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Infrared Spectroscopic Study of CO + H_2 Reaction over TiO_2-Supported Rh Catalysts

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The hydrogenation of CO over TiO_2-supported Rh catalysts has been investigated by using a Fourier-transform infrared spectrometer. The adsorbed hydrocarbon species and surface acetate ions were observed during the CO + H_2 reaction. From the reactivity of these species toward various treatments, it is concluded that these species are not reaction intermediates but are accumulated on the support near Rh metal. Dependences of adsorbed CO on the evacuation or reduction temperature have also been examined in detail.

INTRODUCTION

Infrared spectroscopy is a useful technique in studying reaction intermediates and mechanisms of heterogeneous catalysis because it can be applied under reaction conditions where higher temperatures and pressures are needed, and provides a large amount of information from the vibrational spectra of adsorbed species. A number of papers have been devoted to the infrared spectroscopic studies of the CO + H_2 reaction over various supported catalysts (*1–14*). Blyholder and Neff (*1a*) observed infrared bands in the C–H and O–H stretching regions and considered the existence of oxygen-containing intermediates such as CHO(a) or HCHO(a). However, recent studies have provided experimental evidence contradicting the mechanism of oxygen-containing species as an intermediate of hydrocarbon synthesis. Dalla Betta and Shelef (*2*) observed bands attributable to surface hydrocarbon, formate, and carbonate structures, but found out that these species were ascribed to reaction products adsorbed on the support. Furthermore, Ekerdt and Bell (*3*) reported that these hydrocarbon species did not appear to be the reaction intermediates of the hydrocarbon synthesis. On the other hand, Yamasaki *et al.* (*5a*) demonstrated that surface hydrocarbon species formed on Ru/SiO_2 during CO + H_2 reaction play a role as a reservoir of carbon atoms for hydrocarbon synthesis, which may be supplied as C_1 species through the scission of their carbon–carbon bonds. Previously, we have examined the CO + H_2 reaction over SiO_2-supported Rh catalysts by combining infrared spectroscopy with the isotope tracer method and demonstrated that a part of surface hydrocarbons play an intermediate for both hydrocarbon synthesis and acetaldehyde formation (*14*). In spite of these numerous studies (*1–14*), the precise features of adsorbed species under reaction conditions are not understood very well.

Metal–support interaction is a topic of great importance in current research involving supported transition-metal cata-

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lysts. To cite a few recent examples, Vannice and Garten (*15*) showed that Ni/TiO_2 catalysts are more active in methanation than Ni/Al_2O_3 or Ni/SiO_2 catalysts and produce higher-molecular-weight paraffins. Solymosi *et al.* (*9*) studied the hydrogenation of CO on various supported Rh catalysts. They found that the support exerts a marked influence on the specific activity of Rh, the order being $TiO_2 > Al_2O_3 > SiO_2 > MgO$. They assumed that TiO_2, which is an *n*-type semiconductor, provides much greater electronic interaction with Rh than Al_2O_3, SiO_2, or MgO.

Infrared spectroscopic studies of TiO_2-supported catalysts have not been carried out as extensively as those of Al_2O_3-supported catalysts because of low transmittance of TiO_2 support. In the present work, we have measured infrared spectra of adsorbed species on TiO_2-supported Rh catalysts during the $CO + H_2$ reaction by using a Fourier-transform infrared spectrometer and examined the reactivities of the adsorbed species toward various treatments in detail. It has been found that adsorbed hydrocarbon species and surface acetate ion are not reaction intermediates but are accumulated on the support near Rh metal. Furthermore, dependences of adsorbed CO during $CO + H_2$ reaction on the temperature of H_2 reduction treatment have also been investigated.

EXPERIMENTAL

The catalysts were prepared by impregnating aqueous solutions of metal salts ($RhCl_3$, $Rh(NO_3)_3$, Na_3RhCl_6, or a mixture of $RhCl_3$ and alkaline chlorides) onto TiO_2 (P-25, Nippon Aerosil, anatase ≈ 90%, 50 m^2/g). After the impregnation, the catalysts (5 wt% Rh) were dried in air at 383 K for ≈ 12 h. The dried catalysts were ground to a fine powder and pressed into self-supporting disks (2 cm in diameter and ≈100 mg in weight) at 150 atm. One disk was placed into an infrared cell, which was connected to a gas circulation system, and reduced by hydrogen between 473 and 723 K for several hours inside the cell.

