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INFRARED STUDIES OF REACTION OF ETHYLENE WITH SYNGAS ON Ni/SiO$_2$

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Ni/SiO$_2$, a methanation catalyst, has been shown to exhibit CO insertion activity. In situ infrared studies of CO/H$_2$ and C$_2$H$_4$/CO/H$_2$ reactions on Ni/SiO$_2$ show that carbonylation of Ni/SiO$_2$ to Ni(CO)$_4$ leads to an inhibition of methanation in CO hydrogenation but an enhancement of formation of propionaldehyde in the C$_2$H$_4$/CO/H$_2$ reaction.

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_{3+} hydrocarbons, and propionaldehyde, respectively. 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 exhibits a strong CO insertion activity is active for producing C_{2+} 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 an 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$_2$, 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 reaction on Ni/SiO$_2$, in situ infrared (IR) spectroscopic studies of CO/H$_2$ and C$_2$H$_4$/CO/H$_2$ reactions were undertaken.

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2. Experimental

14.4 wt% Ni/SiO_2 was prepared by impregnation of SiO_2 (Strem Chemicals) using $Ni(NO_3)_2 \cdot 6H_2O$ (Johnson Matthey Chemicals). The catalyst was reduced in flowing hydrogen at 400 °C for 24 hours. The Ni crystalline size was determined to be 108 Å by X-ray diffraction line-broadening. Chemical analyses of the Ni catalysts were performed by Galbraith Laboratory, Inc. The catalyst was ground to a fine powder and then pressed into a disk (10 mm in diameter and 0.9 mm in the thickness). After placing the catalyst disk in the IR cell, the catalyst was reduced again at 240 °C. The IR cell design is similar to those reported by Wolf and co-workers [10]. CO/H_2 and $C_2H_4/CO/H_2$ reactions on Ni/SiO_2 were studied in the IR cell at 240 °C and 1 ~ 30 atm. 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 the SiO_2 disk in the cell from the spectra of adsorbed species on the Ni/SiO_2 catalyst.

