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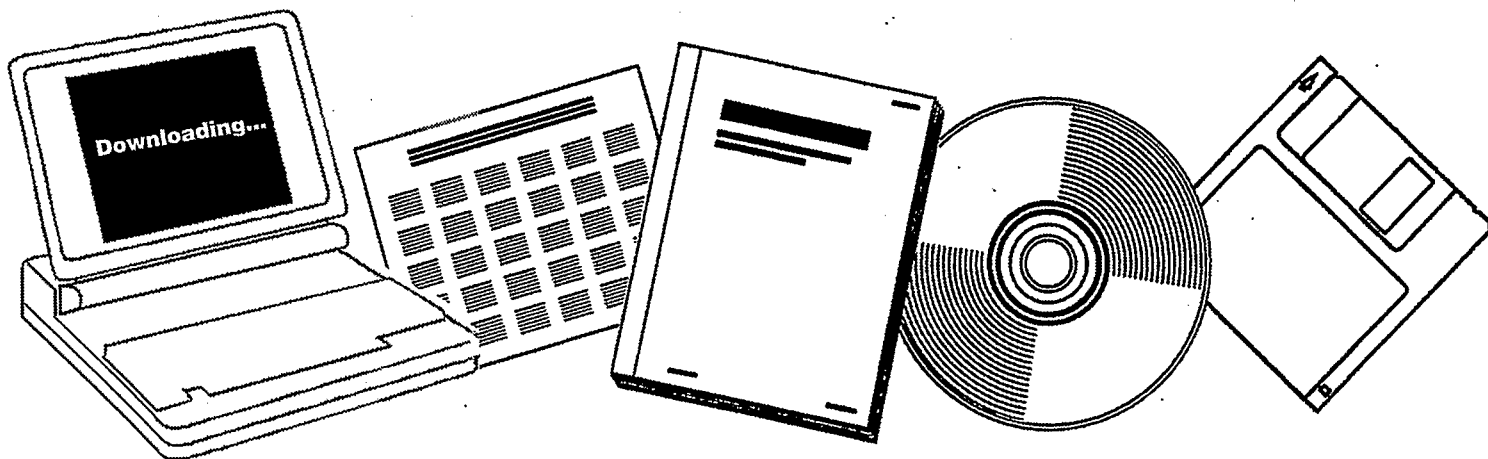
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**EFFECT OF CHEMICAL ADDITIVES ON THE  
SYNTHESIS OF ETHANOL. TECHNICAL PROGRESS  
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**THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL**

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## SUMMARY

The objective of this research is to elucidate the role of 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 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. Reaction of ethylene with syngas is used as a probe to determine CO insertion capabilities of metal catalysts. During the sixth quarter of the project, the mechanism of CO insertion on Ni/SiO<sub>2</sub> was investigated by in-situ infrared spectroscopy.

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## ABSTRACT

Ni/SiO<sub>2</sub>, a methanation catalyst, has been shown to exhibit CO insertion activity. In situ infrared studies of CO/H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> reactions show that the carbonylation of Ni/SiO<sub>2</sub> to Ni(CO)<sub>4</sub> leads to an inhibition of methanation in CO hydrogenation but an enhancement of formation of propionaldehyde in C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> reaction. The results suggest that the sites for propionaldehyde formation is different from those for methanation.

### 1. Introduction

The reaction of ethylene with syngas has been used as a probe reaction for investigating the mechanism of the Fischer-Tropsch (F-T) synthesis and the activity of F-T catalysts for catalyzing the specific reaction steps(1-5). The added ethylene may undergo various specific reactions: (i) hydrogenation, (ii) chain incorporation, and (iii) CO insertion leading to the formation of ethane, C<sub>3+</sub> hydrocarbons, and propionaldehyde. The selectivity of F-T catalysts has been shown to depend on their capabilities for these specific reactions (1-3,6). In general, a catalyst which shows a strong CO insertion activity is active for producing C<sub>2+</sub> oxygenates in the F-T synthesis. The catalysts including Rh, Ru, Co, Fe, and Mo have been shown to exhibit the activity for CO insertion (1-5, 7,8).

Ni is known to be the active catalyst for the F-T synthesis (9). Due to its high methanation activity and selectivity, the catalytic capabilities of Ni catalyst for other syngas related reactions have been overlooked. We have recently found that Ni/SiO<sub>2</sub>, a methanation catalyst, exhibits strong CO insertion activity; its activity for CO insertion is comparable to that of Rh which is known to be the most active for CO insertion. In order to develop a better understanding of the CO insertion on Ni/SiO<sub>2</sub>, in situ infrared (IR) spectroscopic studies of CO/H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> reactions were undertaken.

