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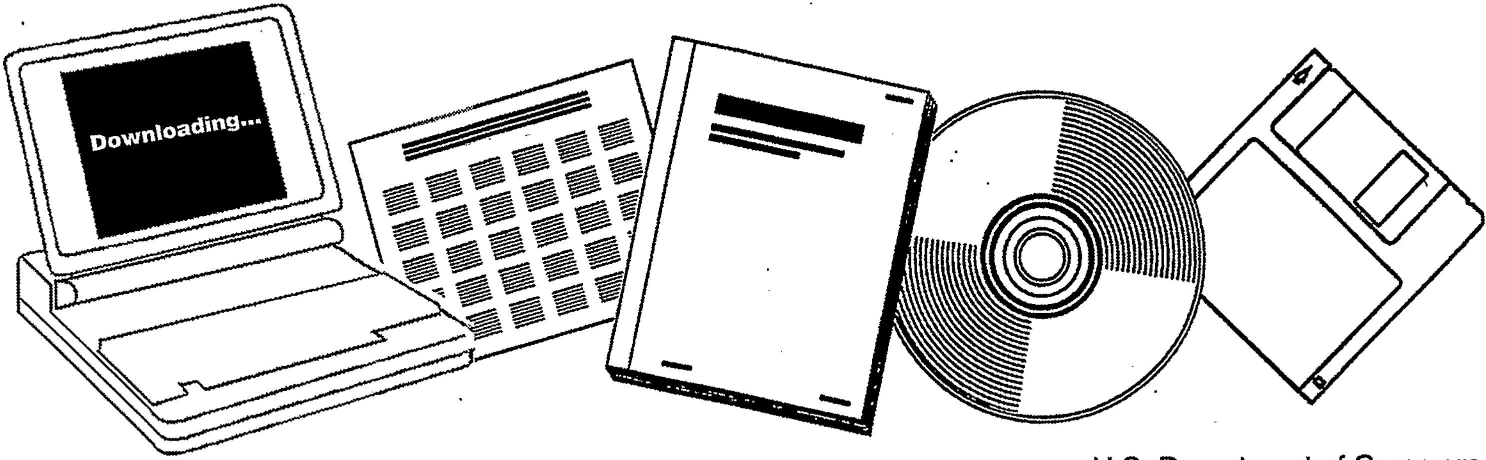

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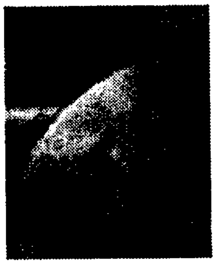

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

Technical Progress Report 5
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by

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SUMMARY

The objective of this research is to elucidate the role of various chemical additives on ethanol 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 including temperature programmed desorption, infrared study of NO adsorption, reactive 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.

RESULTS TO DATE CO insertion is known to be a key step to the formation of acetaldehyde and ethanol from CO hydrogenation over Rh catalysts. Ethylene hydroformylation has often served as a probe to determine CO insertion capabilities of Rh catalysts. However, the mechanism of CO insertion in hydroformylation on the supported Rh is still not well understood. During the fifth quarter of the project, the mechanism of CO insertion in ethylene hydroformylation over Rh/SiO_2 was investigated by in-situ infrared spectroscopy.

Introduction

Hydroformylation, which is a reaction of an olefin with syngas to form an aldehyde, is well known to be a homogeneous reaction catalyzed by metal complexes [1-3]. The reaction was first discovered by Roelen in 1938 while investigating the mechanism of the Fischer-Tropsch (F-T) synthesis by the addition of ethylene to syngas [4]. It was found that a significant amount of added ethylene was converted to propionaldehyde over a heterogeneous cobalt catalyst (a conventional F-T catalyst) under the F-T condition. The selectivity to propionaldehyde was significantly enhanced by increasing reaction pressures over 5.1 MN/m^2 and decreasing temperatures below 423 °K in which the F-T reaction ceased to occur. The overall reaction proceeds according to

$$CO + H_2 + C_2H_4 \text{ ---> } C_2H_5CHO \qquad (1)$$

It was the conventional F-T cobalt catalyst which was first used as a hydroformylation catalyst in a fixed bed reactor [4,5]. It was later recognized that the hydroformylation is a homogeneous reaction catalyzed by the cobalt carbonyls [1,5-7]. The conventional F-T cobalt catalyst (cobalt metal) was indeed a precursor for the generation of cobalt carbonyls for the reaction. The identification of hydroformylation as a homogeneously catalyzed reaction has essentially led to the successful development of commercial hydroformylation processes with Co and Rh complex catalysts [1-3].

