Effect of Potassium Promoter on the Adsorption of Carbon Monoxide on Silica Supported Ruthenium

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We have investigated the infrared spectra for carbon monoxide chemisorbed on silica supported ruthenium with and without potassium coating within the frequency range of 1800-2200 cm^{-1} at various ruthenium concentrations and CO pressures. For the system without potassium coating, three bands were observed in the infrared spectra when CO was adsorbed on both the reduced and oxidized form of supported ruthenium. However, the relative intensities of these three bands were found to have no interdependence. Therefore, we have assigned each of these bands as arising from the CO stretching vibration for carbon monoxide molecules adsorbed on the Ru sites of different nature. On coating with potassium, the 2030 cm^{-1} band observed for the system without potassium coating was found to suffer red shift by 10-30 cm^{-1} and we conclude that this bathochromic shift is caused by enhancement in the capability of back donation of electrons from the metal atom to the antibonding π^* orbitals of CO due to the presence of potassium.

Introduction

Ruthenium is known to exhibit unique catalytic properties among the noble metals. It is found that it is the excellent catalyst for the selective reduction of NO to N_2[1-3] and for the formation of hydrocarbons from CO/H_2 mixtures (Fischer-Tropsch synthesis).[4] Understanding of its catalytic property for the Fischer-Tropsch synthesis should be based on the study of nature of chemical bond between CO molecules and metal surface, and the infrared studies can be a powerful tool for such purpose.

Chemisorption of carbon monoxide on Ru surface has mostly been studied by making use of single crystals or thin films of the metal of interest,[5-7] but to the knowledge of present authors not much investigation has been carried out using supported metals due to the complexity of the latter systems. However, transition metal components are very often supported on high surface area carriers in the chemical industry. This produces highly efficient catalyst with maximum specific metal surface areas and improves its thermal stability and thus the life of the catalyst significantly.[8]

A number of infrared studies concerning carbon monoxide adsorbed on Ru have been reported previously. Lynds[9] observed two bands at 2152 and 2083 cm^{-1} for Ru supported on silica. Guerra and Schulman[10] identified two broad bands for CO adsorbed on silica-supported Ru. The band occurring between 2010 and 1990 cm^{-1} was assigned to the CO bond stretch in Ru-CO while the band occurring between 1910 and 1870 cm^{-1} was assigned to that due to the bridge type species Ru_2CO. Two bands in the region between 2100 and 1900 cm^{-1} were also reported by Kobayashi and Shirasaki[11] for silica-supported Ru. They did not make specific structural assignments for either band but suggested that both might be attributed to multiple adsorption of CO at a single Ru site.

The effect of Ru particle size on the infrared spectrum of CO adsorbed on alumina-supported Ru was discussed by Dalla Betta.[12] For particles of 90 Å or larger in diameter only a single band at 2028 cm^{-1} was observed, while, for particles of 60 Å or smaller, three bands in the vicinity of 2140, 2080, and 2040 cm^{-1} were found. The exact band positions in the latter case showed slight variations with varying particle size. The low-frequency (LF) band was assigned to CO adsorbed on low-coordination edge and corner metal atoms. These band assignments, however, have been questioned by Brown and Gonzalez.[13] They discovered that CO adsorption on a reduced Ru sample produced a strong band at 2030 cm^{-1} and weak bands at 2150 and 2080 cm^{-1}, whereas CO adsorbed on an oxidized silica-supported Ru produced a strong band at 2080 cm^{-1} and medium intensity bands at 2135 and 2030 cm^{-1}. The low-frequency (LF) band was assigned to CO adsorbed as the linear species Ru-CO while high-frequency (HF) and medium-frequency (MF) bands were assigned to CO adsorbed on a surface oxide and CO adsorbed on a Ru atom perturbed by a nearby oxygen atom, respectively. On the contrary Bell[14] assigned HF and MF bands to the symmetric and antisymmetric stretches of two CO molecules bonded to single oxidized Ru site based on his observation that the intensities of these two bands appeared to change in parallel in the process of CO desorption. We attempt to clarify this point also in this work.

In this paper we have investigated the IR spectra of carbon monoxide adsorbed on the reduced and oxidized Ru surface to gain more insight into the nature of chemical bond between chemisorbed CO molecules and metal surface. We have observed the positions and intensities of IR bands for adsorbed CO as a function of w/w percentage of Ru in silica-supported Ru, CO pressure and temperature of the system, respectively. We have also observed the changes in the IR spectra of CO when the surface of silica-supported Ru is covered with potassium as a function of CO pressure and temperature for better understanding of the effect of alkali promoters.