Infrared spectra were recorded at room temperature by a JEOL JIR-03F Fourier-transform infrared spectrometer with an MCT (HgCd–CdTe) detector cooled by liquid nitrogen. Spectral resolution of the spectrometer was fixed at 2 cm^{-1} in the region 4000–1000 cm^{-1}.

Hydrogen gas from a commercial cylinder was purified by passing over an Engelhard Deoxo unit followed by passage through a liquid nitrogen cold trap. Carbon monoxide was passed through a liquid nitrogen cold trap immediately before use in order to remove water impurity.

RESULTS AND DISCUSSION

Infrared Spectra of Adsorbed Species on TiO_2-Supported Rh Catalysts

Infrared spectra of adsorbed species on $Rh–Na/TiO_2$ (Na_3RhCl_6) catalyst (the metal precursors are shown in parentheses) during CO adsorption at room temperature and $CO + H_2$ reaction at 453 K were investigated and are shown in Fig. 1. In the case of CO adsorption at room temperature (Fig. 1a), three types of adsorbed CO were observed: twin CO(a), $Rh(CO)_2$, at 2094 and 2031 cm^{-1}; linear CO(a), Rh(CO), at 2060 cm^{-1}; bridged CO(a), $Rh_2(CO)$, at 1817 cm^{-1}. The band intensity of the bridged

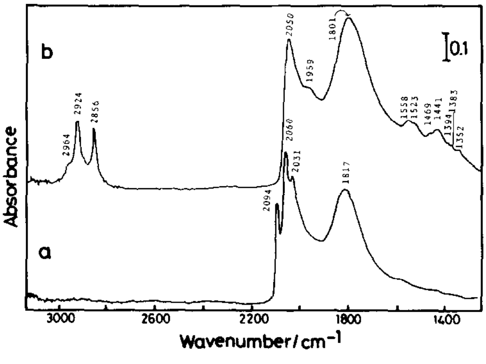


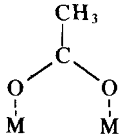
FIG. 1. Infrared spectra of adsorbed species on $Rh–Na/TiO_2$ catalyst: (a) CO adsorption at room temperature (P = 160 Torr); (b) $CO + H_2$ reaction at 453 K for 2.5 h (P° = 240 Torr, CO/H_2 = 2).

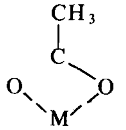
species relative to the linear species was greater for Rh–Na/TiO_2 (I_{br}/I_l = 0.65) than for Rh/TiO_2 ($RhCl_3$) (I_{br}/I_l = 0.27) (*13*) or Rh/TiO_2 ($Rh(NO_3)_3$) (I_{br}/I_l = 0.29), suggesting the modification of the chemical state of rhodium metal by added sodium cations. Addition of alkali is known to result in an increased electron density on the metal (*16*). The increasing charge in the 3*d* band of the metal enhances the π-donation from the metal into the antibonding π-orbital of CO, causing the increase in the metal–CO bond strength and bringing the suitable conditions for the formation of the multiple adsorption sites. By X-ray photoelectron spectroscopy, only sodium in the oxidation state of 1+ was detected on the catalyst surface even after the H_2 reduction. Under the reaction conditions (Fig. 1b), the infrared bands of twin species disappeared, but a new band at 1959 cm^{-1} appeared as a shoulder, which suggested the competitive adsorption of hydrogen to the same site of twin CO(a) (e.g., RhH(CO)) and the increased π-donation from the Rh into the antibonding π-orbital of CO, which resulted in the decrease in CO stretching frequency (*9*). This shoulder also appeared at 1923 cm^{-1} when adsorbed CO was hydrogenated at 373 K.

TABLE 1

Infrared Absorption Wavenumbers of Surface Acetate Ions on Rh–Na/TiO_2 from Hydrogenation of CO or Adsorption of Acetic Acid or Acetaldehyde

Reactions	Bridge acetate[a]		Bidentate acetate[b]	
	ν_{as}	ν_s	ν_{as}	ν_s
$^{12}CO + H_2$[c]	1606	1392	1529	1441
$^{12}CO + D_2$[c]	1597	1381	1514	1423
$^{13}CO + H_2$[c]	1574	1367	1487	1400
$^{13}CO + D_2$[c]	1558	—[e]	1466	1390
CH_3CHO[c]	1603	1394	1527	1437
CH_3COOH[d]	1601	1398	1539	1445

[a]


[b]


[c] T = 453 K.
[d] T = 300 K.
[e] Not determined because of very weak intensity.