While Roelen discovered the hydroformylation by the addition of ethylene to syngas on the F-T catalyst, the approach using olefin addition as a probe reaction has been extensively employed to study reaction intermediates and secondary reactions in the F-T synthesis as well as CO insertion capability of the F-T catalysts [8-15]. The addition of ethylene into syngas was found to increase the rate of formation of propionaldehyde over supported Rh and Ru under the F-T condition in which the F-T reaction continues to proceed [8-10]; the addition of 1-butene led to an increase in the rate of formation of 1-pentanol over Fe/Al_2O_3 under the similar reaction condition [11]. Interestingly, homogeneous counterparts of both supported Rh and Ru (i.e., Rh and Ru complexes) are well known to catalyze homogeneous hydroformylation while Fe complexes are known to be active for hydroformylation with CO/H_2O [1-3]. The homogeneous hydroformylation on metal complexes generally takes place under high CO pressures and low temperatures in which the metal complex catalyst is stable; the reaction is highly selective with hydrogenation products as minor products.

The results of olefin addition to syngas is strikingly similar to those observed for Co catalysts by Roelen. The interesting similarity in the reaction of olefins with syngas to form aldehydes on both supported metals and metal complexes has led to the investigation of the relationships between the (heterogeneous) hydroformylation and the homogeneous hydroformylation. It is important to point out here that the hydroformylation is well accepted as a homogeneous reaction catalyzed by metal complexes. In this paper, we tentatively use the term, heterogeneous hydroformylation, to describe the reaction of olefins with syngas to form aldehydes over supported metal catalysts.

The mechanism of homogeneous hydroformylation has been well established whereas little is known about the mechanism of heterogeneous hydroformylation. To develop a better understanding of heterogeneous hydroformylation, CO adsorption, CO hydrogenation (the F-T reaction), and ethylene hydroformylation on Rh/SiO_2 were studied by in situ infrared spectroscopy (IR). Rh was used for this study because of its high activity for both homogeneous and heterogeneous hydroformylation and existence of voluminous literature data on homogeneous hydroformylation on Rh complexes for comparison with heterogeneous hydroformylation [1-7]. H_2S was used as a selective poison to probe the nature of the reaction since sulfur compounds can severely poison the F-T reaction but only inhibit the homogeneous hydroformylation to a limited extent [16,17]. The results were compared with those for homogeneous hydroformylation to elucidate the relationships between heterogeneous and homogeneous hydroformylation.

Experimental

Catalyst Preparation

Three wt. % Rh/SiO_2 was prepared by impregnation of SiO_2 (Strem Chemicals) using Rh chloride (Alfa Chemicals). After impregnation, the sample was dried overnight in air at 313°K, then reduced in flowing hydrogen at 673°K for 16 hr. Hydrogen flow chemisorption was used to determine the metal surface area of Rh/SiO_2 and sulfur coverage on the sulfided Rh/SiO_2. The crystalline size of the Rh metal was determined to be 130 °A by X-ray line broadening technique.

Reaction Studies

Both CO hydrogenation and ethylene hydroformylation were performed over Rh/SiO_2 before and after sulfidation with H_2S in a differential reactor system under 393 - 573 °K and 1.01 MN/m^2. Product distribution was determined by using an HP-5890A gas chromatograph.

Sulfidation

H_2S (1000 ppm of H_2S in H_2) was passed at 15 cc/min. through the catalyst at 573 or 673 °K for about 30 minutes in order to saturate the catalyst surface with sulfur. Hydrogen was then passed through the catalyst bed for about 1 hour at the same temperature to remove any weakly adsorbed sulfur. Hydrogen chemisorption and temperature programmed desorption study shown that the catalyst was incapable of chemisorbing H_2 after sulfidation indicating that the metal surface may be saturated with adsorbed sulfur [17]. It was found that sulfidation with either pure H_2S or 1000 ppm H_2S in H_2 led to the sulfided catalysts which exhibit the same hydroformylation activities.

