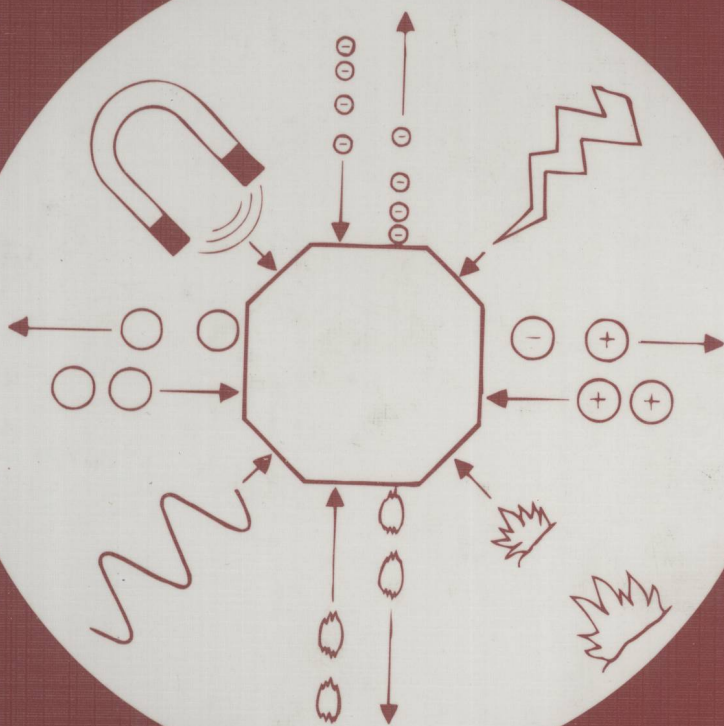


studies in surface science and catalysis



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12th INTERNATIONAL CONGRESS ON CATALYSIS

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***In situ* Infrared Spectroscopic Study of the Reaction between CO and H₂ over an Sm₂O₃ Catalyst**

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The adsorption and reaction of CO and hydrogen over the surface of Sm₂O₃, one of the lanthanide oxides, were investigated by *in situ* infrared spectroscopy. H₂ adsorbed over the surface to form OH and bridged type hydride. The bridged hydride selectively reacted with CO to form three kinds of HCO type species, while the surface species produced from the adsorption of CO were stable and coexisted with the hydrogen adsorbed species under H₂ atmosphere. The HCO species were assigned by infrared spectra to on-top formyl, bridged and dyhapt types. The HCO species were mainly produced under the mixed gas of CO and H₂, where the content of CO is relatively high, below 373 K. Under the mixed gas where the content of H₂ was much higher than CO (H₂/CO>100) over 300 K, production of methoxide(CH₃O-) was confirmed in the time course. The mechanism as well as the dynamics of the formation of surface species are discussed.

1. INTRODUCTION

CO hydrogenation have been carried out over variety of the catalyst systems. Among them, oxide catalysts exhibit characteristic abilities to the activity and the selectivity of products[1-3]. Particularly, when lanthanide oxides are used in this reaction, the specific selectivity to hydrocarbons, such as C₂ to C₄ olefins, has been reported[2,3]. A number of techniques has been applied in order to make clear the reaction over oxide surfaces. Infrared (IR) spectroscopy is one of the useful technique and applied to identification of surface intermediates produced under reaction condition as well as to examine the reaction of the produced intermediates. This technique has been practically applied to the study of CO hydrogenation over such oxide surfaces as ZnO and ZrO₂ [4,5]. However, few investigations of the reaction over lanthanide oxides have been carried out.

We have studied the production and the reactivity of surface species over Sm₂O₃ by IR [6-8]. Particularly, we have investigated the reactivity of C₁ species, such as methoxide and formate, over the surface to characterize the surface species produced under the hydrogenation of CO. We have also observed adsorbed hydrogen and examined their properties.

In this paper, we investigate the reaction between CO and hydrogen over an Sm₂O₃ surface by *in situ* IR technique. Here we report the production and the reactivity of the surface intermediate to clarify the reaction mechanism over the surface.

2. EXPERIMENTAL

The Sm_2O_3 catalyst used in this work was prepared by calcining samarium hydroxide precipitate, obtained by hydrolysis of $\text{Sm}(\text{NO}_3)_3$ with NH_4OH , at 773 K in air. The prepared catalyst (60 mg) was pressed into self-supporting pellet, and placed in an IR cell made of quartz. The IR cell was connected to an iso-volumetric system attached to a vacuum line. The pressure in the system was precisely monitored at the range 0.1 Pa by capacitance manometer (MKS Baratron) to know the pressure change originated from the adsorption and reaction of gases. The catalyst was repeatedly oxidized in O_2 and reduced in H_2 at 873 K until the carboxylate like impurity disappeared in the background spectrum and evacuated at 1000 K before use as pretreatment. IR spectra during the course of the reaction were recorded on an FT-IR (Jasco. 7300) with liquid nitrogen cooled MCT detector. The spectra were typically measured with 100 scans at 4 cm^{-1} resolution, and obtained by subtraction of the background spectrum of Sm_2O_3 from that of containing adsorbed species.

3. RESULTS AND DISCUSSION

IR spectra of adsorbed hydrogen and surface species produced from adsorption and reaction of CO *in vacuo*. and under H_2 atmosphere at various temperatures are shown in Figure 1. Fig. 1(a) shows the IR spectra of surface species formed from the adsorption of H_2 at 300 K. As shown in Fig. 1(a), H_2 was dissociatively adsorbed over the Sm_2O_3 surface to form OH (3658 cm^{-1}) and bridged type hydride species over twin Sm site as Sm-H-Sm ($820, 710$ and 633 cm^{-1}) [8]. Fig. 1(b) shows the IR spectra of surface species formed from adsorption of CO over the surface, where CO in gas phase was evacuated. As in Fig. 1(b), CO adsorbed to form carboxylate and oligomerized CO species, such as oxalate type species, which gave various infrared bands below 2100 cm^{-1} referred to the previous report [9]. These species were stable *in vacuo*. and the shapes of the spectrum gradually changed with changing the states over 400 K.