Experimental

To prepare the adsorbent an adequate amount of $RuCl_3 \cdot 3H_2O$ (Aldrich Chem. Co., reagent grade) was dissolved in distilled water and silica gel (HDK Wacker N20, BET surface area 200 m^2/g) was added to it so that a thin slurry was formed. The resulting slurry was stirred until a homogeneous mixture was obtained. This then was dried at 80-90 °C for 72 hours and was ground to fine powder using an agate mortar and pestle. After grinding, a portion of the powder was reduced at 300 °C for 24 hours under the stream of H_2

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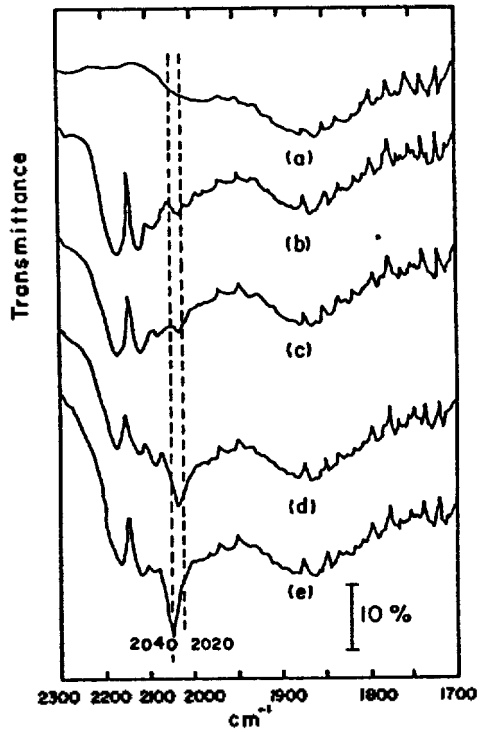

Figure 1. IR spectra for CO adsorbed on Ru-SiO_2 sample at CO pressure of 50 torr as a function of metal contents. Prereduction temperature was gradually increased at a rate of 10 °C/hr to 280 °C. (a) base line. (b) 2%. (c) 4%. (d) 10%. (e) 15%.

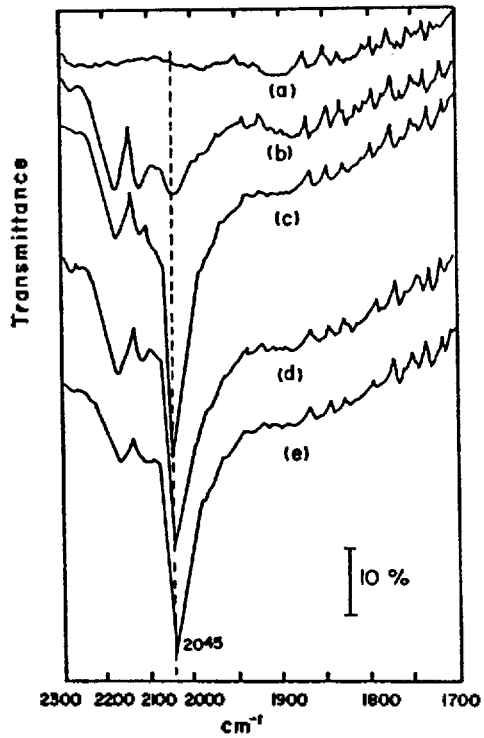

Figure 2. IR spectra for CO adsorbed on Ru-SiO_2 sample at CO pressure of 50 torr as a function of metal contents. Prereduction temperature was 300 °C. (a) base line. (b) 2%. (c) 4%. (d) 10%. (e) 15%.

and another portion of the powder was reduced in the H_2 atmosphere while elevating the temperature at a rate of 10 °C/hr to 280 °C. After this was accomplished, 30-40 mg of each portion of the powder was pressed into a pellet, 2 cm in diameter, using a pressure of 400 kg/cm^2. This pellet was placed in a cell connected to the vacuum system and was reduced at 300 °C for 50 minutes in the H_2 atmosphere and then was evacuated for 10 minutes twice. Finally, the system was cooled down to room temperature for the final evacuation and the adsorption experiment was performed.

The oxidized form of the catalyst was prepared by exposing the pellet, reduced in the manner described above, to oxygen under various conditions (pressures, temperatures, and exposure times).

The infrared cell used in this study was identical with that reported by Chang *et al.*[15] and the method of coating and annealing the sample with thin film of potassium was described by Park.[16] The amount of potassium contained in the catalyst sample was determined by measuring the electrode potential for the solution obtained by dissolving the sample in a known amount of water.

Hydrogen gas used for prereduction was a domestic product of 99.99% in purity while that used for reduction in the cell was the product of 99.9999% in purity obtained from the N. V. Philips Eindhoven Co. The CO and O_2 gases were purchased from the Matheson Gas Products Co., both of 99.99% in purity. These gases were used without further purification. All the IR spectra were recorded on a Perkin-Elmer Model 782 double beam infrared spectrophotometer using an *in situ* cell. To obtain the IR spectra, we have used the so-called differential technique in which a replica of the sample pellet containing the same Ru contents was employed as a filter for the reference beam.