## 2. Experimental

15 wt% Ni/SiO<sub>2</sub> was prepared by impregnation of SiO<sub>2</sub> (strem chemicals) using Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Johnson Matthey Chemicals). The catalyst was reduced in flowing hydrogen at 673° K for 24 hours. The Ni crystalline size was determined to be 108 Å by x-ray diffraction line-broadening. The catalyst was ground to a fine powder and then pressed into a disk (10 mm in diameter and 0.5 mm in the thickness). After placing the catalyst disk in the IR cell, the catalyst was reduced again at 240° C. The design of IR cell is similiar to those reported by Wolf and co-workers (10). CO/H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> reactions on Ni/SiO<sub>2</sub> were studied in the IR cell at 240° C and 1~30 atm. The reactant flow was maintained at steady state. IR spectra of adsorbed species were recorded by a FTIR spectrometer

with a DTGS detector at a resolution of  $4\text{ cm}^{-1}$ . Gas phase CO bands were eliminated by subtracting the absorbance of gas phase CO with  $\text{SiO}_2$  disk in the cell from the spectra of adsorbed species on the  $\text{Rh/SiO}_2$  catalyst. Subsequent to recording each IR spectrum, analysis of composition of reactor effluent was performed using an HP-5890A gas chromatograph with a 12 ft. Porapak PS column.

### 3. Results and discussions

IR spectra of CO/ $\text{H}_2$  reaction on  $\text{Ni/SiO}_2$  at  $240^\circ$ , 1 atm, 10 atm and 20 atm are shown in Figure 1. Table 1 shows the results of rate of CO conversion and product distribution at  $240^\circ\text{C}$  and 1-20 atm corresponding to each IR spectrum taken. Two major bands were observed for CO/ $\text{H}_2$  reaction at 1 atm: linearly adsorbed CO at  $2046\text{ cm}^{-1}$  and bridge-bonded CO at  $1890\text{ cm}^{-1}$ . Methane was identified to be the major product while no oxygenates were observed under this condition. As the reaction pressure was slowly increased to 10 atm, a band at  $2055\text{ cm}^{-1}$  became prominent whereas the band at  $2046\text{ cm}^{-1}$  shrank. The increases in reaction pressure also led to marked decreases in the rate of CO conversion. Shutting off the reaction inflow and outflow and maintaining the reaction pressure at 10 atm led to further growth of the band  $2055\text{ cm}^{-1}$ . This band corresponds to the vibrational frequency of gaseous  $\text{Ni(CO)}_4$ . Gas sample collected from the effluent of IR reactor cell was found to contain large amounts of  $\text{Ni(CO)}_4$ .

indicating that carbonylation of Ni surface to  $\text{Ni}(\text{CO})_4$  occurred at  $240^\circ \text{C}$  and 10 atm.

After resuming reaction study at steady state, further increases in the reaction pressure resulted in completely elimination of all the adsorbed CO and  $\text{Ni}(\text{CO})_4$  bands as well as the loss of CO hydrogenation activity. These results suggest that the active site, i.e., the reduced Ni surface atom, for CO hydrogenation has been completely removed from  $\text{Ni}/\text{SiO}_2$  by carbonylation. It appears that carbonyl formation can be one of the major causes for deactivation of Ni-based catalysts for the F-T reaction.

The possible formation of carbonyl species under F-T condition has been noted by the Pichler's work which led to the suggestion that the best pressure range for F-T reaction on Ni is less than 1 atm (11). Storch et. al (12) have also suggested that removal of active metal from catalysts by carbonyl formation is probably one of the factors limiting the Fischer-Tropsch synthesis to relatively low pressures as compared with the alcohol synthesis.