Fig. 1(c)-(e) show the IR spectra of surface species formed when the CO preadsorbed surface was exposed to H_2 (13 kPa) at various temperatures. As shown in Fig. 1(c), under H_2 atmosphere at 300 K, infrared bands at 3656, 815, 710 and 633 cm^{-1} that were attributable to adsorbed hydrogen were produced beside the bands due to the surface species produced from CO adsorption. When the temperature was increased, the decrease of the intensities of the bands due to the adsorbed hydrogen was observed, while the spectra of the surface species produced from CO did not change markedly as shown in

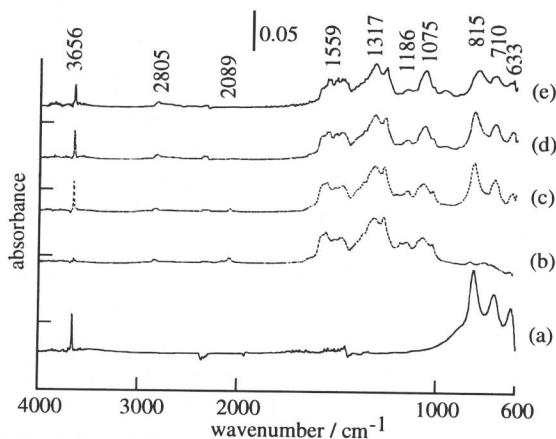


Figure 1, Infrared spectra of adsorbed hydrogen and CO under various conditions; (a):hydrogen adsorbed species at 300 K, (b):surface species from CO adsorption at 300 K, and surface species from CO under H_2 at (c):300 K, (d):323 K, and (e):373 K.

Figs. 1(d) and (e). Any significant changes of the spectrum, such as production of new bands originated from the reaction between the surface species, were not observed when time dependence spectra were examined at various temperatures. These results clearly show that the surface species produced from CO show poor reactivity toward hydrogen. Moreover, the adsorption sites of hydrogen are different from that of the surface species produced from CO adsorption.

Fig. 2 shows time dependence IR spectra of surface species formed when the hydrogen preadsorbed surface was exposed to CO (650 Pa) at 203 K. The hydrogen adsorption was carried out at 273 K under 13 kPa of H_2 and the gas phase was evacuated at 203 K. Fig. 2(a) shows the IR spectra of preadsorbed hydrogen after evacuating the gas phase at 203 K. The hydrogen adsorbed species were relatively stable *in vacuo*. below 243 K. After evacuating the gas phase, CO (650 Pa) was introduced. Fig. 2(b)-(e) show time dependence IR spectra of the surface species under CO atmosphere at 203 K. As shown in Fig. 2 (b)-(e), the production of bands in $\nu(C-H)$ (3019, 2809 and 2671 cm^{-1}) and $\nu(C-O)$ or $\delta(C-H)$ (1580, 1272, 1211, 1108, and 853 cm^{-1}) were observed, and their intensity increased in the time course. These bands indicate the formation of C-H bond containing surface species. Simultaneously, intensity of the bands attributed to bridged hydride decreased, while that of OH remained unchanged. The bands of bridged hydride almost disappeared after 60 min. from introducing CO, where the band intensities of the produced species were almost saturated. The decrease of the bridged hydride is well corresponding to the increase of the produced species. Therefore, it was found that bridged hydride species selectively reacted with CO to form surface species possessing C-H bond.

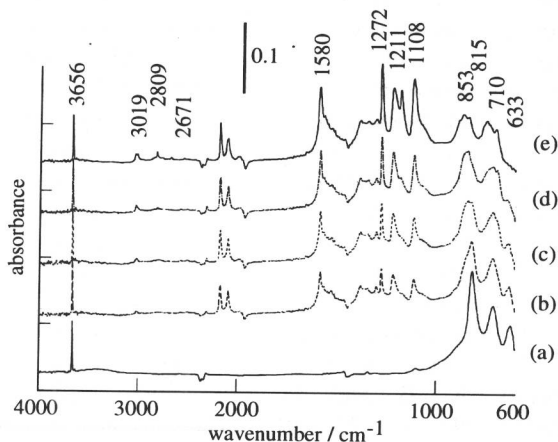


Figure 2, Time dependence infrared spectra of surface species formed when the hydrogen preadsorbed surface is exposed to CO at 203 K; (a) before exposure, and (b):0.5 min., (c):1 min., (d):3 min., and (e):60 min. from introducing CO.

In order to know the stoichiometry of the species, the amount of preadsorbed hydrogen and reacted CO with hydride were examined from the relation between IR intensity of the corresponding bands and the amount of consumed gases. The amount of hydride preadsorbed over the surface was estimated to be 9 mmol/g. The amount of CO concerned the reaction with surface hydride can be estimated to be 9 mmol/g. This value is in good agreement with that of preadsorbed hydride over the surface. These strongly suggest that HCO type species were formed from one to one reaction between CO and bridged hydride.

