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Ethylene Addition to CO Hydrogenation over Sulfided Ni, Rh, and Ru

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The effect of H_2S on ethylene addition to CO hydrogenation has been studied over Ni/SiO_2, Rh/SiO_2, and Ru/SiO_2 catalysts at 300°C and 10 atm. The major products of the ethylene addition on the unsulfided catalysts are ethane and propionaldehyde which result from ethylene hydrogenation and the insertion of CO into adsorbed ethylene species, respectively. Sulfidation of the catalysts led to the suppression of ethylene hydrogenation and CO hydrogenation. CO insertion over Ni/SiO_2 and Rh/SiO_2 catalysts was insensitive to sulfidation, whereas CO insertion on Ru/SiO_2 was inhibited by sulfidation. Infrared studies of CO adsorption reveal that sulfidation of the catalysts led to the disruption of neighboring surface atoms for bridge CO resulting in the formation of isolated atom sites which may be responsible for CO insertion on the sulfided Ni and Rh catalysts.

CO insertion has been demonstrated to be a key step for the formation of higher oxygenates in CO hydrogenation over Fe (*1*), Rh (*2–4*), Ru (*5*), and Mo (*6*) catalysts. One effective way to determine CO insertion activity is the use of ethylene addition as a probe reaction (*2–4, 6, 7*). In ethylene addition to CO hydrogenation, the added ethylene may undergo various specific reaction steps: (i) hydrogenation, (ii) CO insertion (carbonylation), (iii) hydrogenolysis, and (iv) chain incorporation, which lead to the increase in the rate of formation of ethane, propionaldehyde, methane, and higher hydrocarbons, respectively.

Most of these specific reaction steps involving syngas are known to be highly sensitive to sulfur poisoning (*8–10*). A dramatic decrease in the rate of ethylene hydrogenation, ethane hydrogenolysis, and CO hydrogenation has been observed on the sulfided metals (*8–11*). In contrast, sulfidation has been found to hardly affect the rate of CO insertion in the ethylene addition reaction over Rh/SiO_2 at 300°C and 10 atm (*12*). The failure of H_2S to poison CO insertion has also been observed in the ethylene hydroformylation on the Rh/SiO_2 catalyst at 180°C and 1 atm (*13*). The purpose of this paper is to investigate the effect of adsorbed sulfur on the CO insertion over Ni/SiO_2, Rh/SiO_2, and Ru/SiO_2 under CO hydrogenation conditions.

EXPERIMENTAL

The 15 wt% Ni/SiO_2, 3 wt% Ru/SiO_2, and 3 wt% Rh/SiO_2 were prepared by impregnation of large pore SiO_2 (SA: 350 m^2/g, Strem Chemicals, #14-7420) using $Ni(NO_3)_2 \cdot 6H_2O$, $RhCl_3 \cdot 3H_2O$, and $RuCl_3 \cdot 3H_2O$ (Johnson Matthey). After impregnation, the sample was dried overnight in air at 40°C, then reduced in flowing hydrogen at 400°C for 16 h. H_2S (1000 ppm of H_2S in H_2) was passed at 15 cc/min through the catalyst in 240–400°C for about 30 min in order to saturate the catalyst surface with sulfur. Hydrogen was then passed through the catalyst bed for about 1 h at 400°C to remove any weakly adsorbed sulfur and also to achieve a uniform distribution of sulfur on the catalyst surface. It was found that catalysts which were sulfided at either 240 or 400°C exhibit the same CO hydrogenation activities.

The crystallite size of metal was determined by X-ray diffraction (XRD) line-

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TABLE 1

Catalyst Characterization

Metal	Crystallite size (A°)	H_2 (Uptake (μmol/g)	Sulfided metal	S/M[a] ratio	H_2 Uptake (μmol/g)
15 Wt% Ni/SiO_2	92	110	$S-Ni/SiO_2$	0.46[b]	—[c]
3 wt% Rh/SiO_2	130	9.8	$S-Rh/SiO_2$	0.12	—
3 wt% Ru/SiO_2	80	18.8	$S-Ru/SiO_2$	0.2	—

[a] S/M: sulfur/metal.