Over Rh–Na/TiO_2 catalyst, C_2-oxygenated compounds (acetaldehyde and ethanol) were produced in relatively high selectivity from CO + H_2 reaction below atmospheric pressure (*17*). The selectivities in CO + H_2 reaction at 453 K (in carbon efficiency, %) were as follows: methane, 24; C_{2+} (hydrocarbons higher than methane), 57; acetaldehyde, 12; ethanol, 6 for Rh–Na/TiO_2: methane, 16; C_{2+}, 84 for Rh/TiO_2. Other bands due to accumulated hydrocarbon species and surface acetate ions were also observed in Fig. 1b. The bands at 2856 and 2924 cm^{-1} can be assigned to the symmetric and asymmetric C–H stretching vibration modes of methylene group, and the shoulder at 2964 cm^{-1} to the asymmetric C–H stretching vibration mode of methyl group. In the region 1600–1400 cm^{-1}, several bands appeared, which can be assigned to the asymmetric and symmetric modes of O–C–O stretching vibration of two types of adsorbed acetate ions (bridge and bidentate structures) (*18*). To confirm these assignments, the experiments using isotopes such as ^{13}CO and D_2 and the adsorption of acetaldehyde or acetic acid were carried out. The infrared absorption wavenumbers of produced acetate ions are summarized in Table 1. The reasonable isotope shifts were observed (*19*) in all the cases, and adsorption of acetaldehyde or acetic acid caused the formation of surface acetate ions which exhibited the same wavenumbers as those from CO + H_2 reaction. In order to confirm where these hydrocarbon species and acetate ions were located, the adsorption of olefinic hydrocarbons and acetaldehyde on TiO_2 reduced at 523 K by hydrogen was carried out at 473 K. By infrared spectroscopy, similar bands

TABLE 2

Reduction Temperature Dependence of Adsorbed CO on Rh–Na/TiO_2 Catalyst During CO + H_2 Reaction

H_2 reduction (temp(K) × time(h))	IR band position of CO(a) (cm^{-1}) absorbance in parenthesis		
	Linear	Bridged	I_{br}/I_l[a]
523 × 2[b]	2042 (0.62)	1807 (0.59)	0.94
573 × 1[c]	2044 (0.52)	1797 (0.39)	0.75
623 × 1[c]	2048 (0.36)	1798 (0.22)	0.61
673 × 1[c]	2056 (0.13)	1799 (0.04)	0.33
723 × 1[b,c]	—[d]	—[d]	

[a] The ratio of absorbance of bridged CO(a) to that of linear CO(a).

[b] Reaction temperature = 453 K.

[c] Reaction temperature = 473 K.

[d] Not observed.

attributing to surface hydrocarbons and acetate ions were observed in considerable intensity on TiO_2 support alone. Consequently, it can be considered that hydrocarbon species and acetate ions during CO + H_2 reaction were accumulated on TiO_2.

Table 2 shows the dependence of adsorbed CO on Rh–Na/TiO_2 during the CO + H_2 reaction upon the temperatures of H_2 reduction treatment before the reaction. As the reduction temperature increased, the absorbance of both the linear and the bridged CO(a) decreased and the catalytic activity in CO + H_2 reaction did, too. However, the selectivity and activation energy of product formation from the CO + H_2 reaction remained almost unchanged (*17*). This phenomenon is considered to be related to the SMSI (strong metal–support interaction) (*13*). The SMSI effect blocked the multiple adsorption sites (i.e., bridged CO(a)) preferentially, but had little influence on the band positions of adsorbed CO. After the oxidation at 723 K followed by reduction at 473 K, the ability of the catalyst to adsorb CO and the catalytic activity in CO + H_2 reaction could be recovered.

As mentioned above, the band intensity and/or position of adsorbed CO are very dependent on the compositions and pretreatments of the catalysts. Therefore, we can use the infrared spectra of adsorbed CO as the probe of the chemical state of supported rhodium.