Figure 2 shows IR spectra of  $\text{C}_2\text{H}_4/\text{CO}/\text{H}_2$  reaction. Comparison of IR spectra of  $\text{C}_2\text{H}_4/\text{CO}/\text{H}_2$  with those of  $\text{CO}/\text{H}_2$  (Figure 1) shows that the addition of ethylene to syngas caused a downward shift of both linear and bridge CO bands. The downward shift of CO bands may be attributed to the dilution of the adsorbed CO layer caused by adsorbed



ethylene species (13). As shown in Table 2, the major product of the reaction is ethane which is resulted from ethylene hydrogenation. Appreciable amounts of propionaldehyde and 1-propanol was also observed at the pressure above 1 atm. As the pressure was increased to 10 atm, the bands at 1732 and 1676  $\text{cm}^{-1}$  began to appear. The former corresponds to adsorbed propionaldehyde. The band at 1676  $\text{cm}^{-1}$  may be assigned to adsorbed acyl species ( $\text{Ni}(\text{CO})\text{C}_2\text{H}_5$ ). Although the vibrational frequency of acyl group in the Ni complex has not be reported, this assignment is in line with the wave number of acyl band of a number of Rh and Ir acyl complexes (14-16). The possible presence of adsorbed acyl species suggests that the propionaldehyde may be formed via CO insertion pathway on Ni.

Comparison of the IR spectra as well as product formation rate in Figure 2 and Table 2 shows several interesting features of pressure effect on the IR spectra and the rate of product formation. Increases in total reaction pressure led to (i) increases in the intensity of  $\text{Ni}(\text{CO})_4$  band (ii) increases in the intensity of both linear and bridge CO for the pressure from 1 to 10 atm and decreases in intensity of both adsorbed CO for the pressure above 10 atm. (iii) increases in the rate of formation of propionaldehyde and 1-propanol, and (iv) decreases in the rate of ethane formation.

Carbonylation of Ni/SiO<sub>2</sub> which was observed in CO hydrogenation (the F-T reaction) was also observed in reaction of ethylene with syngas as indicated by the formation of Ni(CO)<sub>4</sub> at high pressure. Although the intensity of Ni(CO)<sub>4</sub> band is in parallel with the rate of formation of propionaldehyde, Ni(CO)<sub>4</sub> is well known to be inactive for homogeneous hydroformylation (17). The active sites for the formation of propionaldehyde appears to be on the surface of the Ni/SiO<sub>2</sub> catalysts. The difference in the pressure effect on the product formation suggests that the active sites for the formation of propionaldehyde are different from those for ethane formation.

It has been shown that reduction of Ni oxide to the zero-valent Ni is the required step for the carbonylation of ore or oxides to Ni(CO)<sub>4</sub> (18). Our infrared studies of CO adsorption on unreduced Ni catalysts reveal that carbonylation does not occur on the unreduced catalysts (19). Carbonylation of Ni/SiO<sub>2</sub> under reaction conditions, especially at high pressure, appears to lead to the removal of the reduced Ni which is known to be responsible for CO hydrogenation and ethylene hydrogenation. The removal of the reduced Ni surface atoms could result in an increase in the relative concentration of Ni<sup>δ</sup>, which may be responsible for CO insertion, leading to increases in rate of propionaldehyde. This proposition appears to be consistent with our experimental observation. The

proposition is also in line with the suggestion that CO insertion is favored at isolated  $\text{Rh}^{\delta}$  sites (20).

In contrast to  $\text{C}_2$  oxygenate synthesis catalyst such as Rh (1,2,4), Ni/SiO<sub>2</sub>, which exhibits strong methanation activity during CO/H<sub>2</sub> reaction, is active for catalyzing the formation of propionaldehyde in the reaction of ethylene with syngas. The absence of correlation in the oxygenate selectivity between CO/H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> reactions on the Ni/SiO<sub>2</sub> suggests that the CO insertion site may not be accessible to CH<sub>x</sub> which is produced on CO dissociation and hydrogenation sites during the CO/H<sub>2</sub> reaction whereas ethylene may directly land on the CO insertion site during C<sub>2</sub>H<sub>4</sub>/CO/H<sub>2</sub> reaction. Work is under way to prepare a Ni-based catalyst of which CO insertion site should be in the proximity of CH<sub>x</sub> formation site so that the insertion of CO into adsorbed CH<sub>x</sub> can take place during the F-T reaction.