In Situ Infrared Spectroscopic (IR) Studies

Adsorption of CO, CO hydrogenation, and ethylene hydroformylation on Rh/SiO_2 and sulfided Rh/SiO_2 were studied in an IR cell at 510 °K and 1.01 MN/m^2. The IR cell is made of stainless steel with CaF_2 window using Grafoil o-rings (Union Carbide). The catalysts for the study were grounded to a fine powder and pressed into a disk (10 mm in diameter and 2 mm in thickness with 25 mg). IR spectra of adsorbed species were recorded by a Nicolet 5SXC FTIR spectrometer with a DTGS detector at a resolution of 4 cm^{-1}. Gas phase CO bands were eliminated by subtracting the absorbance of gas phase CO with SiO_2 disk in the cell from the spectra of adsorbed species on the Rh/SiO_2 catalyst.

Results

Addition of Ethylene to Syngas

Addition of ethylene to syngas over Rh/SiO_2 was studied using a feed consisting of 5% ethylene in the mixture of syngas with $CO/H_2=1$ in 393-573 °K and 1.01 MN/m^2. Table I shows the product distribution for the reaction. At temperatures below 453 °K, the major products of the reactions are propionaldehyde and ethane indicating that ethylene hydroformylation and hydrogenation are dominant. At temperatures above 513 °K, methane and C_{2+} hydrocarbons were observed. Ethylene hydroformylation and hydrogenation appear to accompany with the F-T reaction. A recent study by Sze in our laboratory showed that the concentration of added ethylene did not affect the selectivity of ethylene hydroformylation; the rate of formation of ethane and propionaldehyde increased proportionally with the concentration of added ethylene [13].

In Situ IR study

Figure 1 shows IR spectra of CO adsorption, CO hydrogenation, and ethylene hydroformylation on Rh/SiO_2 at 513 °K and 1.01 MN/m^2. Two major bands were observed for CO adsorption and CO hydrogenation: linearly adsorbed CO at 2043 m^{-1} and bridge-bonded CO near 1890 cm^{-1}. Methane was identified as the major product ; acetaldehyde and C_{2+} hydrocarbons were observed as the minor products during the CO hydrogenation under this condition.

When ethylene was added to CO/H_2 to initiate hydroformylation, both linear- and bridge CO-bands shifted downward in wave number and decreased in the absorbance compared to both CO bands before ethylene addition. The downward shift in both linear- and bridge-CO wave number has been attributed to the decrease in the dipole-dipole coupling between adsorbed CO as a result of dilution of adsorbed CO by adsorbed ethylene species [18]. The decrease in the absorbance of both linear- and bridge-CO appears to be due to a decrease in CO partial pressure as a result of ethylene addition. A new set of bands was also observed during the hydroformylation. IR bands near 1466 and 1416 cm^{-1} may be assigned to the bend vibration of hydrocarbons or alkyl part of propionaldehyde [19]; bands around 2880-2980 cm^{-1} may be assigned to C-H stretching vibrations of hydrocarbon species [19,20]. IR bands at 1722 cm^{-1} are assigned to adsorbed propionaldehyde on the catalyst. The assignment was confirmed by IR spectra of adsorption of propionaldehyde on the catalyst and SiO_2 support. The band of interest at 1678 cm^{-1} may be assigned to a surface acyl group ($CH_3CH_2(CO)$-Rh). This assignment is in line with the observation of 1670 cm^{-1} which was identified as an acyl compound {$Rh_6(CO)_{15}(CH_3CH_2CO[NMe_4]$}, in a homogeneous hydroformylation study [21].

IR studies of ethylene hydroformylation was repeated on a fresh catalyst under 1.01 MN/m^2 and 513 °k. Following the reaction study, the reactant flow was stopped; the reactor pressure and temperature was decreased to $1.01X10^5$ N/m^2 and 298 °K. Spectra taken subsequently showed that the spectra of adsorbed species remained almost the same as those under reaction conditions except that the acyl band showed an increase in the absorbance. The reactivity of all of the adsorbed species to hydrogen was examined by temperature programmed reaction with hydrogen. The study was carried out by introduction of a flow of H_2 into the IR cell at 10 cc/min. and the reactor was heated at 3.5 °K/min. Spectra taken is shown in the Figure 2. Absorbance of acyl band was rapidly decreased while the absorbance of propionaldehyde band was slowly attenuated as temperature increased. Gas chromatograph analysis of the gas phase product in the reactor effluent showed that propionaldehyde and CH_4 are major products during temperature programmed reaction. The band near 1722 cm^{-1} which remained almost unchanged after more than 1 hr. of reduction in H_2 at 513 °K may be attributed to the adsorbed propionaldehyde on SiO_2.