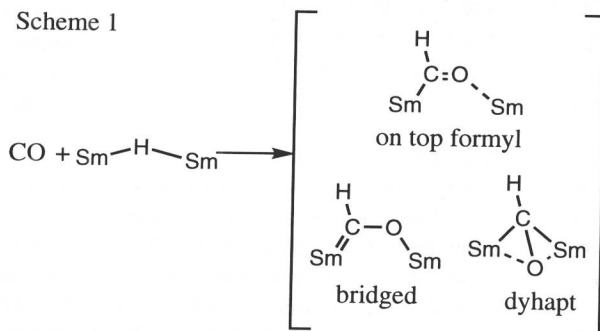
The rate of production of each band was examined from the time dependence IR spectra in order to assign the bands in more detail. The results are arranged to Arrhenius plots and then estimated the activation energy (E_a) for production. If the bands are originated from the same

The rate of production of each band was examined from the time dependence IR spectra in order to assign the bands in more detail. The results are arranged to Arrhenius plots and then estimated the activation energy (E_a) for production. If the bands are originated from the same

species, Ea shows the same value. From the quantitative analysis through the Arrhenius plots, the bands can be separated into three groups as A(2671 and 1580 cm^{-1}), B(3019, 1211 and 853 cm^{-1}) and C(2809, 1272 and 1108 cm^{-1}) on the basis of the values of Ea; 9, 7 and 12 kJ/mol, respectively. The IR bands of the species produced from CO with hydride and deuteride that are separated into three groups as A, B and C from the values of Ea are listed in Table 1. The bands in each group can be assigned to ν (C-H), ν (C-O) and δ (C-H). These suggest that three kinds of HCO species based on the IR bands in group A, B and C were formed as species A, B and C, respectively. Various kinds of HCO species can be expected from the spectrum. Particularly, this work deals with the reaction between surface bridged hydride with CO, and thus, HCO species that interact with twin Sm site can be expected. According to the previous reports of organometallic chemistry about the reaction between CO and hydride complexes [10,11], the IR bands of group A are in good agreement with on-top type formyl complex where the O atom in carbonyl group interact with alkali ion in the solution [10], so that species A can be assigned to on-top formyl where O atom in the carbonyl group interact with one of the Sm ion in the twin Sm site. On the other hand, the production of two kinds of HCO species, bridged and dyhapt type, were confirmed from the reaction between CO and bridged hydride complex [11]. The IR bands in group B is in agreement with the structure of bridged type HCO and those in group C is in agreement with the structure of dyhapt one. Therefore, species B and C can be assigned to bridged and dyhapt HCO, respectively. The reaction are summarized in Scheme 1. These species were relatively stable *in vacuo*. and under H_2 atmosphere and gradually decomposed to form carboxylate species over 373 K.

Table 1, IR frequencies (cm^{-1}) of surface species from CO and adsorbed hydrogen over Sm_2O_3

Group	IR frequencies		Isotopic ratio	Assignment
	CO+H (a)	CO+D(a)		
A	2671	1993	1.34	ν (C-H)
	1580	1567	-----	ν (C-O)
B	3019	2252	1.34	ν (C-H)
	1211	1223	-----	ν (C-O)
	853	640	1.33	δ (C-H)
C	2809	2096	1.34	ν (C-H)
	1272	964	1.32	δ (C-H)
	1108	1110	-----	ν (C-O)



complexes [10,11], the IR bands of group A are in good agreement with on-top type formyl complex where the O atom in carbonyl group interact with alkali ion in the solution [10], so that species A can be assigned to on-top formyl where O atom in the carbonyl group interact with one of the Sm ion in the twin Sm site. On the other hand, the production of two kinds of HCO species, bridged and dyhapt type, were confirmed from the reaction between CO and bridged hydride complex [11]. The IR bands in group B is in agreement with the structure of bridged type HCO and those in group C is in agreement with the structure of dyhapt one. Therefore, species B and C can be assigned to bridged and dyhapt HCO, respectively. The reaction are summarized in Scheme 1. These species were relatively stable *in vacuo*. and under H_2 atmosphere and gradually decomposed to form carboxylate species over 373 K.

Figure 3 shows IR spectra of surface species produced under the mixed gas of H_2 and CO (26 kPa) in various ratio at 323 K. As shown in Fig. 4, when the surface was exposed to the

mixed gas where the content of CO was relatively high, HCO species preferentially produced as shown in Fig 3(a) and (b), while under that of the low content of CO, surface species, which give the IR bands attributable to $\nu(\text{C-H})$ (2921, 2810, 2757, 2695 and 2560 cm^{-1}) and $\nu(\text{C-O})$ (1580, 1140, 1049 and 966 cm^{-1}), preferentially produced instead of the IR bands attributed to bridged or dyhapt HCO species. These bands are in agreement with that of methoxide($\text{CH}_3\text{O-}$) over the surface referred to our previous works[6,7]. These suggest that hydrogenation proceeded further under the mixed gas in low CO content to form methoxide. Nearly the same tendency was observed when the exposed temperature changed; at relatively low temperatures HCO species preferentially produced. As mentioning above, once HCO type species produced over the surface, the species were relatively stable. The production of methoxide was not observed from the HCO species under H_2 .

Figure 4 shows the time dependence IR spectra of surface species formed under the mixed gas of H_2 and CO ($\text{H}_2/\text{CO}=300$) at 323 K. When the surface was exposed to the mixed gas, surface species attributable to OH and bridged hydride immediately produced and, besides the adsorbed hydrogen, production of the bands attributed to on-top formyl and methoxide were confirmed as shown in Fig. 3(a). The bands attributed to bridged hydride decreased with passing time, while the bands attributed to the produced surface species were increased as shown in Fig. 3(b)-(d).

The bands of bridged hydride almost disappeared after 90 min. from introducing the mixed gas, where the bands of the produced species were saturated. The rate of production of the bands of methoxide were examined at various temperatures and the results were arranged to Arrhenius plots as the same manner as producing HCO species. The activation energy (E_a) for production was 36 kJ/mol. This value is 3 to 5

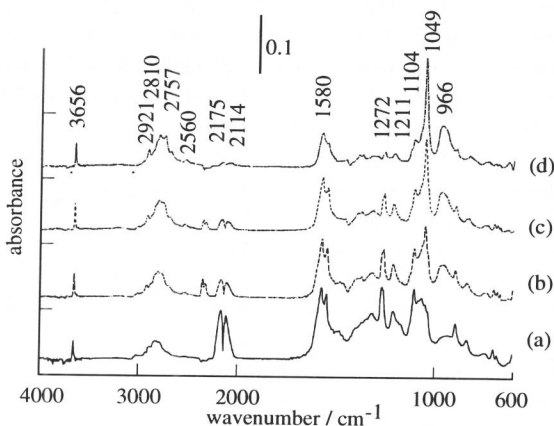


Figure 3, Infrared spectra of surface species formed at 323 K under the mixed gas of H_2 and CO (26 kPa) in various ratio; the H_2/CO ratios are (a):10, (b):50, (c):100, and (d):300.