Reactivity and Stability of Adsorbed Species toward Various Treatments

The reactivities of adsorbed species on Rh–Na/TiO_2 toward evacuation and reduction were examined after the CO + D_2 reaction at 453 K for 13.25 h, and the results are shown in Table 3 and Fig. 2. On evacuation up to 453 K (Fig. 2b), the bands of the linear and bridged CO(a) decreased in intensity and shifted to lower wavenumbers. However, their responses to evacuation were considerably different from each other: (i) the linear CO(a) decreased monotonically, but the bridged CO(a) increased at first and then decreased; (ii) the shift of the linear CO(a) to lower wavenumber (81 cm^{-1}) was larger than that of the bridged CO(a) (44 cm^{-1}); and (iii) the linear CO(a) almost disappeared after evacuation at 453

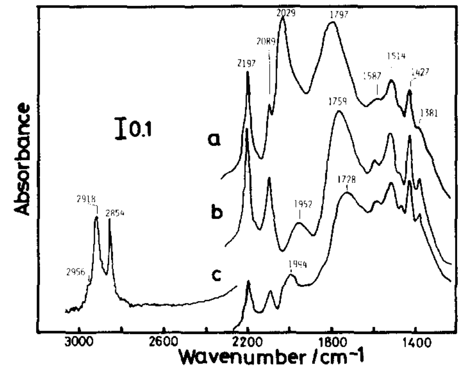


FIG. 2. Infrared spectra of adsorbed species on Rh–Na/TiO_2 catalyst: (a) CO + D_2 reaction at 453 K for 13.25 h (P° = 240 Torr, CO/D_2 = 2); (b) evacuation at 453 K for 1 h after (a) followed by evacuation at 373 K for 0.75 h; (c) H_2 reduction at 373 K for 0.5 h after (b) followed by further evacuation at 453 K for 1 h (P = 110 Torr).

TABLE 3

Reactivity of Adsorbed Species on Rh–Na/TiO_2 Catalyst from CO + D_2 Reaction at 453 K for 13.25 h toward Various Treatments

Treatment	IR band position (cm^{-1}), absorbance in parentheses					
	CD_2(a)	CO(a)			Acetate-d_3[a]	
	ν_{as}	Linear	Bridged	I_{br}/I_l[c]	ν_{as}	ν_s
CO + D_2 at 453 K for 13.25 h[b]	2197 (0.29)	2029 (0.45)	1797 (0.43)	0.97	1514 (0.10)	1427 (0.10)
Evacuation at 373 K for 0.75 h	2197 (0.32)	2019 (0.38)	1793 (0.48)	1.3	1516 (0.13)	1427 (0.13)
Evacuation at 453 K for 1 h	2197 (0.33)	1952 (0.06)	1759 (0.38)	6.6	1518 (0.14)	1427 (0.15)
Evacuation at 453 K for 2 h	2197 (0.33)	1948 (0.04)	1753 (0.36)	9.3	1518 (0.14)	1427 (0.16)
	CH_2(a)	CD_2(a)	Acetate-d_3[a]		Acetate-h_3[a]	
	ν_{as}	ν_{as}	ν_{as}	ν_s	ν_{as}	ν_s
H_2 reduction at 373 K for 0.5 h	2918 (0.26)	2195 (0.11)	1516 (0.10)	1427 (0.11)		
H_2 reduction at 373 K for 1 h	2916 (0.26)	2195 (0.09)	1518 (0.09)	1427 (0.11)		
H_2 reduction at 453 K for 0.5 h	2916 (0.06)	2195 (0.03)			1533 (0.07)	1439 (0.07)
H_2 reduction at 473 K for 0.5 h					1533 (0.05)	1437 (0.06)

[a] Bidentate structure.

[b] The spectrum remained almost unchanged by evacuation at 300 K for 0.5 h.

[c] The ratio of absorbence of bridged CO(a) to that of linear CO(a).

K for 2 h, whereas ≈80% of the initial amount of the bridged CO(a) remained on the catalyst. These results suggest that at lower coverage of CO the catalyst surface is covered mainly by bridged CO(a) and that the adsorption sites for the linear and bridged CO(a) are interchangeable.

On the other hand, the accumulated hydrocarbon species and surface acetate ions remained almost unchanged on evacuation (the first evacuation at 373 K caused the small increase in the band intensities of these species, which is probably due to the change of background spectrum of TiO_2 support). During the H_2 reduction at 373 K (Fig. 2c), C–H stretching vibrations were observed with the corresponding decrease in band intensity of CD_2(a), indicating that CH_2(a) and CH_3(a) species were formed by a rapid hydrogen exchange reaction between CD_2(a) or CD_3(a) and H_2 gas, especially in the absence of the inhibition by adsorbed CO. On the contrary, the hydrogen exchange reaction between deuterated acetate ions and H_2 gas was observed at temperatures higher than 453 K, but the hydrogenation of surface species proceeded simultaneously and the band intensities decreased considerably. Some acetate ions remained on the catalyst even after H_2 reduction at 473 K, whereas other surface species disappeared completely.