A slight shift in the wave number of both linear and bridge CO to lower wave numbers was observed as the temperature increased to 473 °K. Both types of adsorbed CO were almost completely desorbed at 513 °K while substantial amount of adsorbed hydrocarbons remained on the surface.

Figure 3 shows the IR spectra of CO adsorption, CO hydrogenation, and ethylene hydroformylation on sulfided Rh/SiO_2. Comparing IR spectra in the Figure 3 with those in the Figure 1 showed that (i) adsorbed sulfur inhibited adsorption of CO in the bridged form and shifted the wave number of linear CO to a higher wave number, (ii) a shoulder near 2020 cm^{-1} appeared on the CO adsorption and CO hydrogenation and became a dominant band in the ethylene hydroformylation on the sulfided Rh catalyst; the absorbance of the band appears to be independent of the CO partial pressures, and (iii) acyl band was not observed on the sulfided catalyst. Analysis of gas phase products for the hydroformylation showed that propionaldehyde and ethane were major products and only trace of methane was observed. The results agree well with our previous study on the same Rh/SiO_2 catalyst showing that sulfur poisoned methanation, slightly inhibited the ethylene hydrogenation, but essentially had no effect on the rate of formation of propionaldehyde [22].

Discussion

Adsorption of CO on the Rh/SiO_2 and the sulfided Rh/SiO_2

Two forms of adsorbed CO, linear and bridge CO, have been observed during the CO adsorption and CO hydrogenation on Rh/SiO_2 at 513 °K and 1.01 MN/m^2. Similar observations have been reported on the CO hydrogenation studies on La-Rh/SiO_2 [23] and Rh-Ir-Mn-Li/SiO_2 [24]. In contrast, three forms of adsorbed CO (linear, bridge, and twin) have been identified on the supported Rh catalyst. Twin carbonyl was generally considered to bond to isolated Rh sites [25]. Solymosi and Pasztor [26] has reported that H_2 prevent the formation of isolated Rh sites at temperature above 373 °K. In addition, twin carbonyl is more reactive toward hydrogen than linear CO and bridge CO [27]. It appears that the formation of stable dicarbonyl species is not favorable under CO hydrogenation and hydroformylation conditions.

Sulfidation of the catalyst led to modification of adsorbed CO: an upward shift of linear-CO wave number, a significant decrease in bridge-CO absorbance and downward shift of bridge CO wave number , and the appearance of a new band at 2020 cm^{-1}. The shift of the CO wave number has often been used to characterize the electronic state of metal catalysts. The adsorbed CO gave a higher wave number on the metal ion (or metal with partial positive charge) than that on the zero-valent metal surface [9]. The linear bands at 2043 cm^{-1} for Rh/SiO_2 and at 2061 cm^{-1} for sulfided Rh/SiO_2 observed in this study are in the range of 2073-

2040 cm^{-1} which has been assigned to linear CO on the zero-valent Rh surface [25,26]. The small upward shift (18 cm^{-1}) of linear CO band appears to be insufficient to justify the possible formation of Rh^+ (or partial positive Rh) on the surface of the sulfided Rh catalysts.

The decreased bridge-CO absorbance on the sulfided catalyst suggests that adsorbed sulfur disrupts ensemble site for bridge CO and CO hydrogenation without blocking sites for linear CO and hydroformylation. It clearly indicates that the bridge CO is not responsible for the hydroformylation; hydroformylation is less structure sensitive than hydrocarbon synthesis of the CO hydrogenation.