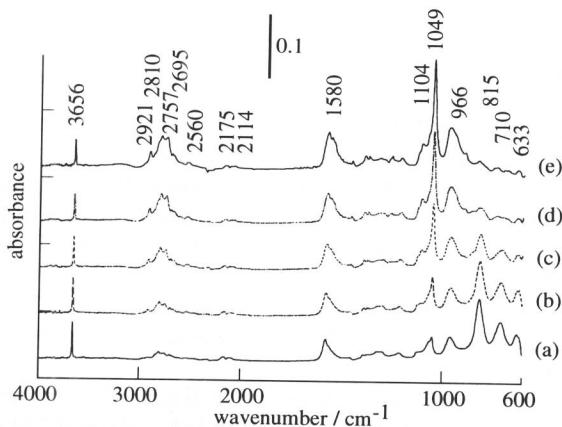
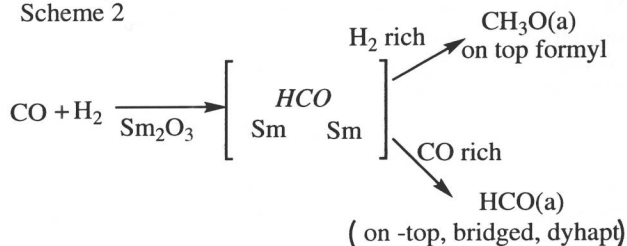


Figure 4, Time dependence infrared spectra of surface species formed under the mixed gas of H_2 and CO ($\text{H}_2/\text{CO}=300$) at 323 K for (a) 1 min., (b) 3 min, (c) 10 min, (d) 30 min., and 90 min from introducing CO.

times larger than that of production of HCO. These results suggest that the intermediate of HCO species are the same as that of methoxide and the formation over the surface proceeded competitively. Here, *HCO* type intermediate can be proposed. Bridged and dyhapt HCO produced when the intermediate was stabilized over the surface and, under the H_2 rich atmosphere, this intermediate hydrogenated further to form methoxide. Scheme 2 summarize the reaction between CO and H_2 over the surface under the present condition.

We have already demonstrated that methoxide is one of the important intermediates of CO hydrogenation over the surface but, under the reaction condition ($H_2/CO=3$), methoxide can be confirmed over the surface over 523 K [7]. This work clearly demonstrate the formation of methoxide over the surface under relatively mild condition as well as, under the conventional reaction condition ($H_2/CO=3$), formation of the stable surface products disturbs the formation of methoxide.

Scheme 2



REFERENCES

1. K. Maruya, T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, and T. Onishi, Bull. Chem. Soc. Jpn., 61 (1988) 667.
2. R. Kieffer, J. Varela, and A. Deluzarche, J. Chem. Soc., Chem. Commun., (1983) 763.
3. T. Arai, K. Maruya, K. Domen, and T. Onishi, Bull. Chem. Soc. Jpn., 62 (1989) 349.
4. J. Saussey, J-C. Lavalley, J. Lamotte, and T. Rais, J. Chem. Soc., Chem. Commun., (1982) 287.
5. H-Y. He and J. G. Ekerd, J. Catal., 87 (1984) 381
6. Y. Sakata, M. Yoshino, H. Imamura, and S. Tsuchiya, J. Chem. Soc., Faraday Trans., 86 (1990) 3489.
7. Y. Sakata, M. Yoshino, T. Fukuda, H. Yamaguchi, H. Imamura, and S. Tsuchiya, L. Gucci et. al (eds.), New Frontiers in Catalysis, KIADO Budapest (1993) 1519.
8. Y. Sakata, H. Imamura, and S. Tsuchiya, Chem. Lett., (1991) 349.
9. A. Zecchina, S. Coluccia, G. Spoto, D. Scarano, and L. Marchese, J. Chem. Soc., Faraday Trans., 86 (1990) 703.
10. B. B. Wayland, A. Puttaahmed, and B. A. Woods, J. Chem. Soc., Chem. Commun., (1983) 142.
11. P. A. Belmonte, F. G. N. Cloke, and R. R. Schrock, J. Am. Chem. Soc., 105 (1983) 2643.

***In situ* Infrared Spectroscopic Investigation of 12-Tungstphosphoric Acid and its Cesium Hydrogen Salts in Relation to Catalytic Activity**

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The nature of hydroxyl groups of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ has been investigated by means of IR spectroscopy. Novel behavior of protons in $\text{HPW} \cdot n\text{H}_2\text{O}$ was observed with the change of the amount of water molecules, n , and the acidic OH band was identified. A good correlation between the surface acidity and the catalytic activity was confirmed for the Cs hydrogen salts by low temperature CO adsorption.

1. INTRODUCTION

Heteropoly compounds are efficient solid "super" acid catalysts for a wide variety of reactions [1]. It is known that various polar molecules are easily incorporated into the bulk of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and catalyzed by protons in the bulk, i. e., "pseudoliquid" catalysis. Water molecules are also incorporated into the bulk to form stable hydrates. Catalytic activity of HPW changes with the number of water molecules in the bulk (n in $\text{HPW} \cdot n\text{H}_2\text{O}$), [2]. Hence interactions between H^+ and water molecules are of great concern for the understanding of its acidity and catalytic activity. It is confirmed by XRD and neutron diffraction [3] that, at $n = 6$, H^+ is associated with two water molecules to form H_3O_2^+ cation connecting four HPW anions. But IR spectra of OH band of heteropolyacids having variations of water content are not well understood.