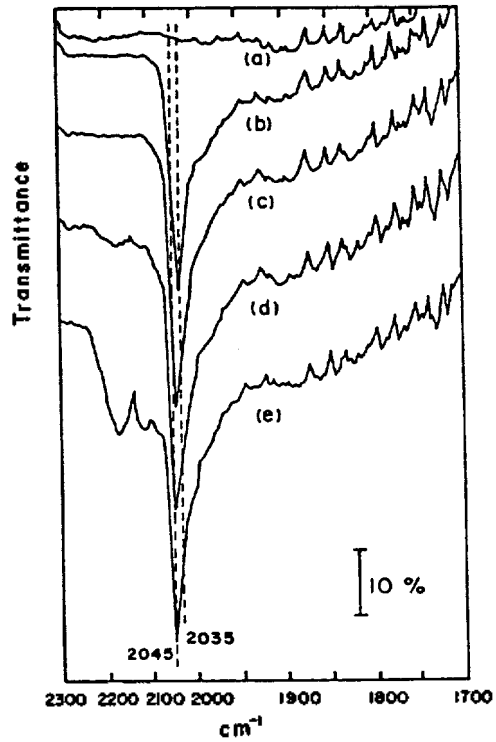

Figure 3. IR spectra for CO adsorbed on 4.0% Ru-SiO_2 sample at 20 °C as a function of CO pressure. (a) base line. (b) 0.1 torr. (c) 1.0 torr. (d) 10 torr. (e) 50 torr.

Results

(A) Adsorption of CO on silica-supported Ru without potassium coating. Shown in Figure 1 and Figure 2 are

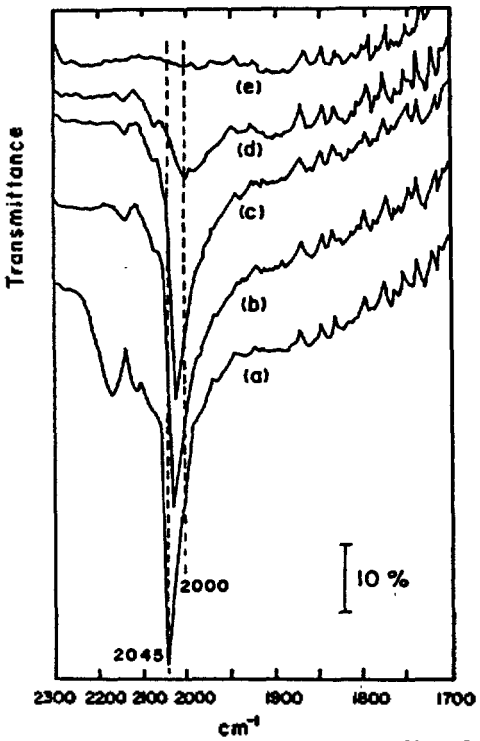

Figure 4. IR spectra for CO adsorbed on 4.0% Ru-SiO_2 sample after pumping at 20 °C. (a) CO pressure of 50 torr. (b) 5 min. of pumping. (c) 30 min. of pumping. (d) 12 hrs. of pumping. (e) base line.

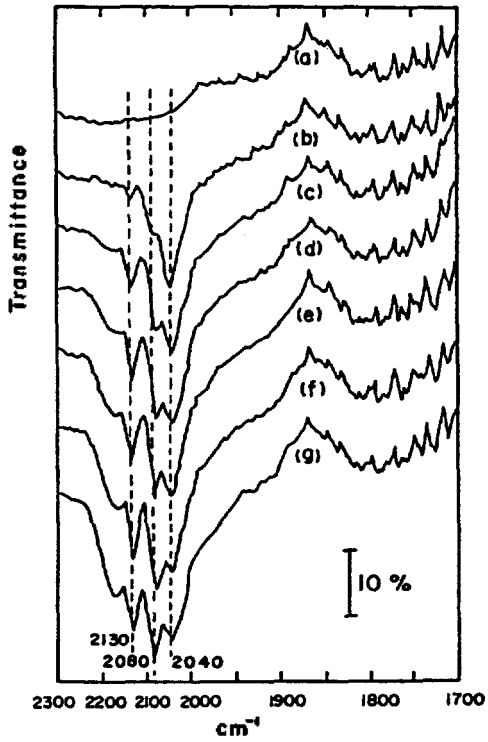

Figure 5. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample at 20 °C as a function of CO pressure. (Oxygen pressure; 10 torr, oxidation temperature; 300 °C, exposure time; 15 sec.). (a) base line. (b) below 0.1 torr. (c) 0.1 torr. (d) 1.0 torr. (e) 10 torr. (f) 20 torr. (g) 50 torr.