The band observed at 2020 cm^{-1} on sulfided Rh/SiO_2 appear to be different from that at 2016 cm^{-1} for hydroformylation on Rh/SiO_2. The wave number and absorbance of the former appears to be relatively insensitive to the change in CO partial pressure from .26 MN/m to 1 MN/m as hydrogen and ethylene were added to the reactant stream. This band at 2020 cm^{-1} could be assigned to a surface carbonyls species. The band resembles those of $Rh(CO)_4$ which was reported to give bands at 2020 and 2010 cm^{-1} [28]; it is also in line with the observed IR band of CO vibration of the proposed $C_2H_5Rh(CO)_4$ which was considered to be a reaction intermediate in the homogeneous hydroformylation [29]. It is known that sulfur overlayer tends to promote the formation of metal carbonyl form metal [30]. Our recent study has also shown that H_2S enhances the formation of $Ni(CO)_4$ from Ni/SiO_2 catalyst during CO adsorption, CO hydrogenation, and hydroformylation.

Comparison of in situ IR results with those of our current and previous reaction studies [13,22] revealed that in spite of the absence or presence of carbonyl band at 2020 cm^{-1} and the difference in the wave number of linear-CO band on the Rh catalysts, both Rh/SiO_2 and sulfided Rh/SiO_2 exhibited essentially the same activity for the ethylene hydroformylation. It remains unclear about the role of surface carbonyl species in the hydroformylation on the supported Rh. Our results are not able to provide definitely evidence to clarify the current controversy on the state of active sites for the CO insertion step in both hydroformylation and CO hydrogenation on supported metal catalysts [31-34].

Mechanistic Relationships Between Homogeneous and Heterogeneous Hydroformylation

Mechanistic studies of homogeneous hydroformylation have revealed that the reaction proceeds via (i) activation of catalyst by transformation of the parent carbonyl into a hydridocarbonyl, (ii) a formal insertion of an olefin into a metal-H bond of the hydridocarbonyl to from an alkylmetal complex , (iii) a formal migratory insertion of a CO into an alkyl-metal bond of alkylmetal complex to form an acyl species, and (iv) hydrogenolysis of the acyl species to give an aldehyde with the regeneration of the catalysts [1-7,35,36].

The key step in the homogeneous hydroformylation which can be used to develop mechanistic relationship between homogeneous and heterogeneous hydroformylation appears to be the migratory insertion of CO into an alkyl-metal bond to form an acyl-metal complex Take rhodium complex catalyst as an example.

$$CH_3CH_2Rh(CO)_3 + CO \longrightarrow CH_3CH_2Rh(CO)_4 \longrightarrow CH_3CH_2(CO)Rh(CO)_3 \qquad (2)$$

A number of in-situ infrared spectroscopic studies on the homogeneous hydroformylation have shown that the migratory CO insertion takes place in Rh carbonyl system [29,37]. King et al. [29] found that $C_2H_5Rh(CO)_4$ is the most abundant reaction intermediate in ethene hydroformylation over alkylrhodium tetracarbonyl derivative catalysts. Although the acyl complex has not been observed during hydroformylation by in situ IR, the acyl-complex intermediates in the reaction have been isolated and characterized by IR [21]. The observation of acyl band indicates that the acyl intermediate, $CH_3CH_2(CO)$-Rh, is present on the surface of Rh/SiO_2 during the heterogeneous hydroformylation. The results suggest the migratory CO insertion may take place on the supported Rh catalysts leading to the formation of acyl intermediate. Temperature programmed reaction study (shown in Figure 2) revealed that the acyl species can be hydrogenated to form propionaldehyde. It is important to point out that our IR study was carried out under steady state condition which provides the spectra of all the adsorbed species including reaction intermediates and spectator species (surface species which do not involve in the reaction). An isotopic transient FTIR study incorporated with mass spectroscopy is under way to distinguish reaction intermediates from spectator species.

It is important to note that the incapability of sulfur compounds to poison hydroformylation over supported metal is, in some respects, similar to that observed with hydroformylation over metal carbonyl. Freund and Marko [16] have shown that metal carbonyls remain active in catalyzing hydroformylation in the presence of sulfur species which slowly deactivate the reaction. Sulfided Rh catalysts appears to exhibit more catalytic property similarities to Rh carbonyls and complexes than Rh metal; both sulfided Rh and Rh complexes are inactive for the hydrocarbon synthesis of the CO hydrogenation while Rh metal is active for CO hydrogenation; acyl species which was not observed in in situ IR studies on both sulfided Rh and Rh carbonyl systems [29]. The acyl species is probably not the abundant intermediate in the hydroformylation over both sulfided Rh and Rh carbonyl.