Cesium hydrogen salts of HPW, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ (denoted by CsX , $X = 0 \sim 3$), particularly $\text{Cs}_{2.5}$, show very high activities for various acid-catalyzed reactions due to its high surface acidity [4, 5]. In this case, the determination of the surface acidity is an important subject to understand the catalytic activity. According to thermal desorption of NH_3 and pyridine [1, 5-9], calorimetric titrations with NH_3 [10-12], and indicator tests [6, 13, 14], CsX 's as well as HPW are very strong acids. These measurements, however, involve strong interactions between the surface and the probe molecules, so that the reactions other than acid-base interaction may be involved [15]. In addition, the basic molecules are often absorbed into the bulk of heteropolyacids [1, 5, 6], so that it is difficult to measure the surface acid sites separately. The surface acidity of CsX has not been directly determined for these reasons. We recently reported that the surface acidity could be measured by using low temperature CO adsorption [16].

In the present study, we investigated in detail the state of H^+ in HPW and CsX by means of IR spectroscopy. At $n = 6$ in $\text{HPW} \cdot n\text{H}_2\text{O}$, a novel large continuum expanding

from 1300 cm^{-1} to 3400 cm^{-1} was observed, and for $0 \leq n \leq 6$, the acidic OH band was assigned. It has been shown that the Cs^+ and H^+ on the surface of CsX can be distinguished from each other by the IR bands of the adsorbed CO, and that the numbers of H^+ on the surface thus measured varied in parallel with the catalytic activity.

2. EXPERIMENTAL

Number of water molecules in the bulk of $\text{HPW} \cdot n\text{H}_2\text{O}$ was determined by using a microbalance. Cesium hydrogen salts, CsX ($X = 2, 2.3, 2.5, 2.8$, and 3), were prepared by the titration of an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ with an aqueous solution of Cs_2CO_3 , as in the previous works [4, 7].

IR spectra were recorded after the heteropoly compounds (ca. 20 - 30 mg) dispersed in water was spread on a Si plate and dried in air at room temperature. IR spectra of $\text{HPW} \cdot n\text{H}_2\text{O}$ were measured at 298 K after evacuation at various temperatures for 1 h with a JASCO FT-IR 550 spectrometer. IR spectra of CsX were recorded at 110 K. Prior to the measurements, CsX was evacuated at 523 K for 1 h to remove adsorbed water and was cooled to about 110 K, and a predetermined amount of CO was introduced. For the determination of the heat of CO adsorption, the measurement was carried out changing the temperature from 110 K to 150 K.

3. RESULTS AND DISCUSSION

3.1. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW)

Fig. 1 shows the IR spectra of $\text{HPW} \cdot n\text{H}_2\text{O}$. $\text{HPW} \cdot n\text{H}_2\text{O}$ ($n > 6$) showed a broad band at around 3300 cm^{-1} and a band at 1720 cm^{-1} in OH stretching and bending regions, respectively, after evacuation at room temperature (not shown). These bands which are characteristic of the adsorbed water disappeared after evacuation at 343 K, and a broad continuum expanding from 1300 cm^{-1} to 3400 cm^{-1} appeared (spectrum a in Fig. 1, $n = 6$). This continuum band shifted to lower wavenumber ($\sim 2200\text{ cm}^{-1}$) by H_2O - D_2O exchange, showing that this large band is due to hydroxyl groups. The position of the continuum band indicates that the OH group is strongly hydrogen-bonded. Brown et al. [3] reported that H^+ in hexahydrate ($n = 6$) is associated with two water molecules to form H_5O_2^+ connecting four polyanions. This was also confirmed by ^1H -NMR [17]. Hence the continuum band corresponds to this H_5O_2^+ . The $\text{O} \cdots \text{O}$ distance of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond in H_5O_2^+ is about 2.37 \AA [3]. Zundel's group reported based on the quantum calculation that when the $\text{O} \cdots \text{O}$ distance is as short as 2.39 \AA , the energy

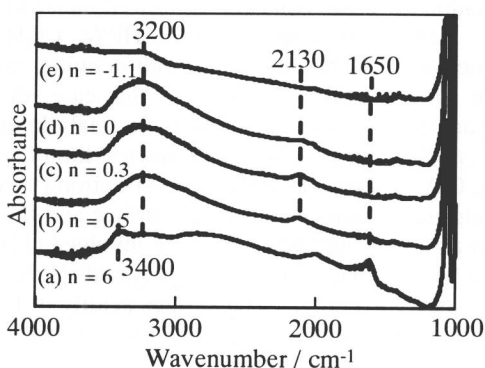


Fig. 1 IR spectra of $\text{HPW} \cdot n\text{H}_2\text{O}$. $\text{HPW} \cdot n\text{H}_2\text{O}$ ($n > 6$) was evacuated at (a) 343 K, (b) 373 K, (c) 423 K, (d) 553 K, and (e) 673 K.

barrier of double minimum potential of the hydrogen bond becomes very small to be a shallow broad potential [18]. The broad OH band of this type has been discussed for zeolites [19]. The very broad IR band of H_5O_2^+ may be understood in this way.

Further evacuation of $\text{HPW} \cdot 6\text{H}_2\text{O}$ (spectrum a) at 373, 423, and 553 K caused a decrease of the continuum band and the appearance of a broad band at around 3200 cm^{-1} (spectrum b - d). Correspondingly, the number of hydrogen bonds of H_5O_2^+ to $\text{W}=\text{O}$ decreased upon dehydration as observed by the shift of a part of the $\text{W}=\text{O}$ band at 975 cm^{-1} to 1005 cm^{-1} [20]. This dehydration process is also consistent with the observation by ^{31}P - and ^1H -NMR, which characterized the behavior of acidic proton as a function of n [17]. The broad band ($\sim 3200\text{ cm}^{-1}$) shifted to lower wavenumber ($\sim 2400\text{ cm}^{-1}$) by H_2O - D_2O exchange. From these results, we can assign this broad band to acidic OH (Brønsted acid site, BAS, or isolated acidic H^+ [17]). Usually IR bands of BAS of zeolites are observed around $3500 \sim 3650\text{ cm}^{-1}$. The very low wavenumber of the OH band ($\sim 3200\text{ cm}^{-1}$) may be explained by the strong hydrogen bonding to the neighboring oxygen or the high mobility of H^+ on the surface of heteropolyanion. The peak at 2130 cm^{-1} is possibly overtone or combination vibration of skeletal vibration mode of heteropolyanion [21].

