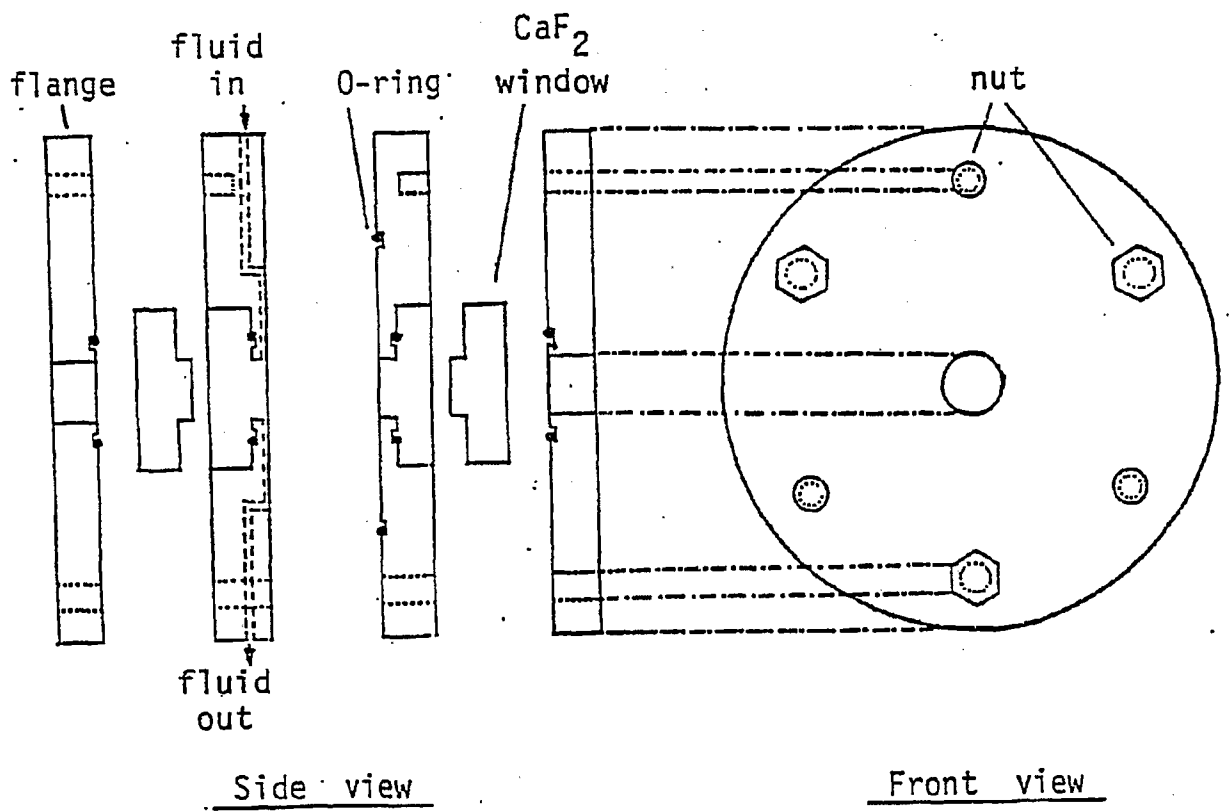
High Pressure and Temperature IR Cell

ABSORBANCE

1.54 1.25 1.1 .96 .67 .38 .09

2988
2950
2090

2003
2025
1866
1733
1560
1001
2033

70 min

40 min

10 min

5 min

3200 2900 2600 2300 2000 1700 1400

WAVENUMBER

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