Conclusions

Adsorbed acyl species was observed on Rh/SiO_2 catalyst during ethylene hydroformylation by in situ IR technique. The results suggest that the insertion of CO into adsorbed ethyl specie takes place on the Rh/SiO_2. Addition of H_2S on the Rh/SiO_2 blocked the bridge-CO sites and inhibited the formation of hydrocarbons from CO hydrogenation. In contrast. H_2S addition slightly affected the vibrational frequency of linear CO, and essentially had no effect on the hydroformylation activity. Adsorbed sulfur also promoted the formation of carbonyl species which roles in catalysis remains unclear. Hydroformylation on sulfided Rh/SiO_2 appears to resemble homogeneous hydroformylation to a greater extent compared to the hydroformylation on Rh/SiO_2.

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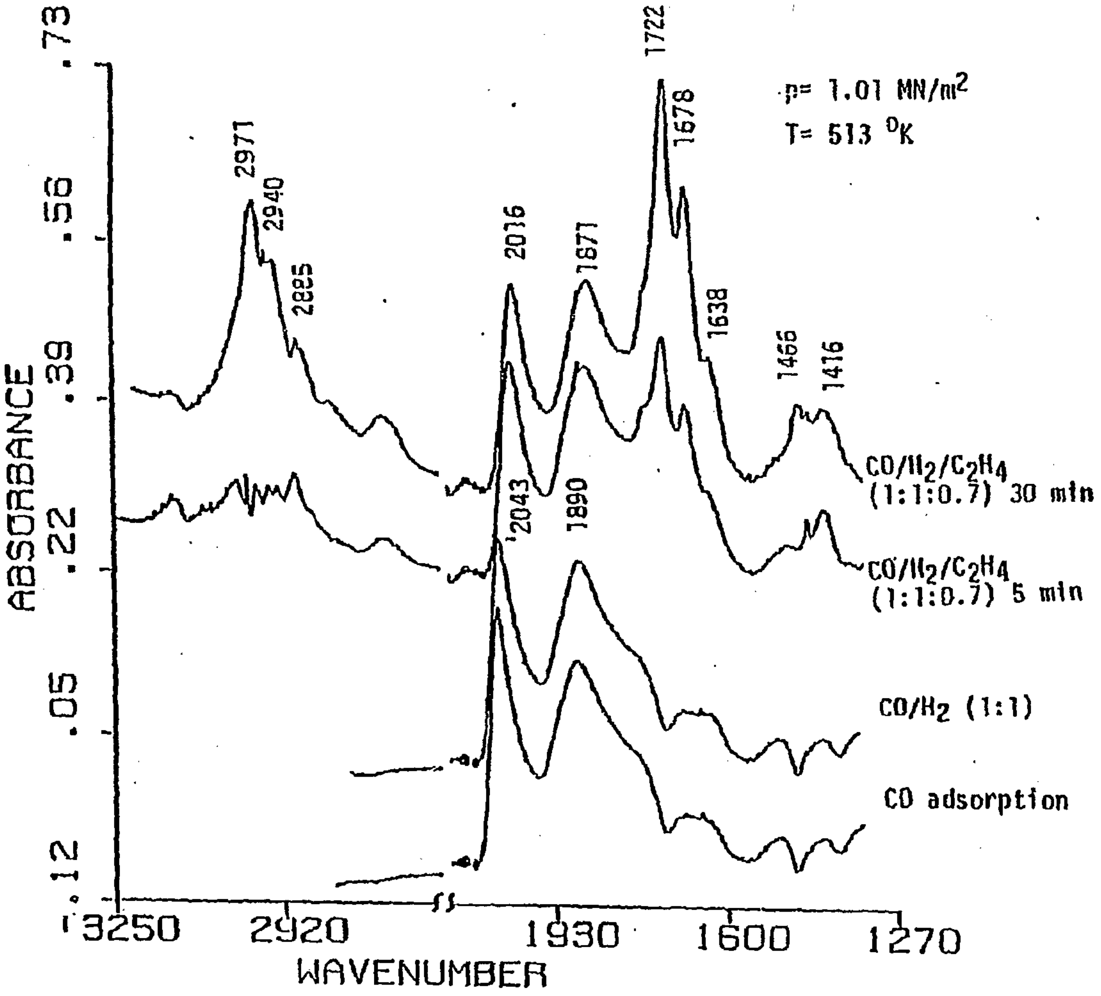
Table 1. Product Selectivity of $CO/H_2/C_2H_4$ Reaction over Rh/SiO_2