After evacuation at 673 K for 1 h, the number of water of crystallization, n , calculated from the weight decrease became -1.1 , close to the result reported previously [22], and the peak area of this band (3200 cm^{-1}) decreased much, which suggests that the weight decrease was due to the removal of H^+ as water molecule. However, the evacuation at 673 K caused the decrease of the $\text{W}-\text{O}_c-\text{W}$ stretching band at 900 cm^{-1} and broadening of $\text{W}-\text{O}_c-\text{W}$ band at around 800 cm^{-1} , showing partial destruction of Keggin structure.

3.2. CsX ($2 \leq X \leq 3$)

Fig. 2 shows the changes in IR spectra measured at 110 K with the amount of CO adsorbed on Cs3, which has no residual H^+ . When CO corresponding to 1.5 molecules per anion of the bulk was introduced to Cs3 at 110 K, two bands at 2154 and 2139 cm^{-1} appeared (spectrum b). No peak was observed in this region in the case of the Si plate alone. The band at 2154 cm^{-1} is assigned to the CO adsorbed on Cs^+ , since Cs-ion exchanged mordenite and ZSM-5 show the peak at this position [23]. The band at 2139 cm^{-1} is attributed to physisorbed CO as in the case of zeolites and silica [15, 23, 24]. No peak was observed for Cs3 in the OH stretching region ($3000\text{--}3700\text{ cm}^{-1}$), showing that no residual H^+ existed after evacuation at 423 K (spectrum a in Fig. 2A). Peak areas of those peaks increased with the amount of CO adsorbed (spectra b - f in Fig. 2B).

The same measurement was applied to Cs2.5 (Fig. 3). Broad

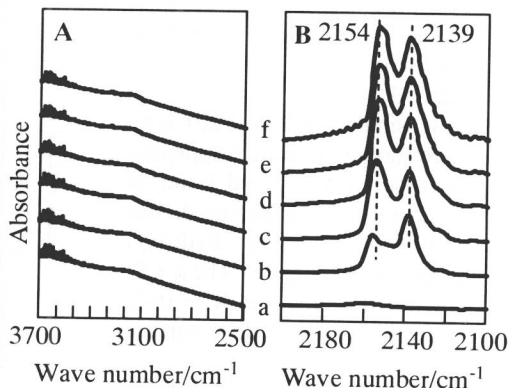


Fig. 2 Changes in IR spectra of Cs3 by CO adsorption at 110 K. Amount of CO adsorbed were (a) 0.0×10^{-6} mol, (b) 6×10^{-6} mol, (c) 9×10^{-6} mol, (d) 20×10^{-6} mol, (e) 25×10^{-6} mol, and (f) 34×10^{-6} mol. Catalyst: 32mg.

peaks at 3600 and 1620 cm^{-1} , corresponding to adsorbed water, together with a peak at around 3200 cm^{-1} , were observed before evacuation (not shown), and the former two peaks disappeared by evacuation at 523 K (spectrum a in Fig. 2B). According to TG analysis, the adsorbed (or absorbed) water of Cs2.5 desorbs below 423 K [22]. The broad peak 3200 cm^{-1} shifted to around 2400 cm^{-1} by H_2O - D_2O exchange. Taking into account that the broad band at around 3200 cm^{-1} of Cs2.5 was similar to that of $\text{HPW} \cdot n\text{H}_2\text{O}$, this band may be assigned to BAS of CsX.

IR spectrum of CO adsorbed at 110 K on Cs2.5, which had been evacuated at 423 K, is shown in spectra b – f in Fig. 3B. Other CsX (Cs2, Cs2.3, Cs2.75, and Cs2.8) showed essentially the same bands as Cs2.5. When CO was introduced to Cs2.5 at 110 K, a new band appeared at 2165 cm^{-1} in addition to the two bands at 2154 and 2139 cm^{-1} observed for Cs3. The new band at 2165 cm^{-1} was observed for Cs2 – Cs2.8 and can be considered to be CO adsorbed on BAS, since CO adsorbed on BAS of zeolites and silanol of SiO_2 are observed around 2160 – 2178 cm^{-1} [15, 23, 24]. When the amount of CO adsorption was changed, the broad band at around 3200 cm^{-1} decreased in intensity in proportion to the increase of the band at 2165 cm^{-1} . This correlation also supports the assignment of the broad band at 3200 cm^{-1} to BAS. The decrease of the band at 3200 cm^{-1} was also obvious in other samples but Cs3.

A new small band at 3220 cm^{-1} (Fig. 3, spectrum b-f), which appeared with a decrease in the broad band at 3200 cm^{-1} is not well understood, but possibly corresponds to some hydroxyl species interacting with CO. These CO bands were not detected for X = 0–2, probably due to their very low surface areas.

After the three peaks at 2165, 2154, and 2139 cm^{-1} were deconvoluted by assuming Lorentzian function, isotherms for each peak were obtained as shown for example in Fig. 4. In the higher pressure region, the peak

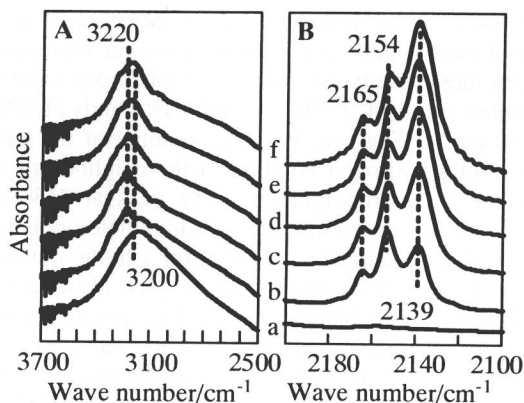


Fig. 3. Changes in IR spectra of Cs3 by CO adsorption at 110 K. Amount of CO adsorbed were (a) 0.0×10^{-6} mol, (b) 6×10^{-6} mol, (c) 9×10^{-6} mol, (d) 13×10^{-6} mol, (e) 20×10^{-6} mol, and (f) 30×10^{-6} mol. Catalyst: 18 mg.