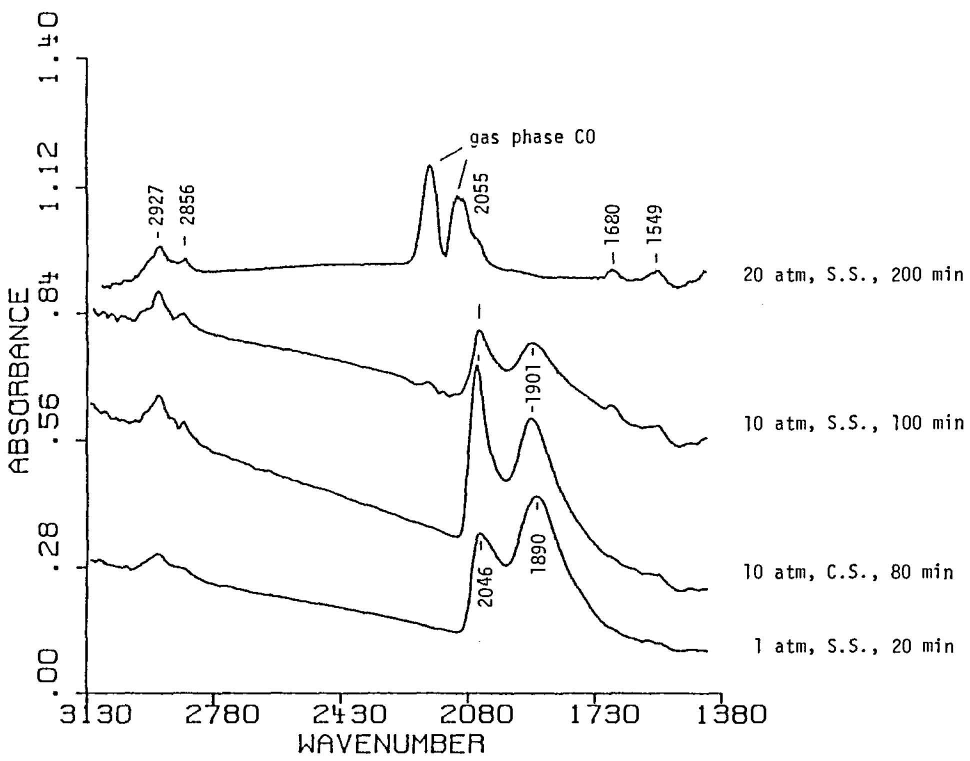

Fig. 1. Infrared spectra of CO/H_2 reaction on Ni/SiO_2. S.S. (steady state): The spectrum was taken while the reactant flow was maintained at steady state. C.S. (closed system): The spectrum was taken while both the inlet and outlet of the IR reactor was closed.

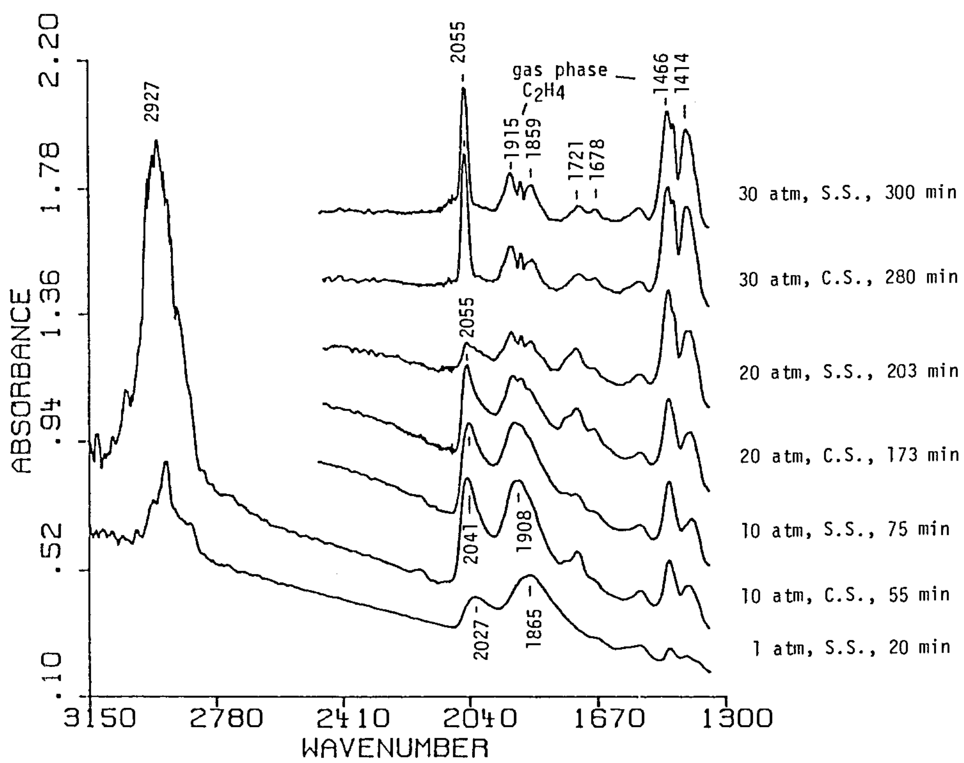

Fig. 2. Infrared spectra of $C_2H_4/CO/H_2$ reaction on Ni/SiO$_2$.

IR spectra (as shown in figs. 1 and 2) were taken under steady-state (S.S.) flow condition and closed system (C.S.). Steady-state IR spectra were recorded after reactant flow was maintained at steady state for 20 min. Subsequent to recording each S.S. IR spectrum, analysis of the reactor effluent composition was performed using an HP-5890A gas chromatograph with a 12 ft Porapak PS column. The reaction pressure was raised by sutting off the reactor effluent and maintaining constant inlet flow rate. Once the desired pressure was reached, the reactor inlet was closed to maintain the pressure at constant for 5 min prior to recording the C.S. IR spectrum.