T (°K)	393	453	513	573
Overall Rate of C_2H_4 (gmol/kg-hr)	6.1E-2	4.9E-1	5.1E0	3.3E1
Product Selectivity (mol %)				
CH_4	0.0	0.0	4.3	7.8
C_2 Oxyg.	0.0	0.0	2.2	2.4
C_{3+} HC	0.0	0.0	0.3	0.5
C_2H_6	35.2	46.3	60.9	76.4
C_2H_5CHO	64.8	52.8	30.7	8.0
C_3H_7OH	0.0	0.9	2.0	4.9

Pressure = 1.01 MN/m^2.

5 mol% C_2H_4 in $CO/H_2 = 1$.

LIST OF FIGURES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.56
.39
.22
.05
.12
WAVENUMBER
3250
2920
1930
1600
1270
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T= 513 °K
2971
2940
2885
2016
1871
1722
1678
1638
1466
1416
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CO/H₂/C₂H₄ (1:1:0.7) 30 min
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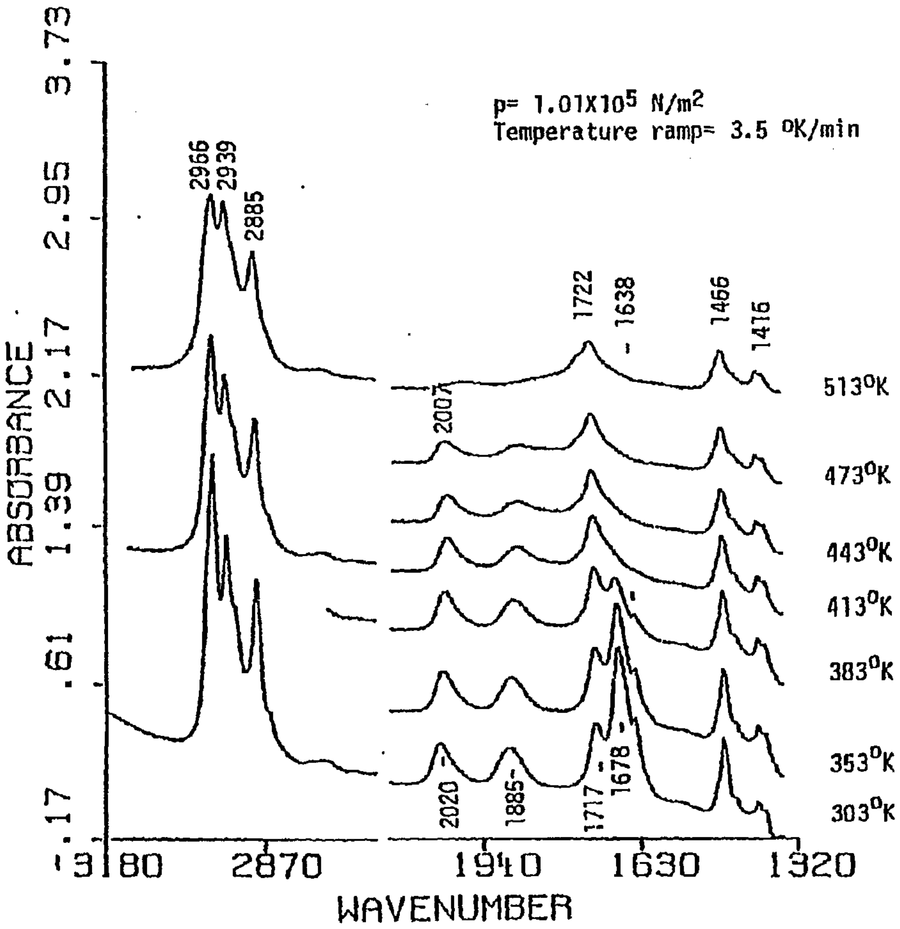
CO/H₂ (1:1)
CO adsorption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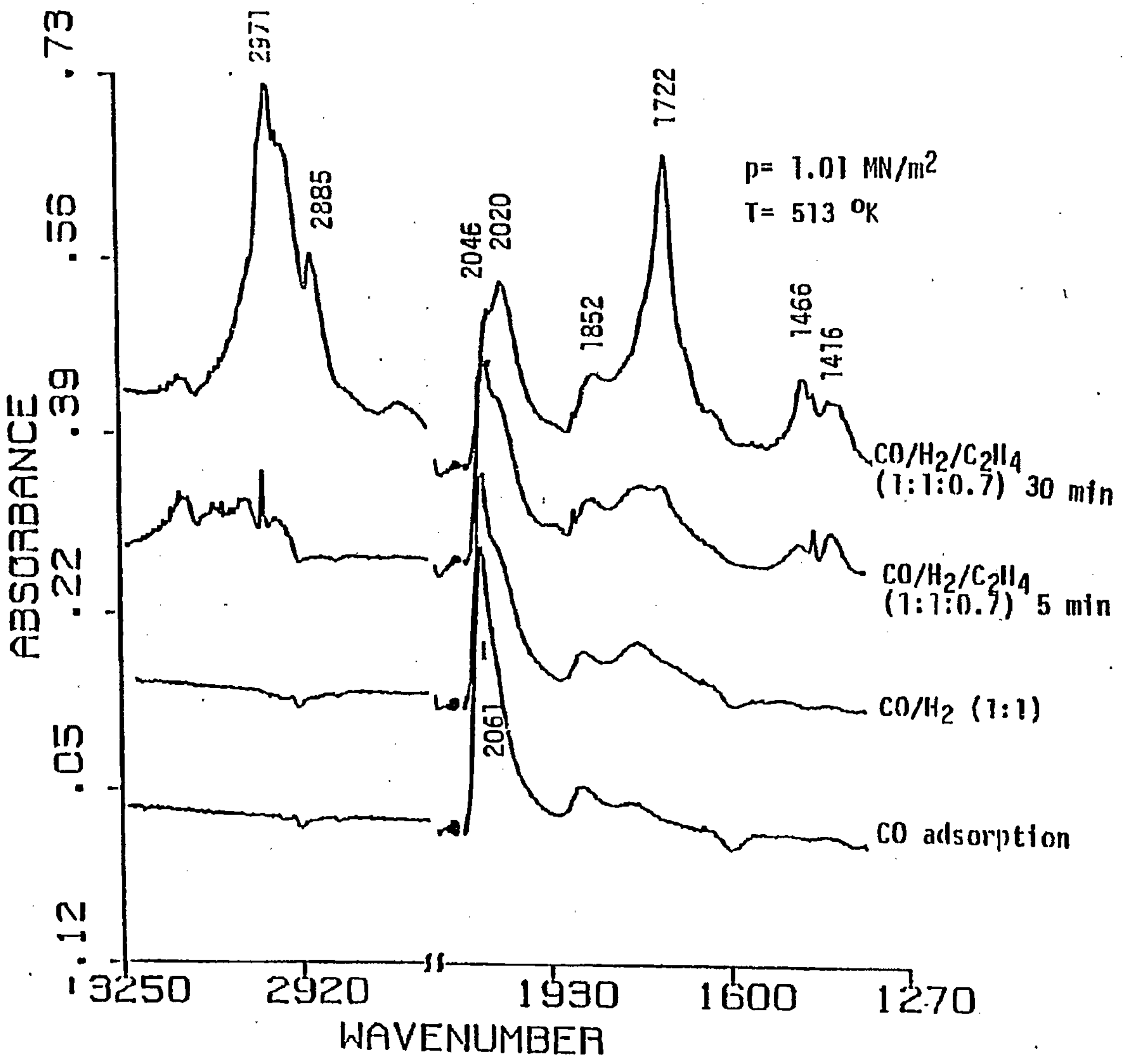
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p= 1.01 MN/m^2
T= 513 ^oK
CO/H$_2$/C$_2$H$_4$ (1:1:0.7) 30 min
CO/H$_2$/C$_2$H$_4$ (1:1:0.7) 5 min
CO/H$_2$ (1:1)
CO adsorption

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