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Table 1

Product Selectivity of CO/H<sub>2</sub> Reaction over Ni/SiO<sub>2</sub>

Pressure (atm)	1	10	20
Overall rate			
(mol/kg-hr)	0.22	0.36	0.14
Selectivity			
(mol%)			
C <sub>1</sub> HC	65.2	30.9	26.0
C <sub>2</sub> HC	25.8	65.9	73.9
C <sub>3</sub> HC	6.2	3.2	0.0
C <sub>4</sub> HC	2.8	0.0	0.0

Reaction Temperature: 240° C

CO : H<sub>2</sub> = 1:1

HC = Hydrocarbons

Table 2

Rate of Product Formation from  $C_2H_4/CO/H_2$  Reaction on  $Ni/SiO_2$

Pressure (atm)	1	10	20	30
Rate (mole/kg-hr)				
$C_2H_4$	36.6	62.3	51.5	48.7
$C_2H_5CHO$	0.96	1.52	4.26	6.18
1- $C_2H_7OH$	0.038	0.13	0.11	0.14

Temperature = 240° C

$C_2H_4 : CO : H_2 = 1 : 1 : 1$

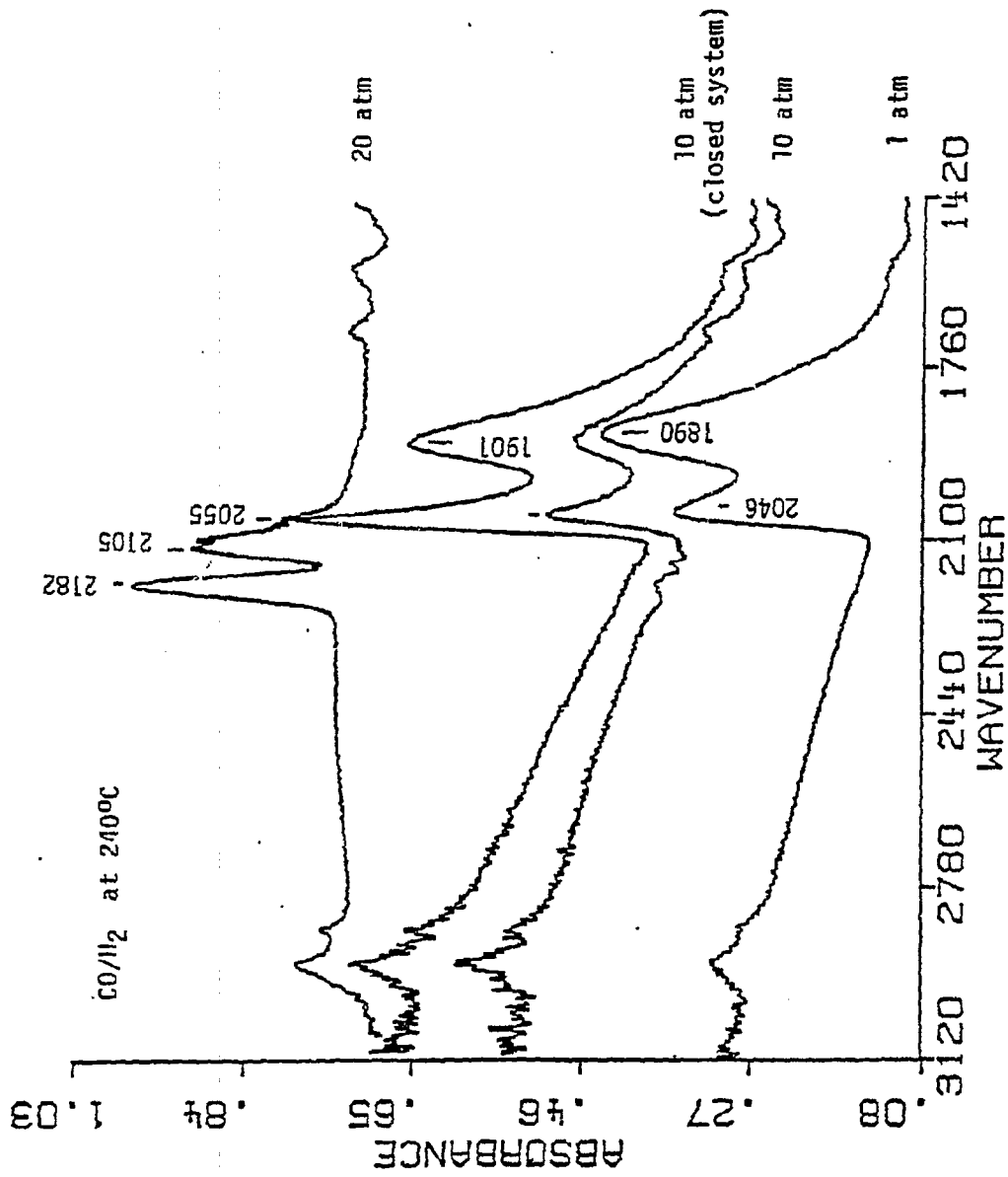


Figure 1. Pressure effect on CO/H<sub>2</sub> over Ni/SiO<sub>2</sub> catalyst



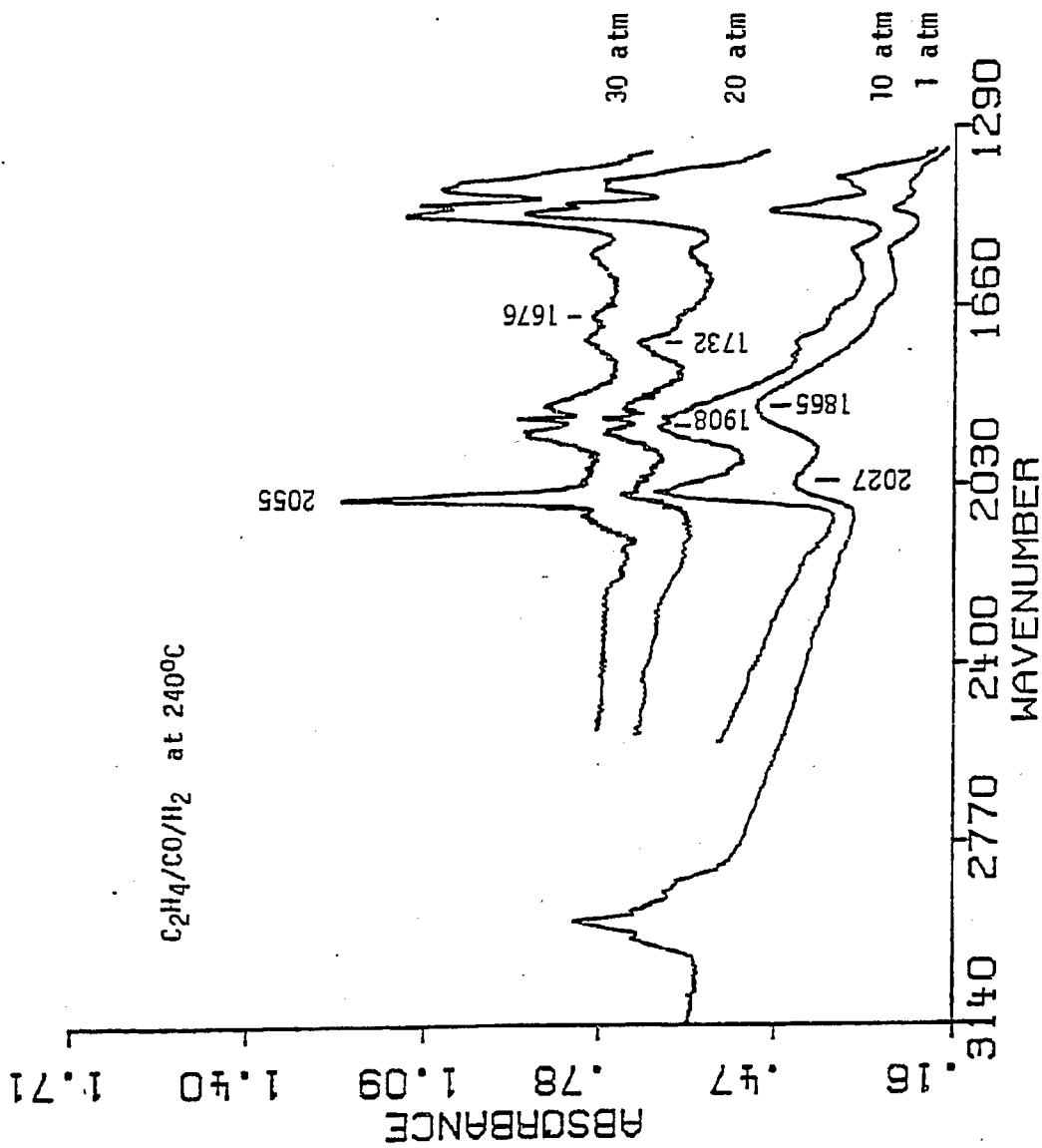


Figure 2. Pressure effect on  $C_2H_4/CO/H_2$  over Ni/SiO<sub>2</sub> catalyst

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