[b] EDS was performed by ETEC Scanning Electron Microscope with Kevex DELTA V X-ray analyzer using ZAF correction.

[c] H_2 uptake is less than 0.5 μmol which is beyond the sensitivity of our thermal conductivity detector.

broadening technique. Hydrogen uptake of the catalysts was measured by hydrogen temperature-programed desorption (TPD). Sulfur content of the sulfided catalysts was measured by energy-dispersive spectroscopy (EDS). Infrared (IR) spectroscopy of CO adsorption was used to probe the effect of sulfidation on the metal surface of the catalysts. IR spectra of adsorbed CO 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 SiO_2-supported metal catalyst (*14*).

Both CO hydrogenation ($CO : H_2 = 1 : 1$) and ethylene addition studies were performed in a differential reactor system in 180–300°C and 10 atm. Product distribution was determined using an HP-5890A gas chromatograph with a 6-ft Porapak PS column in series with a 6-ft Porapak QS column.

RESULTS AND DISCUSSION

Results of hydrogen TPD, XRD, and EDS are listed in Table 1. No hydrogen desorption peak was observed for the sulfided catalysts. Sulfidation of Ni/SiO_2, Rh/SiO_2, and Ru/SiO_2 appears to result in the loss of hydrogen chemisorption capabilities. A number of studies on the sulfided metals have suggested that the fraction of metal surface which adsorbs hydrogen is inversely proportional to the fractional coverage of adsorbed sulfur (*8–11*). The loss of hydrogen chemisorption capability of the sulfided metals indicates that a significant fraction of metal surface was covered with adsorbed sulfur. EDS results show that the approximate ratio of sulfur to metal atom is 0.46 for sulfided Ni/SiO_2, 0.12 for sulfided Rh/SiO_2, and 0.2 for sulfided Ru/SiO_2. It should be noted that EDS results provide information about the bulk composition rather than the surface composition. Both CO hydrogenation and ethylene addition reactions did not lead to any significant change in the ratio of sulfur to metal.

Infrared Spectra of CO Adsorption

Figure 1 shows IR spectra of CO adsorption on the fresh and sulfided catalysts at 240°C and 1 atm. Two major bands were observed for CO adsorption on the fresh catalysts: linear CO at 2063 cm^{-1} and bridge CO at 1911 cm^{-1} for the Ni/SiO_2; linear CO at 2044 cm^{-1} and bridge CO at 1890 cm^{-1} for the Rh/SiO_2; and linear CO at 2036 cm^{-1} and a broad bridge-CO band around 1782 cm^{-1} for the Ru/SiO_2. The observed wave numbers of adsorbed CO are in good agreement with those reported for SiO_2-supported Ni (*15, 16*), Rh (*17, 18*), and Ru (*19–21*). Sulfidation of the catalysts resulted in (i) an inhibition of CO adsorption in the bridge form on the Ni, Rh, and Ru catalysts, (ii) a reduction in the intensity of linear-CO band for Ni and Ru catalysts and

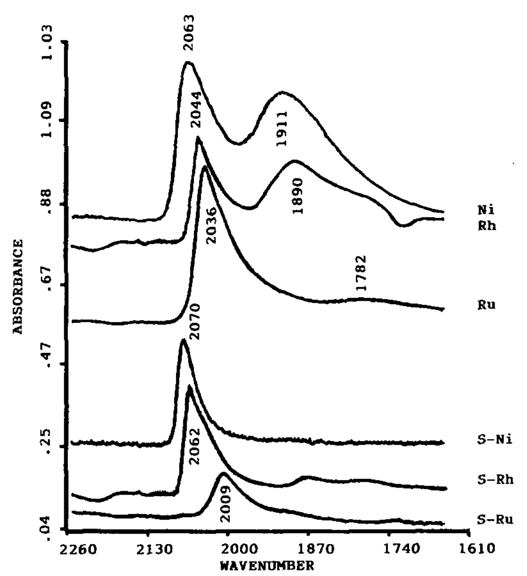

FIG. 1. Infrared spectra for CO adsorption on Ni/SiO_2, Rh/SiO_2, Ru/SiO_2, and their sulfided catalyst (240°C, 1 atm).