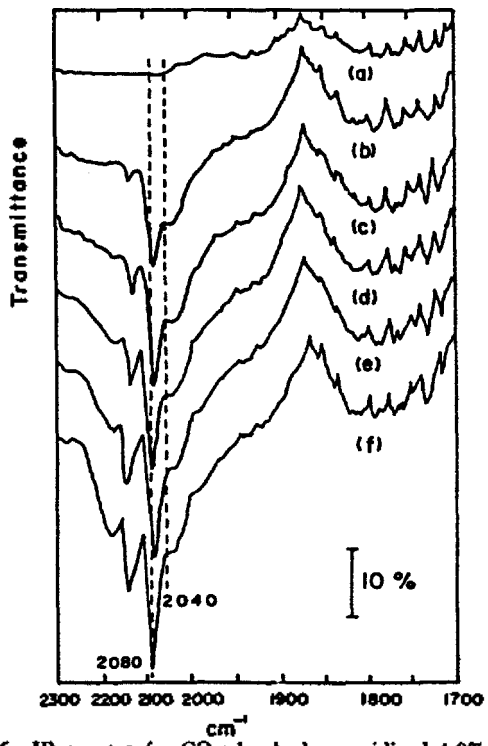

Figure 6. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample at 20 °C as a function of CO pressure. (Oxygen pressure; 150 torr, oxidation temperature; 20 °C, exposure time; 15 sec.) (a) base line (b) below 0.1 torr (c) 0.1 torr. (d) 1.0 torr. (e) 10 torr. (f) 50 torr.

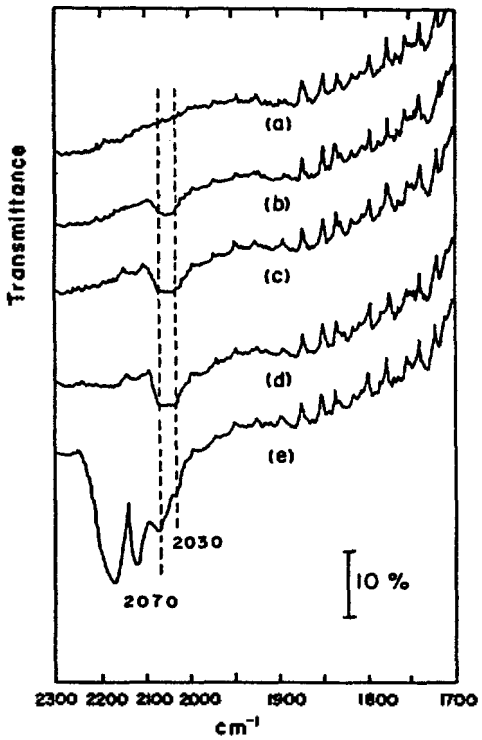

Figure 7. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample at 20 °C as a function of CO pressure. (Oxygen pressure; 50 torr, oxidation temperature; 300 °C, exposure time; 15 sec.) (a) base line. (b) 0.1 torr. (c) 1.0 torr. (d) 10 torr. (e) 50 torr.

the IR spectra taken at 20 °C and under CO pressure of 50 torr using the sample of several different Ru contents. The IR spectra shown in Figure 1 was obtained for the sample reduced in the H_2 while elevating the reduction temperature gradually at a rate of 10 °C/hr to 280 °C and those shown in Figure 2 was obtained for the sample reduced at 300 °C for

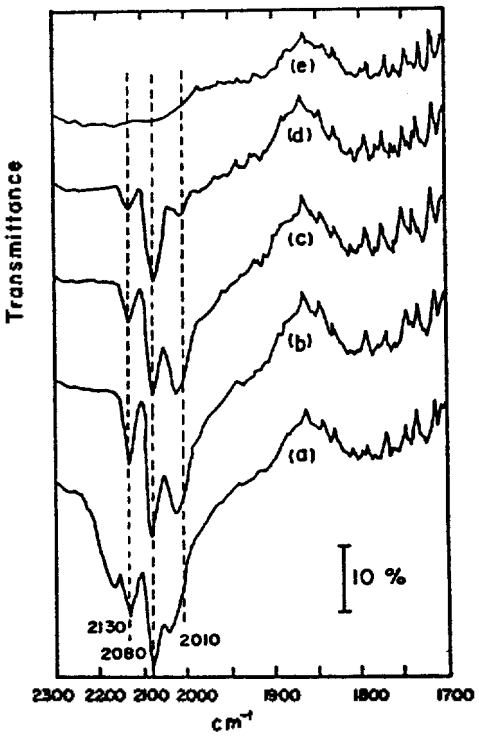

Figure 8. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample at 20 °C as a function of pumping time. (a) CO pressure of 50 torr. (b) 5 min. (c) 30 min. (d) 12 hrs. (e) base line.

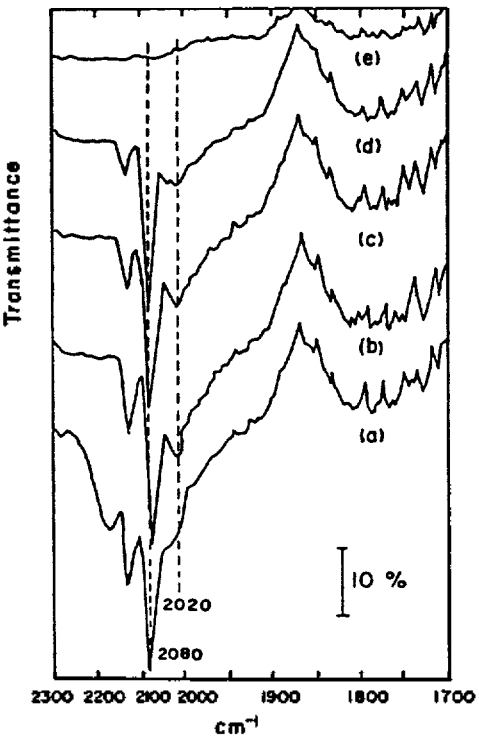

Figure 9. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample at 20 °C as a function of pumping time. (a) CO pressure of 50 torr. (b) 5 min. (c) 30 min. (d) 12 hrs. (e) base line.