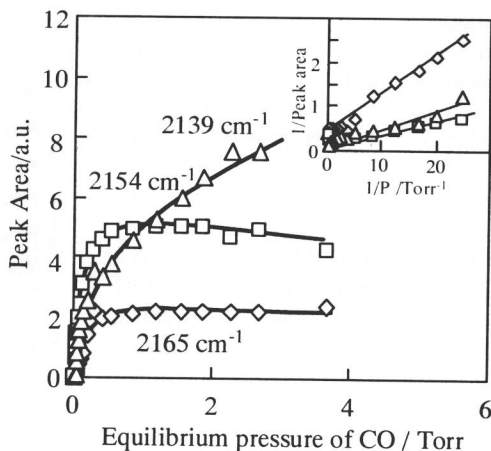


Fig. 4. Isotherms of the CO adsorption on Cs2.5 at 110 K. The inset shows the Langmuir plots for the low pressure region.

intensity at 2154 cm^{-1} a little decreased with an increase in pressure. This may be explained by solvent depolarization effects [24]. This effect was less significant at higher temperatures and for the other two peaks. Langmuir plots can fairly be applied for the low pressure region (e. g., the inset in Fig. 4). The peaks due to CO on H^+ (2165 cm^{-1}) and Cs^+ (2154 cm^{-1}) leveled-off at the amount of CO adsorbed were over 9 and $16\text{ }\mu\text{mol}$, respectively. These values were a little larger than the number of cation sites ($\text{H}^+ + \text{Cs}^+$, Cs2.5: $6.5\text{ }\mu\text{mol}$, Cs3: $9.7\text{ }\mu\text{mol}$) estimated from BET surface area (Cs2.5: $135\text{ m}^2\text{ g}^{-1}$, Cs3: $114\text{ m}^2\text{ g}^{-1}$) [5].

The heat of adsorption was estimated at each site, based on van't Hoff equation, K , the equilibrium constant at each temperature, K , being estimated from the Langmuir plots. The value of K was $\text{Cs}^+, \text{H}^+ >$ physisorption at $110 - 150\text{ K}$. Heat of adsorption of physisorbed CO was about 6 kJ mol^{-1} , which is close to the heat of vaporization [25]. Heats of adsorption on BAS and Cs^+ were ca. 4 kJ mol^{-1} higher than that of physisorbed CO, and were similar to those on MgO [26] or silanol of silica [24].

If the leveled-off peak intensities in the isotherms are taken as full CO coverages of each site, the intensities reflect the number of each site. Actually, the relative intensities of the 2165 cm^{-1} peak to that of the 2154 cm^{-1} peak, I_{2165}/I_{2154} , at high CO pressures changed linearly with $(3-X)/X$, that is, the bulk H^+/Cs^+ ratio [16]. It has previously been concluded on the basis of ^{31}P -NMR that $\text{Cs}X$'s ($X = 2\sim 3$) after heat treatment are nearly uniform solid solutions of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and the surface H^+/Cs^+ ratio reflects the ratio in the bulk. The change of the peak intensity with X obtained in the present work supports the previous conclusion.

The intensity of the 2165 cm^{-1} band (CO on BAS) and the catalytic activity for alkylation changed in a very similar way with the change of the Cs content, X [16]. Here, the catalytic activity for dehydration of 2-propanol at 383 K [4] is plotted against the number of surface acid sites evaluated from the peak area of IR measurement (Fig. 5). The trends agree also with the number of the surface H^+ estimated from the surface area and the chemical formulas [5]. The excellent agreement confirms the conclusion that the catalytic activity of $\text{Cs}X$ ($X = 2 - 3$) is governed by the surface acidity and further shows the usefulness of the present method for the measurement of the surface acid sites of $\text{Cs}X$.

4. CONCLUSION

We have clearly demonstrated the presence of an extra broad IR band of hydroxyl group of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$, which is due to a unique planer conformation H_5O_2^+ in $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$, and was explained by a very short $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond with a broad single potential. The variation of the band was measured as a function of water content. For $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 0\text{H}_2\text{O}$, a broad

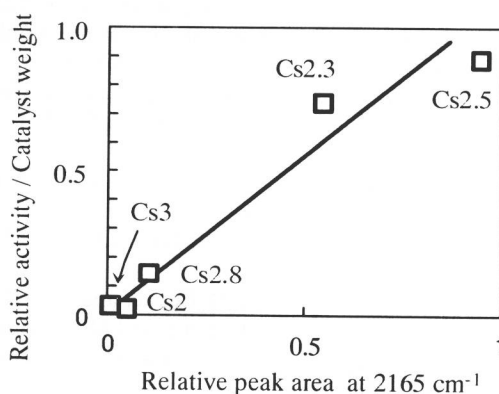


Fig. 5 Correlation between surface acidity observed by low temperature CO adsorption and catalytic activity for dehydration of 2-propanol at 383 K [4].

band due to acidic hydroxyl group was observed.

The H^+ and Cs^+ sites on the surface of Cs hydrogen salts were successfully distinguished by using IR measurement of CO adsorption at low temperature. Heat of adsorption for these sites was slightly greater than that of physisorbed CO. The surface acidity measured by this method exhibited an excellent correlation with the catalytic activity reported previously.