an increase in the linear-CO intensity for Rh catalyst, and (iii) an upward shift of the linear-CO wave number on the Ni and Rh catalyst and a downward shift of the linear-CO wave number on the Ru catalyst.

The variation of the linear-CO intensity has been found to depend on the coverage of sulfur on the metal and the extent of metal–sulfur interactions (*8, 10, 22*). The upward shift of linear-CO frequency can be attributed to the weakening of metal–CO bond. Such a shift has been observed on the sulfided Ni and Rh (*8, 10*). In contrast, sulfidation of Ru led to a slightly downward shift of the linear-CO wave number. The effect of adsorbed sulfur on CO adsorption on Ru has been shown to differ from those on Pt and Ni catalysts (*23*). Binding energy of CO on the sulfided Ru was found to be constant up to a certain concentration of adsorbed sulfur and adsorbed CO (*23*). The downward shift of 27 cm^{-1} of linear CO may be due to the reduction in the dipole–dipole coupling as a result of the decrease in the concentration of adsorbed CO on the sulfided Ru.

CO Hydrogenation

Table 2 lists results of CO hydrogenation. The results were obtained after 2 h of CO hydrogenation under steady-state flow conditions. Both Rh and Ru show stable activities for the reaction after long periods of reaction studies. In contrast, the activity of Ni catalyst continuously declines after the onset of the reaction. The deactivation of Ni was found to be primarily due to the loss of Ni metal atoms via formation of $Ni(CO)_4$ under reaction conditions (*24–26*). Ni/SiO_2 exhibited high methanation activity; Rh/SiO_2 demonstrated the highest C_2 oxygenate selectivity; and Ru/SiO_2 showed good activities and selectivity toward C_{2+} hydrocarbons. The results are consistent with those reported in the literature (*27–32*). Sulfidation of these catalysts resulted in the severe suppression of the overall CO hydrogenation. Methane was the major product. The poisoning effect of sulfur compounds on CO hydrogenation has been attributed to the suppression of hydrogen chemisorption as well as to the inhibition of dissociative chemisorption of CO brought about by the adsorbed sulfur (*8–10*).

The activation energies for CO conversion determined from Arrhenius plots for the unpoisoned and poisoned reaction are shown in Table 2. Due to the deactivation of Ni/SiO_2 during CO hydrogenation under 10 atm and 300°C, the activation energy for the Ni/SiO_2 cannot be measured accurately. Sulfidation not only decreased the activation energy but also reduced the overall reaction rate. The similar behavior for CO hydrogenation has been observed on sulfided Co catalysts (*8*).

Ethylene Addition

Table 3 shows the rate of product formation from ethylene addition to CO hydrogenation. The observation of C_3 oxygenates (propionaldehyde and propanol), ethane, methane, and C_2 oxygenates (acetaldehyde and ethanol) indicates that CO insertion, ethylene hydrogenation, and CO hydrogenation take place at the same time. The rates

TABLE 2

CO Hydrogenation

Catalyst	Rate of CO conv. (mol/kg-h)	Activation energy for CO conv. (kcal/mol)	Product formation rate (mol/kg-h)					
			CH_4	C_2H_4	C_2H_6	$C_{3+}HC$	CH_3CHO	C_2H_5OH
Ni/SiO_2	36.3	—	32.9	0.02	1.1	0.32	—	—
Rh/SiO_2	1.58	28.5	0.69	0.03	0.03	0.025	0.29	0.06
Ru/SiO_2	14.6	20.5	4.14	0.32	0.26	1.5	0.28	0.04
$S–Ni/SiO_2$	0.04	—	0.04	—	—	—	—	—
$S–Rh/SiO_2$	0.02	2.4	0.02	—	—	—	—	—
$S–Ru/SiO_2$	0.05	1.4	0.04	0.001	—	—	—	—