3. Results and discussions

IR spectra of CO/H_2 reaction on Ni/SiO$_2$ at 240 °C, 1 atm, 10 atm and 20 atm are shown in fig. 1. Table 1 shows the results of rate of CO conversion and product distribution at 240 °C and 1 ~ 20 atm corresponding to each IR spectrum taken under steady-state (S.S.) condition. Two major bands were observed for CO/H_2 reaction at 1 atm: linearly adsorbed CO at 2046 cm^{-1} and bridge-

Table 1
Product selectivity of CO/H_2 reaction over Ni/SiO_2

Pressure (atm)	1	10	20
Overall rate (mol/kg-hr)	0.22	0.36	0.14
Selectivity (mol%)			
CH_4	65.2 (0.099) *	30.9 (0.064)	26.0 (0.021)
C_2H_4	17.7	43.0	60.3
C_2H_6	8.1	22.9	13.7
C_3HC	6.2	3.2	0.0
C_4HC	2.8	0.0	0.0

Reaction temperature: 240 ° C Fresh Ni/SiO_2: 14.4%
CO: $H_2 = 1:1$ Used Ni/SiO_2: 6.9%
HC: Hydrocarbons, $C_3 \sim C_4$ olefins and paraffins can not be separated by Porapak PS column.
* : Value in parentheses is the rate of methane formation.

bonded CO at 1890 cm^{-1}. Bands around 2927 cm^{-1} can be assigned to the C–H stretching vibration of hydrocarbon species. Methane was identified to be the major product while no oxygenates were observed under these conditions. As the reaction pressure was slowly increased to 10 atm, a band at 2055 cm^{-1} became prominent whereas the band at 2046 cm^{-1} was attenuated. 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 cm^{-1}. This band corresponds to the wave number of gaseous $Ni(CO)_4$. Resuming the S.S. flow condition and keeping in the reaction pressure at 10 atm resulted in a marked decrease in the intensity of both $Ni(CO)_4$ and bridge-CO band. The band at 2055 cm^{-1} was also observed in the gas sample collected from the effluent of the IR reactor cell. These observations indicate that $Ni(CO)_4$ produce from carbonylation of Ni surface was transported with reactant stream from the catalyst to the reactor effluent.

As shown in fig. 1, increasing reaction pressure from 10 atm to 20 atm and maintaining the steady-state reaction flow resulted in reduction of all the adsorbed CO and $Ni(CO)_4$ bands. This increase in the reaction pressure also led to the decrease in CO hydrogenation activity as shown in table 1. Chemical analysis of the Ni catalysts also revealed that the Ni loading decreased from 14.4% (fresh catalyst) to 6.9% during the entire period of CO hydrogenation study. These results suggest that part of the Ni atoms for CO hydrogenation have been removed from Ni/SiO_2 by carbonylation. Carbonyl formation can be one of the major causes for deactivation of Ni-based catalysts for the F-T reaction [11–13].

A fresh Ni/SiO_2 was used for IR studies of $C_2H_4/CO/H_2$ reaction. Figure 2 shows IR spectra of $C_2H_4/CO/H_2$ reaction. Gaseous ethylene bands appeared around 1915, 1859, 1466, and 1414 cm^{-1}. Comparison of IR spectra of $C_2H_4/CO/H_2$ with those of CO/H_2 (fig. 1) shows that the addition of ethylene

Table 2
Rate of product formation from $C_2H_4/CO/H_2$ reaction on Ni/SiO_2

Pressure (atm)	1	10	20	40
rate (mole/kg-hr)				
CH_4	0.80	0.95	0.63	0.30
C_2H_6	36.6	62.3	51.5	48.7
C_{3+} HC	0.94	1.03	0.79	0.38
C_2H_5CHO	0.96	1.52	4.26	6.18
1-C_3H_7OH	0.038	0.13	0.11	0.14