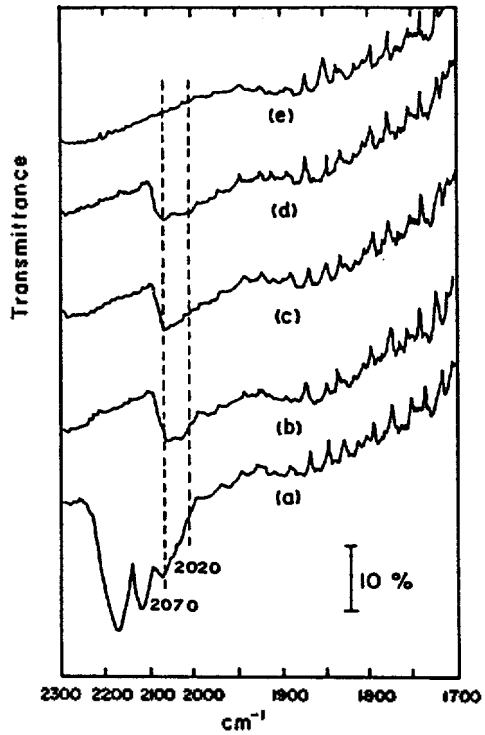

Figure 10. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample at 20 °C as a function of pumping time. (a) CO pressure of 50 torr. (b) 5 min. (c) 30 min. (d) 12 hrs. (e) base line.

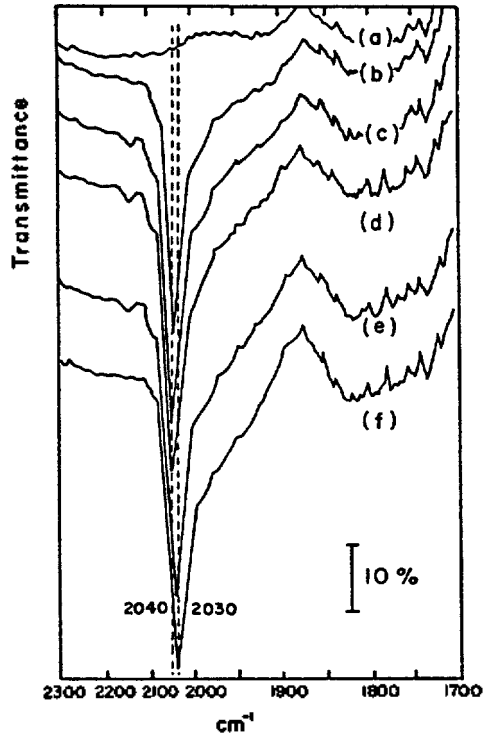

Figure 11. IR spectra for CO adsorbed on reduced 4.0% Ru-SiO_2 sample at 1.0 torr as a function of temperature. (a) base line. (b) 25 °C. (c) 50 °C. (d) 100 °C. (e) 150 °C. (f) 200 °C.

24 hours. It is evident from these figures that the degree of band frequency shift depends on the prereduction method. The results shown in Figure 3 and thereafter are all obtained for the sample reduced for 24 hours at 300 °C. Figure 3 shows us the IR spectra for CO adsorbed on silica-supported Ru at various pressures. Also shown in Figure 4 are the IR spectra obtained when pumped to vacuum (10^{-5} torr or lower). We see from Figure 4 that the LF band suffers red shift by 45 cm^{-1} as the CO pressure is gradually decreased. The IR spectra for increasing amounts of CO chemisorbed

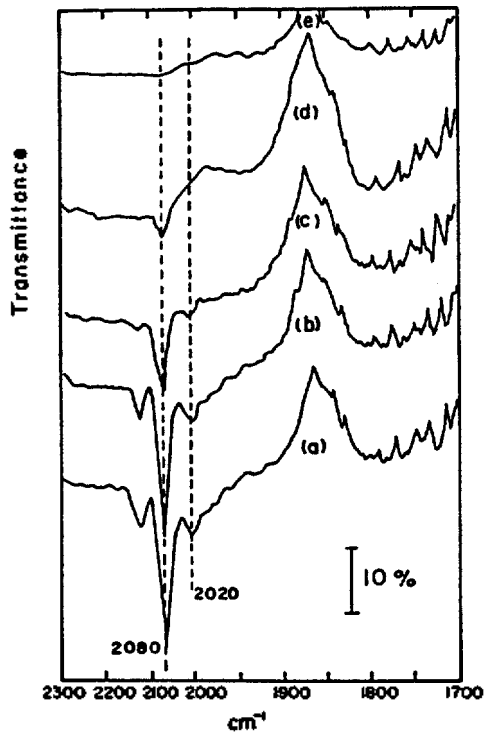

Figure 12. IR spectra for CO adsorbed on oxidized 4.0% Ru-SiO_2 sample after pumping as a function of temperature. (a) 25 °C (b) 100 °C (c) 150 °C. (d) 200 °C. (e) base line.

