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Methanol Synthesis from CO and CO_2 Hydrogenations over Supported Palladium Catalysts

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The hydrogenation of CO and CO_2 was carried out over palladium catalysts supported on various metal oxides. A significant support effect of Ga_2O_3 on the methanol synthesis activity from CO_2 hydrogenation was observed. On the other hand, a Pd/ZrO_2 catalyst showed high methanol synthesis activity from CO hydrogenation. Furthermore, the hydrogenation reaction over Pd/Ga_2O_3 and Pd/ZrO_2 catalysts was investigated by in situ infrared spectroscopy in order to understand the active sites and the reaction mechanism. On the Pd/Ga_2O_3 catalyst, surface formate and methoxy species were observed during CO and CO_2 hydrogenation. In contrast, the reaction pathway was clearly different between CO and CO_2 hydrogenation over the Pd/ZrO_2 catalyst. That is, surface formaldehyde and methoxy species were observed as intermediates during CO hydrogenation, while surface formate and methoxy species were detected during CO_2 hydrogenation. It was thus found that the reaction mechanisms of methanol synthesis from CO and CO_2 hydrogenation were strongly dependent on the types of supports over the Pd catalysts.

Methanol synthesis from CO/CO_2/H_2 is an important industrial process, and Cu/ZnO-based catalysts are well known to be active for this reaction.[1,2] Numerous investigations concerning the active sites in the Cu/ZnO catalyst and the role of ZnO have been carried out over the past few decades. On the other hand, palladium catalysts are also known to be active for methanol synthesis from carbon monoxide and hydrogen as well as from carbon dioxide and hydrogen.

Ponec et al. pointed out that although Pd^+ species on the surface are active in methanol synthesis from CO and H_2, stabilization of the species by promoters was not successful.[3,4] Bell et al. reported a support effect of palladium catalysts containing a metal oxide, such as SiO_2, TiO_2, MgO, Al_2O_3, La_2O_3, and ZrO_2, on the activity of methanol formation from carbon monoxide and hydrogen, and found that the Pd/La_2O_3 catalyst showed the highest activity, while Pd/ZnO exhibited the highest selectivity toward methanol formation.[5] Recently, Matsumura et al. reported that the cationic palladium species, mainly present in Pd/CeO_2 prepared by a coprecipitation method, are active for methanol synthesis from carbon monoxide and hydrogen at a low reaction temperature.[6] It has been found that the palladium-support interaction can enhance the reaction activity and selectivity involving the hydrogenation of CO.

Furthermore, the reaction mechanisms of CO and CO_2 hydrogenation were investigated over palladium on various supports. Diagne et al.[7] studied CO hydrogenation over Pd/CeO_2 and CeO_2 catalysts, and concluded that formyl species are involved in methanol synthesis on the Pd/CeO_2 surface, whereas on CeO_2, the formate species were detected as intermediates. Baiker et al.[8,9] investigated CO and CO_2 hydrogenation over Pd/ZrO_2 catalysts. They concluded that a rapid formation of surface formate was observed upon exposure to CO_2/H_2. On the other hand, the surface reactions proceeded via an adsorbed CO, π-bonded formaldehyde, surface-bound methylate, and gas-phase methanol as a product from CO/H_2. However, the differences in the support effect and the reaction mechanisms between the hydrogenation of CO and CO_2 over palladium catalysts were not fully understood. In this study, we examined the differences in the support effect and the reaction mechanisms of methanol synthesis between CO and CO_2 hydrogenation of over palladium catalysts supported on various metal oxides.