Note. Reaction conditions: 10 atm, 300°C, $CO : H_2 = 1 : 1$. $S–Ni/SiO_2$ represents the sulfided Ni catalyst.

of C_3 oxygenates formation reflect the CO insertion activities of the catalysts. The mechanism for the CO insertion has been suggested to resemble homogeneous ethylene hydroformylation (*3*, *4*). For Rh/SiO_2 and Ru/SiO_2 catalysts, the high rate of methane formation can be attributed to both CO hydrogenation and the hydrogenolysis of C_2 species, i.e., ethylene and ethane. In the case of Ni/SiO_2, the results of ethylene addition show low rates of formation of methane and C_{3+} hydrocarbons. This is due to the severe deactivation of Ni/SiO_2 during the reaction. Since the ethylene addition was conducted after 3 h of CO hydrogenation study, an appreciable amount of Ni was removed from the surface of the catalyst via formation of $Ni(CO)_4$ during the CO hydrogenation (*24*). Interestingly, such a deactivation for the hydrocarbon formation did not decrease the rate of propionaldehyde formation.

Comparison of results of ethylene addition on the unsulfided catalysts with those on the sulfided catalysts (see Table 3) shows that sulfidation has little effect on the rates of formation of propionaldehyde over Ni and Rh. Sulfidation resulted in a decrease in the rates of formation of CH_4, C_2H_6, C_2 oxygenates, and C_3 hydrocarbons on Ni, Rh, and Ru catalysts. The suppression of formation of hydrocarbons, especially for ethane, and a slight enhancement of CO insertion activity greatly increased the selec-

TABLE 3

Ethylene Addition to CO Hydrogenation

Catalyst	Product formation rate (mol/kg-h)							
	CH_4	C_2H_6	$C_{3+}HC$	CH_3CHO	C_2H_5OH	C_2H_5CHO	C_3H_7OH	$[C_3\ oxyg.]/[C_2H_6]$
Ni/SiO_2	0.5	14.4	0.11	—	—	1.1	0.05	0.077
Rh/SiO_2	2.5	25.5	0.2	0.62	0.2	2.7	1.7	0.17
Ru/SiO_2	11.7	17.5	5.8	0.9	0.08	2.2	0.42	0.15
$S–Ni/SiO_2$	0.1	3.6	0.004	—	—	1.4	0.08	0.41
$S–Rh/SiO_2$	0.08	5.1	0.04	0.009	—	2.5	0.24	0.53
$S–Ru/SiO_2$	0.1	0.3	0.001	—	—	0.03	—	0.1

Note. Reaction conditions: 10 atm, 300°C, $CO : H_2 : C_2H_4 = 1 : 1 : 0.02$.

tivity toward C_3 oxygenates for sulfided Ni and Rh as indicated by the increase in the ratio of C_3 oxygenates to C_2H_6.

In summary, sulfidation of Ni/SiO_2 and Rh/SiO_2 resulted in (i) blockage of bridge-CO sites, (ii) enhancement of CO insertion, and (iii) suppression of CO and ethylene hydrogenation. Although results of this study are not able to clarify the state of CO insertion sites (*2, 33–35*), the blockage of bridge-CO sites and enhancement of CO insertion brought about by adsorbed sulfur suggests that isolated Ni and Rh atoms may be responsible for catalyzing CO insertion. Adsorbed sulfur appears to disrupt the adjacent pairs of metal atoms acting as bridge-CO sites. Therefore, the remaining surface metal may form isolated atoms which only permit adsorption of CO in the linear form.

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