Temperature = 240 ° C
$C_2H_4:CO:H_2=1:1:1$

Fresh Ni/SiO_2: 14.4%
Used Ni/SiO_2: 7.2%

to syngas caused a downward shift of both linear and bridge CO bands at 1 atm. The downward shift of CO bands may be attributed to the dilution of the adsorbed CO layer caused by adsorbed ethylene species [14]. As shown in table 2, the major hydrocarbon products of the reaction are methane and ethane. High ethane formation rate indicates that the majority of ethane are formed from ethylene hydrogenation. Hydrogenolysis of C_2 hydrocarbons appears to occur to a significant extent as indicated by high methane formation rate in the $C_2H_4/CO/H_2$ reaction compared with that in the CO/H_2 reaction. Appreciable amount 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 1721 and 1678 cm^{-1} began to appear. The former corresponds to adsorbed propionaldehyde. The band at 1678 cm^{-1} may be assigned to adsorbed acyl species ($Ni(CO)C_2H_5$). Although the vibrational frequency of the acyl group in the Ni complex has not been reported, this assignment is in line with the wave number of acyl band of a number of Rh and Ir acyl complexes [15–17]. 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 fig. 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 $Ni(CO)_4$ band under C.S. condition, (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, (iv) decreases in the rate of ethane formation from 10 to 30 atm, and (v) decreases in the rate of methane formation. It is important to point out that the $Ni(CO)_4$ band observed under S.S. condition is always smaller than that of $Ni(CO)_4$ observed under C.S. condition. This is due to the removal of gaseous $Ni(CO)_4$ by the steady-state reactant flow. The removal of Ni from the Ni/SiO_2 is also evidenced by the decrease of Ni loading from 14.4% to 7.2% during $C_2H_4/CO/H_2$ study.

Carbonylation of Ni/SiO_2 which was observed in CO hydrogenation was also observed in reaction of ethylene with syngas as indicated by the formation of $Ni(CO)_4$ at high pressure. Comparison of transmission electron microscopy of both fresh and used catalysts shows no obvious difference in the size of Ni particle [18]. Carbonylation of Ni/SiO_2 under reaction conditions, especially at high pressures, led to the removal of the reduced Ni atoms resulting in decreases in rates of CO hydrogenation and ethylene hydrogenation as well as in the IR intensity of adsorbed CO band.

At the end of both CO/H_2 and C_2H_4/CO/H_2 reaction studies, almost 50% of Ni was removed from the Ni/SiO_2 catalysts and the catalysts exhibited very weak bands of adsorbed CO indicating that part of the Ni remains on the Ni/SiO_2 may not be in the reduced state. This may be due to incomplete reduction of the Ni catalyst at the reduction temperature of 400 ° C. It has been shown that reduction of Ni oxide to the zero-valent Ni is the required step for the carbonylation of Ni oxides to $Ni(CO)_4$ [19]. Our infrared studies of CO adsorption on unreduced Ni catalysts revealed that carbonylation did not occur on the unreduced catalysts [18].

Although the intensity of the $Ni(CO)_4$ band is in parallel with the rate of formation of propionaldehyde, $Ni(CO)_4$ is well known to be inactive for homogeneous hydroformylation [20]. The active sites for the formation of propionaldehyde appear to be on the surface of the Ni/SiO_2 catalysts. Nevertheless, the results of this study do not provide sufficient information for elucidating the state of active sites. In contrast to C_2 oxygenate synthesis catalysts such as Rh (1,2,4), Ni/SiO_2, which exhibits strong methanation activity during CO/H_2 reaction, is active for catalyzing the formation of propionaldehyde in the reaction of ethylene with syngas. The reason for the absence of a correlation in the oxygenate selectivity between CO/H_2 and C_2H_4/CO/H_2 reactions on the Ni/SiO_2 remains unclear. Further investigation on the CO insertion sites of Ni catalysts is required for clarifying the above issue.

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