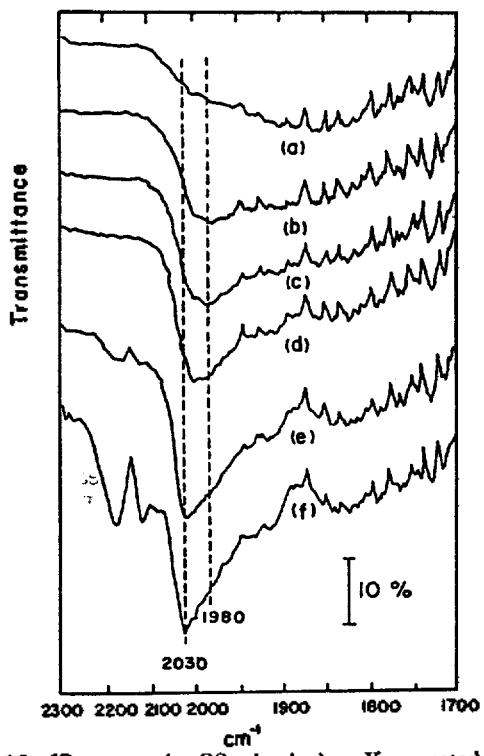

Figure 13. IR spectra for CO adsorbed on K-promoted 4.0% Ru-SiO_2 sample at 20 °C as a function of CO pressure. (a) base line. (b) below 0.1 torr. (c) 0.1 torr. (d) 1.0 torr. (e) 10.0 torr. (f) 50 torr.

on an oxidized 4% Ru-SiO_2 surface are shown in Figure 5 through Figure 7 while the corresponding desorption spectra are shown in Figure 8 through Figure 10, Figure 11 shows us the spectra for CO adsorbed on the reduced Ru sample at various temperatures. We see from this that above 150 °C the

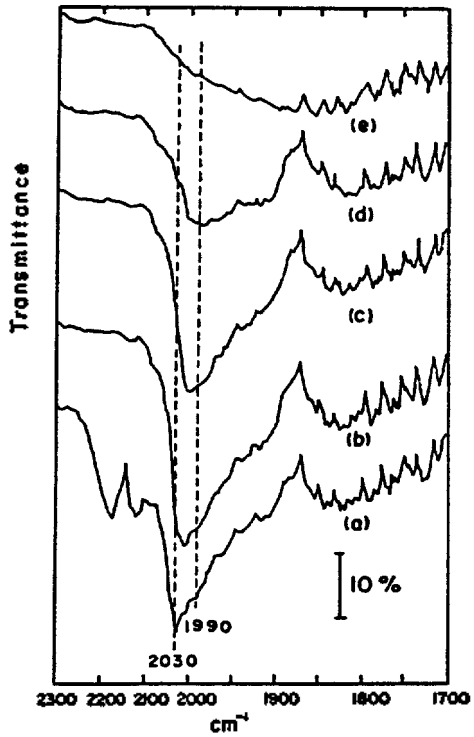

Figure 14. IR spectra for CO adsorbed on K-promoted 4.0% Ru-SiO_2 sample at 20 °C as a function of pumping time. (a) CO pressure of 50 torr. (b) 5 min. (c) 30 min. (d) 12 hrs. (e) base line.

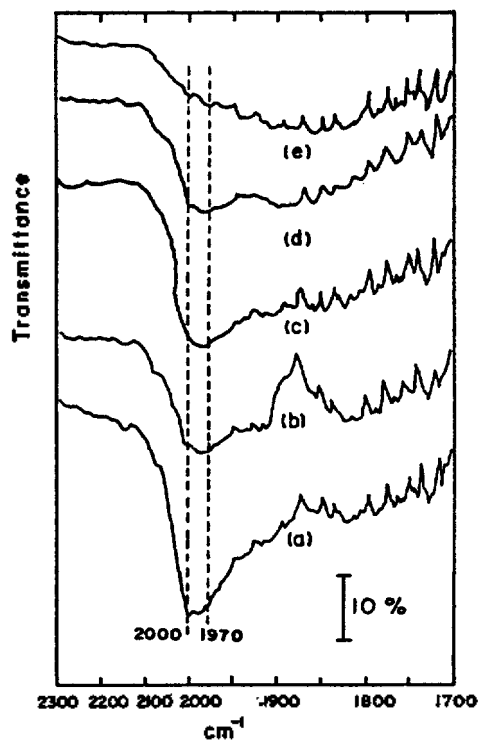

Figure 15. Desorption IR spectra for CO adsorbed on K-promoted 4.0% Ru-SiO_2 sample after evacuation for 12 hours as a function of potassium content in Ru-SiO_2 (potassium amount in g per mg of Ru). (a) 0.0. (b) 1.3×10^2. (c) 3.65×10^2. (d) 3.88×10^2. (e) base line.