Experimental

Catalyst Preparation. A series of palladium catalysts were prepared by a coprecipitation method[10], where the final composition of the Pd:metal oxides weight ratios was 5:95. A 200 mL sample of a mixed aqueous solution of palladium(II) nitrate hydrate and metal nitrate oxide at a total concentration of 1.0 mol/L and 200 mL of an aqueous solution of sodium carbonate (1.0 mol/L) were simultaneously added dropwise to 400 mL of distilled water over a period of 40 min with vigorous stirring at room temperature. The dropping rates of both solutions were carefully controlled at 0.5 mL/min using microfeeders, which kept the pH of the suspension at 6.8–7.2. The suspension was further aged for 48 h with stirring at room temperature to form precipitates. The precipitates were then washed, filtered, and dried at 393 K for 24 h; this procedure was repeated five times to remove any Na ions contained in the precipitates. As the final stage, calcination of the precursors was carried out at 673 K for 3 h in air. We examined the catalytic activity of the Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts in order to compare them with those of various supported Pd catalysts. Cu-based catalysts were also prepared by a coprecipitation method. The loadings of Cu, ZnO and Al_2O_3 of the prepared Cu/ZnO and Cu/ZnO/Al_2O_3 were 5:95 wt% and 50:40:10 wt%, respectively.

Catalytic Activity Test and Catalyst Characterization. Reactions were carried out at 50 atm and 473–553 K with a specific velocity of 20000 – 60000 mL/g cat·h in a high-pressure fixed-bed flow reactor. The compositions of the gas feeds were CO_2/H_2 = 25/75 and CO/H_2 = 33/67. The yield of methanol for both hydrogenation procedures was ~ 5%, which is far from an equilibrium yield at 523 K and 50 atm (CO_2 hydrogenation, 22.0%; CO hydrogenation, 54.5%). Before activity measurements, the catalyst was reduced with 10 vol% hydrogen in helium at 50 atm, 523 K for 2 h, with a specific velocity of 30000 mL/g cat•h. A mass-flow controller controlled the flow rate. The effluent gases were analyzed using an on-line gas chromatograph with thermal-conductivity and flame-ionization detectors. The reaction products were methanol and CO by CO_2 hydrogenation, while methanol and a small amount of CO_2 were observed by CO hydrogenation under these conditions. No methane or higher alcohols were produced by either hydrogenation reaction. The catalytic activities were evaluated in terms of the mass time yield (MTY), defined as the number of moles of the product molecules per catalyst weight per time (mol/kg-cat h).

For an in situ FT-IR study, a Fourier transform infrared spectrometer (Mattson Infinity) was connected to a flow reactor (Spectra Tech model 0030-102) to observe the behavior of the adsorbates during the methanol synthesis reaction. The samples were placed in a sample cup without further dilution. A thermocouple was inserted in the reaction cell, which reached the catalyst bed.

The surface areas of the metallic Pd in the catalysts were measured by the chemisorption of CO at 323 K by the pulse method with an Ohkura Riken Model R6015H instrument. The surface area of the metallic Cu was evaluated by monitoring the reaction of N_2O with copper atoms, which is called reactive frontal chromatography.[11]

Results and Discussion

Catalytic Activity. The reaction data for the hydrogenation of CO_2 and the palladium metal surface area over various supported palladium catalysts are summarized in Table 1. The activities under a steady state of the reaction at 523 K and 50 atm were measured after passing the reactants over catalysts for 2 h. The catalytic activity and Cu surface area of the Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts are also shown in Table 1 to compare with those of various supported Pd catalysts.

The effect of the support on the methanol formation rate was found to be significant with different support metal oxides in the following order: $Ga_2O_3 > ZnO > ZrO_2 > La_2O_3 > CeO_2 > Al_2O_3$. It is clear that Pd/ZnO and Pd/Ga_2O_3 show a high methanol formation rate from CO_2 and H_2, which was well reproduced in our previous study.[10] In particular, the specific activity of the Pd/Ga_2O_3 catalyst was 7-times larger than that of the Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts. No significant dependence on the supports was seen in the apparent activation energy for both methanol and CO formation reactions over Pd catalysts. The significant difference in the TOF between the various metal oxides used as a support suggests that the active species involve the Pd^{n+} species, as reported by Driessen et al.,[3] who have clearly shown a liner relationship between the methanol synthesis activity from CO hydrogenation and the amount of Pd^{n+} measured by X-ray Fluoresence on a La or Mg-doped Pd/SiO_2 catalyst. That is, the amount of Pd^{n+} may be quite different for palladium catalysts containing various metal oxides. On the other hand, we have reported[12–14] that the ZnOx species migrate onto the Cu surface and dissolve into Cu particles to form a Cu–Zn alloy; also, Cu–Zn and metallic Cu cooperatively catalyzed methanol synthesis from CO_2 and H_2 over the Cu/ZnO-based catalysts. We also found[15] that Cu/Ga_2O_3 is more active than Cu/ZnO for methanol formation from CO_2 and H_2. It was shown that Ga_2O_3 formed a Cu–Ga alloy in a manner similar to Cu and ZnO, and that the Cu–Ga species acts as active sites for methanol synthesis from CO_2 hydrogenation. Because the ZnO and Ga_2O_3 supports also show high methanol formation rates from CO_2 and H_2 when using the palladium catalysts, we postulate that a surface alloy, such as the Pd–Zn and Pd–Ga species, acts as active sites for the methanol synthesis from CO_2 hydrogenation.