REFERENCES

- 1 E. g., T. Okuhara, N. Mizuno, and M. Misono, *Advan. Catal.*, 41 (1996) 113; M. Misono, *Catal. Rev. Sci.-Eng.*, 29 (1987) 269.
- 2 E. g., T. Okuhara, T. Hashimoto, T. Hibi, and M. Misono, *J. Catal.*, 93 (1985) 224.
- 3 G. M. Brown, M. R. Nnoe-Spirlet, W. R. Busing, and H. A. Levy, *Acta Cryst. B33* (1977) 1038.
- 4 S. Tatematsu, T. Hibi, T. Okuhara, and M. Misono, *Chem. Lett.*, (1984) 865.
- 5 T. Okuhara, T. Nishimura, H. Watanabe, K. Na, and M. Misono, in: H. Hattori, M. Misono, and Y. Ono (Eds), *Acid-Base Catalysis II*, Kodansha, Tokyo - Elsevier, Amsterdam, 1994, p. 419.
- 6 T. Okuhara, T. Nishimura, H. Watanabe, and M. Misono, *J. Mol. Catal.*, 74 (1992) 247.
- 7 M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara, and Y. Yoneda, *Bull. Chem. Soc. Jpn.*, 55 (1982) 400.
- 8 J. A. Dias, J. P. Osegovic, and R. S. Drago, *J. Catal.*, 183 (1999) 83.
- 9 B. K. Hodnett and J. B. Moffat, *J. Catal.*, 88 (1984) 253.
- 10 F. Lefebvre, F. X. L. Cai, and A. Auroux, *J. Mater. Chem.*, 4 (1994) 125.
- 11 T. Nakato, M. Kimura, S. Nakata, and T. Okuhara, *Langmuir*, 14 (1998) 319.
- 12 L. C. Jozefowicz, H. G. Karge, E. Vesilyeva, and J. B. Moffat, *Microporous Mater.*, 1 (1993) 313.
- 13 M. Otake and T. Onoda, *Shokubai (Catalyst)*, 17 (1975) 13.
- 14 A. K. Ghosh and J. B. Moffat, *J. Catal.*, 101 (1986) 238.
- 15 H. Knözinger, in: R. W. Joyner and R. A. van Santen (Eds), *Elementary Reaction Steps in Heterogeneous Catalysis*, Kluwer Academic Publisher, Netherlands, 1993, p.267.
- 16 G. Koyano, T. Saito, and M. Misono, *Chem. Lett.*, (1999) 1075.
- 17 S. Uchida, K. Inumaru, J. M. Dreppe, and M. Misono, *Chem. Lett.*, (1998) 643.
- 18 R. Jamoschek, E. G. Weidemann, H. Pfeiffer, and G. Zundel, *J. Am Chem. Soc.*, 94 (1972) 2387.
- 19 C. Pazé, S. Bordiga, C. Lamberti, M. Savalaggio, A. Zecchina, and G. Bellusi, *J. Phys. Chem. B*, 101 (1997) 4740.
- 20 K. Y. Lee, N. Mizuno, T. Okuhara, and M. Misono, *Bull. Chem. Soc. Jpn.*, 62 (1989) 1731.
- 21 J. C. Edwards, C. Y. Thiel, B. Benac, and J. F. Knifton, *Catal Lett.*, 51 (1998) 77.
- 22 C. Hu, T. Nishimura, T. Okuhara, and M. Misono, *Sekiyu Gakkaishi*, 36 (1993) 386.
- 23 A. Zecchina, S. Bordiga, C. Lamberti, G. Spoto, L. Carnelli, and C. O. Areán, *J. Phys. Chem.*, 98 (1994) 9577.
- 24 T. P. Beebe, P. Gelin and J. T. Yates, Jr., *Surface Sci.*, 148 (1984) 526.
- 25 *Chem. Soc. Jpn. (Eds), Kagaku Binran Kisohen II 3rd edition*, Maruzen, Tokyo 1984, p. 266.
- 26 E. A. Paukshtis and E. N. Yurchenko, *Russ. Chem. Rev.*, 52 (1983) 242.

The oxidation state of Ru catalysts under conditions of partial oxidation of methane studied by XPS and FTIR spectroscopy

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The oxidation state of Ru catalysts supported on undoped, Ca²⁺-doped and W⁶⁺-doped TiO₂ has been investigated under conditions of partial oxidation of methane employing XPS and FTIR techniques. It is found that the catalytic activity and selectivity toward synthesis gas formation depends on the ability of the support to stabilize Ru in the metallic state under reaction conditions. This ability is affected by the nature of the dopant cation.

1. INTRODUCTION

The catalytic partial oxidation of methane to synthesis gas has received significant attention in recent years since it may offer advantages over steam reforming, which is currently practiced in industry. Depending on the catalyst employed, two alternative reaction pathways have been proposed: (a) an "indirect" scheme, according to which the initial total oxidation of methane is followed by reforming of the unconverted methane with CO₂ and H₂O, and (b) a "direct" scheme where methane conversion to synthesis gas occurs without the intermediate production of CO₂ and H₂O.

Recent investigations in this laboratory [1,2] have demonstrated that TiO₂-supported Ru exhibits a unique catalytic behavior in the reaction of partial oxidation of methane by promoting the direct-conversion scheme, even at relatively low temperatures. This behavior has been correlated with the ability of TiO₂ to stabilize dispersed Ru in its metallic state under reaction conditions [3]. It has been also found that doping of the TiO₂ carrier with cations of lower valence (Ca²⁺) than that of the host cation (Ti⁴⁺) promotes further the direct formation of synthesis gas over Ru catalysts. The opposite is true upon doping TiO₂ with higher valence cations (W⁶⁺).

In the present study, the redox behavior of Ru catalysts supported on undoped, Ca²⁺-doped and W⁶⁺-doped TiO₂ is investigated by XPS and FTIR spectroscopy. Results are related to the unique ability of the Ru/TiO₂ catalyst to promote the direct route of the partial oxidation of methane.

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