high-frequency band disappears. Shown in Figure 12 are the IR spectra for an oxidized Ru sample obtained when evacuated for 12 hours at various temperatures. At high

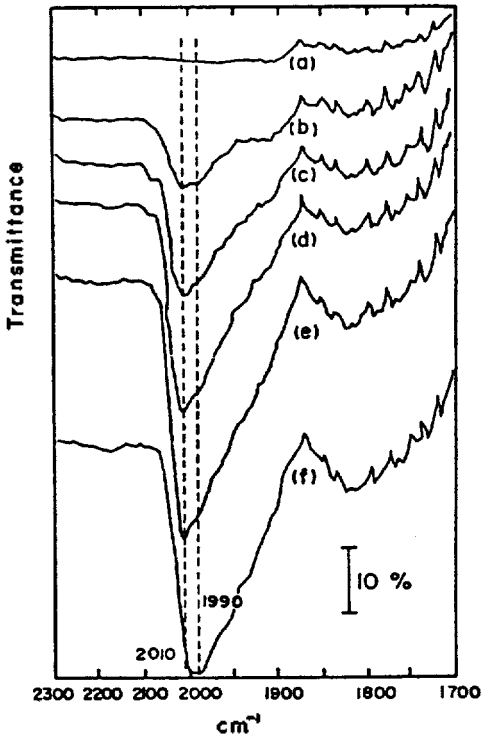

Figure 16. IR spectra for CO adsorbed on K-promoted 4.0% Ru-SiO_2 sample at 1.0 torr as a function of temperature. (a) base line. (b) 25 °C. (c) 50 °C. (d) 100 °C. (e) 150 °C. (f) 200 °C.

temperature only the MF band survives and other bands tend to disappear.

(B) Adsorption of CO on silica-supported Ru with potassium coating. Shown in Figures 13 and 14 are the adsorption and desorption IR spectra for silica-supported Ru (4% content) coated with potassium recorded under various conditions. Shown in Figure 15 are the IR spectra for CO adsorbed on the 4% Ru sample of several different degrees of potassium coverage after pumping for 12 hours at 20 °C. We have found that on coating with potassium the LF band observed for the system without potassium coating suffers red shift by 10-30 cm^{-1} as shown below:

potassium coverage (μg/1 mg of Ru)	0.0	1.3×10^2	3.65×10^2	3.88×10^2
band position (cm^{-1})	2000	1990	1980	1970

Figure 16 shows us the IR spectra for CO adsorbed on the Ru surface with potassium coating at various temperatures. As temperature goes up, the LF band with the strongest intensity shifts toward longer wavelength side and the HF and MF bands tend to disappear.

Discussions

The IR band positions observed in our experiment for carbon monoxide chemisorbed on silica-supported Ru without potassium coating are in good agreement with those reported by Dalla Betta,[12] Brown and Gonzalez,[13] and Bell.[14]

For the reduced Ru-SiO_2 sample the position of 2040 cm^{-1} is found to greatly depend on the Ru concentration in the sample. In the case shown in Figure 1 the 2030 cm^{-1} band suffers blue shift by as much as 15 cm^{-1} as the Ru contents are increased while in the case of Figure 2 virtually no shift is observed for this band. Thus the degree of such blue shift obviously depends on the prereduction method in the sample preparation process. Such dependence may be construed as due to the fact that reduction of $RuCl_3$ with gradual elevation of reduction temperature will produce smaller and better dispersed clusters of Ru particle than reduction at a constant and high temperature. When the surface metal atom on which chemisorption takes place is regarded as a central atom with its chemisorbed CO molecule(s) and surrounding metal atoms constituting ligands, the blue shift of 2030 cm^{-1} band means the increase in the number of surrounding Ru atoms near the Ru site. These surrounding Ru atoms have partially filled d orbitals that can form π bonds with the central atom, and therefore they may compete with the chemisorbed molecules for electrons from the central atom. As the extent for π bonding by back-donation of electrons from the central metal atom to the antibonding π^* orbital of the CO ligands becomes smaller, the M-C bond becomes weaker and the C-O bond stronger, which results in a higher stretching frequency of the C-O bond.[17] In the case shown in Figure 2 the band position of 2045 cm^{-1} band remains constant irrespective of increasing Ru concentrations because the Ru-SiO_2 sample heated at high temperature for 24 hours is not well dispersed and forms large clusters independent of Ru contents.[18]