The same experiments were carried out for nonalkali metal cation doped catalyst

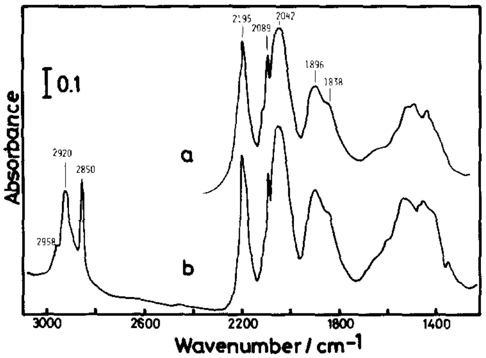


FIG. 3. Infrared spectra of adsorbed species on Rh/TiO_2 ($RhCl_3$) catalyst: (a) $CO + D_2$ reaction at 453 K for 7 h ($P° = 240$ Torr, $CO/D_2 = 1$); (b) $CO + H_2$ reaction at 453 K for 4.5 h after (a) ($P° = 180$ Torr, $CO/H_2 = 1$).

(i.e., Rh/TiO_2 ($RhCl_3$)), and similar reactivities of adsorbed hydrocarbon species and surface acetate ions were observed. Furthermore, the reactivity of CH_x(a) species was also studied for Rh/TiO_2 ($RhCl_3$) in the presence of CO under reaction conditions (Fig. 3). After the formation of CD_2(a) and CD_3(a) species by the reaction of $CO + D_2$ at 453 K, the infrared cell was cooled to room temperature, and the gas phase was evacuated (Fig. 3a). The mixture of $CO + H_2$ was introduced onto the catalyst, and the temperature was raised again to 453 K (Fig. 3b). During this procedure, the amount of CD_2(a) and CD_3(a) species remained almost unchanged but the bands due to CH_2(a) and CH_3(a) species emerged independently of the amount of CD_x(a). Therefore, it is concluded that most of the hydrocarbon species and acetate ions observed during the reaction are not reaction intermediates but are accumulated on the support near Rh metal. In a previous paper (*13*), we have estimated the amounts of surface hydrocarbons on Rh/TiO_2 ($RhCl_3$) and found that adsorbed hydrocarbons grow in a linear form, whose chain length increases up to 30. A similar chain length of surface hydrocarbons was observed for Ru/SiO_2 previously (*5a*), but their reactivities are quite different from those on TiO_2-supported Rh catalysts; surface hydrocarbons on Ru/SiO_2 are much more reactive, readily dehydrogenated to form carbon and hydrogen on evacuation, and also hydrogenated to form mainly methane with some higher hydrocarbon even at 375 K. In the case of Ru/SiO_2, it is considered that the adsorbed hydrocarbons grow in a linear form on a limited part of Ru surface. On Rh/SiO_2 (*14*), much smaller band intensities and chain length of accumulated hydrocarbons were observed previously, and the reactivity of adsorbed hydrocarbons had a much greater resemblance to those on Ru/SiO_2 than on Rh/TiO_2.

CONCLUSIONS

Infrared spectra of adsorbed CO on Rh are very sensitive to the compositions and pretreatments of catalysts. For example, the addition of sodium cations increases the band intensity of bridged CO(a) relative to the linear species. The adsorbed hydrocarbon species and surface acetate ions are observed during $CO + H_2$ reaction and are stable toward evacuation up to 453 K. The hydrogen exchange reaction of adsorbed hydrocarbons with gaseous hydrogen is observed at 373 K but hydrogenation of these species does not occur up to 453 K. The surface acetate ions are the most inactive among all the adsorbed species. When $CO + H_2$ reaction is carried out after $CO + D_2$ reaction, CH_x(a) emerges independently of the amount of CD_x(a) and the band intensity of CD_x(a) is almost unchanged. The adsorption of olefinic hydrocarbons and acetaldehyde on TiO_2 produces the similar infrared spectra of adsorbed species. Therefore, most of the hydrocarbon species and acetate ions are not reaction intermediates but are accumulated on the support near Rh metal.

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