The activities of the methanol synthesis for CO hydrogenation over various Pd catalysts and Cu-based catalysts are reported in Table 2. Under the conditions used in this study, the specific activity was highest with the zirconia-supported catalyst. Although it has been reported that CeO_2 or La_2O_3-supported Pd catalysts showed a high methanol synthesis yield for CO hydrogenation,[5–7] it is evident that the TOF of the Pd/ZrO_2 catalyst prepared by the copreciptation method was 4-times larger than that of the Pd/CeO_2 and Pd/La_2O_3 catalysts. Furthermore, the rate of methanol formation over the Pd/ZrO_2 catalyst was much higher than that of the Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts. The apparent activation energy and specific

Table 1. Catalytic Activity of Methanol Synthesis and Reverse Water Gas-Shift Reaction for CO_2 Hydrogenation over Various Pd Catalysts

Catalysts[a]	CO uptake	Metal surface area	CH_3OH			CO		
			Activity[b]	TOF	Activation energy	Activity[b]	TOF	Activation energy
	mL/g-cat	m^2/g-cat	mol/kg-cat h	h^{-1}	kJ/mol	mol/kg-cat h	h^{-1}	kJ/mol
Pd/Al_2O_3	1.27	4.1	0.8	8.0	60.1	2.4	23.2	58.2
Pd/CeO_2	0.67	2.1	1.3	24.8	90.0	7.2	135.6	63.2
Pd/Ga_2O_3	0.43	1.4	19.7	565.6	57.0	18.5	533.2	66.1
Pd/La_2O_3	0.21	0.7	0.9	52.8	51.1	0.8	48.0	80.7
Pd/ZnO	0.53	1.7	15.0	356.4	67.1	5.8	138.8	89.7
Pd/ZnO_2	0.38	2.2	4.5	84.0	71.8	10.2	188.0	63.6
Cu/ZnO	—	6.8	14.2	83.2	56.7	6.8	39.6	115.6
Cu/ZnO/Al_2O_3	—	38.6	87.3	90.4	53.6	68.4	70.8	115.4

[a] Pd content = 5 wt%, Cu/ZnO = 5/95 wt%, Cu/ZnO/Al_2O_3 = 50/40/10 wt%.

[b] Reaction conditions: Reaction temperature = 523 K, H_2/CO_2 = 3, Total pressure = 50 atm.