In Figure 3 and 4 we see that the band first appearing at 2035 cm^{-1} gradually shifts toward 2045 cm^{-1} as more carbon monoxide is chemisorbed. This frequency shift is typical of CO adsorption on transition metal surfaces and has been interpreted by other authors. Eischens and coworkers[19] suggested the importance of dipole-dipole interactions between adsorbed CO adspecies. This view was also supported by Shigeish and King[20] in explaining the shift of band position from 2065 to 2101 cm^{-1} observed for increasing coverage on a Pt (111) ribbon. They attributed the frequency shift and the virtual invariance of the adsorption band halfwidth with increasing coverage to strong dipole-dipole interactions in the overlayer. In fact, as discussed by Bradshaw and Hoffmann,[21] the dipole-dipole interaction is only one of three possible interactions between adsorbed CO species on metal surfaces, the other two being indirect interaction via electron conduction and intermolecular repulsion. The indirect interaction between adsorbed CO molecules leading to frequency shifts was explained by Blyholder.[17] When the surface coverage by CO is high, the dipole-dipole and indirect interaction, which cause the increasing CO stretch frequency, seem to be dominant as the major interactions among adspecies.

To complement the studies performed using fully reduced sample, spectra were recorded for catalytic samples which had been intentionally oxidized. The IR spectra of CO chemisorbed on an oxidized Ru-SiO_2 surface are shown in Figure 5 through Figure 10. For this system three bands at 2130, 2080, and 2030 cm^{-1} are observed. Further oxidation of the Ru-SiO_2 sample results in a reduction in the band intensities due to decline in the transmittance of the catalyst disk. A similar loss of transmittance due to Ru oxidation has been noted by Brown and Gonzalez.[13] The relative intensities of the bands observed for this oxidized sample are different from those for the reduced sample. The band at 2080 cm^{-1} is

now the dominant feature in the spectrum with the band at 2030 cm^{-1} appearing as a shoulder on this band. A band of medium intensity at 2135 cm^{-1} is also observed. The enhancement in intensity of 2135 and 2080 cm^{-1} band when CO is adsorbed on an oxidized Ru surface suggests that the two high frequency CO bands arise from CO adsorbed on Ru sites perturbed by oxygen atoms. Although both high frequency CO bands are oxygen dependent, desorption experiments and temperature effect on chemisorption as presented in Figures 11 and 12 show that they are not related to each other. It is found that the 2135 cm^{-1} band diminish on desorption more rapidly than 2080 cm^{-1} band. It is important to note that our observation is in disagreement with that of Bell[14] who has reported that two bands behave in parallel in the process of desorption. Our observation is rather close to those of Dalla Betta[12] and Brown and Gonzalez.[13] Therefore, we conclude that the band assignment due to Brown and Gonzalez is more appropriate than that of Bell. Although we cannot determine the exact nature of these oxygen species at this stage, the appearance of 2140 and 2080 cm^{-1} band for the reduced Ru-SiO_2 sample suggests that oxygen atoms in silica are somehow involved in perturbing Ru sites.

As shown in Figures 13 and 14, for Ru-SiO_2 sample coated with potassium only the presence of 2030 cm^{-1} band is discernible and its band width is much broader than for the case of no potassium coating. Such band profile suggests that the C-O bond strength is weaker in comparison with the case of no potassium coating. Figure 15 tells us that the position of 2030 cm^{-1} band gradually shifts toward longer wavelength side as the amount of coating potassium is increased. This indicates that as the surface coverage by potassium increases, the C-O bond strength is weakened which in turn means that the M-C bond is fortified. The stronger M-C bonding on the K-promoted catalyst surface may be attributable to the electron donation properties of potassium.[22] An increase in the electron density on Ru surface sites, which are in close proximity to the promoter atoms, would result in an increase in the strength of carbon-metal bond by virtue of the back donation of electrons from d orbitals of the metal atom to the antibonding π^* molecular orbitals of CO. These K-promoted surface sites which bind carbon monoxide more strongly are responsible for the red shift of IR bands shown in Figure 15.

Conclusions

The following important conclusions emerge from this study:

(1) The 2030 cm^{-1} band for the reduced Ru-SiO_2 sample may or may not exhibit blue shift as the Ru contents is increased depending on the prereduction method in the sample preparation process and this shift can be understood on the basis of argument due to Blyholder.[17]

(2) As the surface coverage by CO increases, dipole-dipole and indirect interactions, which are responsible for increasing of the CO stretch frequency, seem to become dominant factors in the interactions between adspecies.

(3) We conclude that two high frequency CO bands observed for the oxidized Ru-SiO_2 sample arise from CO adsorbed on the Ru sites perturbed by nearby oxygen atoms, but desorption experiment tells us that these two bands are not related to each other.

(4) The promoter effect comes from the electron donation properties of potassium. Enhancement in the capability of back donation of electrons from the central metal atom to the antibonding π^* orbital of CO results in the stronger metal-carbon bond which in turn weakens the carbon-oxygen bond. This effect is visualized by the red shift exhibited by the 2030 cm^{-1} band as the amount of coating potassium is gradually increased.

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