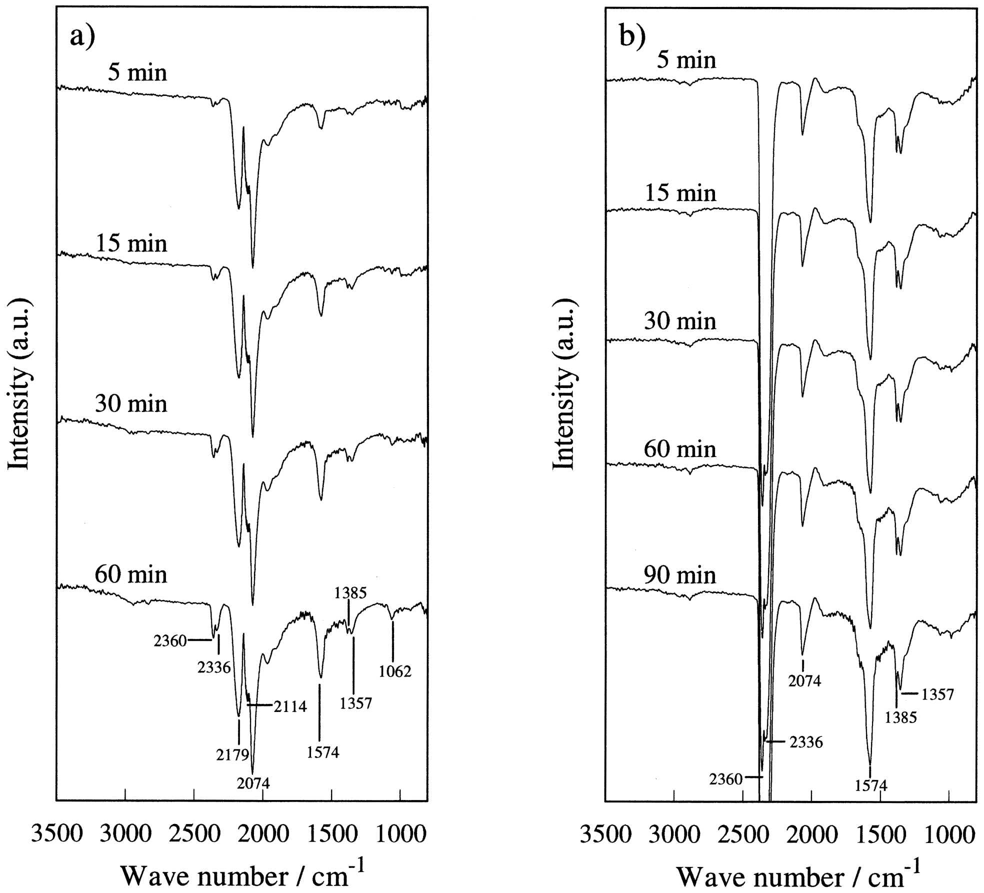

Fig. 1. FT-IR spectra of CO (a) and CO_2 (b) hydrogenations over a Pd/Ga_2O_3 catalyst.
(a): the sample was exposed to a H_2/CO flow (2:1), (b): the sample was exposed to a H_2/CO_2 flow (3:1), The spectra were recorded at a reaction temperature of 523 K and a pressure of 1 atm.

Table 2. Catalytic Activity of Methanol Synthesis for CO Hydrogenation over Various Pd Catalysts

Catalysts[a)]	Activity[b)]	TOF	Activation energy
	mol/kg-cat h	h^{-1}	kJ/mol
Pd/Al_2O_3	0.6	6.3	49.7
Pd/CeO_2	2.3	42.5	91.5
Pd/Ga_2O_3	0.3	7.1	57.2
Pd/La_2O_3	0.8	47.2	88.0
Pd/ZnO	1.5	35.2	90.8
Pd/ZrO_2	8.9	164.5	84.7
Cu/ZnO	1.9	11.1	94.0
$Cu/ZnO/Al_2O_3$	9.7	10.8	86.5

a) Pd content = 5 wt%, Cu/ZnO = 5/95 wt%, $Cu/ZnO/Al_2O_3$ = 50/40/10 wt%.
b) Reaction conditions: Reaction temperature = 523 K, H_2/CO = 2, Total pressure = 50 atm.

activity of supported Al_2O_3 and Ga_2O_3 were found to exhibit very low values.

It was found that the support effect of Pd catalysts was different between the CO_2 and CO hydrogenation reactions. We, accordingly, considered that the reaction mechanisms of methanol synthesis by the hydrogenation of CO and CO_2 over palladium catalysts were distinct from each other. Thus, we examined the reaction mechanism over the Pd/ZrO_2 and Pd/Ga_2O_3 catalysts by CO and CO_2 hydrogenation using in situ FT-IR.

Pd/Ga_2O_3 Catalyst. Figures 1 (a) and (b) show the in situ FT-IR spectra of the CO and CO_2 hydrogenations at 523 K and 1 atm over the Pd/Ga_2O_3 catalyst. In flowing CO/H_2 hydrogenation, peaks appeared at 1062, 1357, 1385, 1574, 2074, 2114, 2179, 2336 and 2360 cm^{-1}. From the literature data,[8,9] the peaks at 1357 and 1385 cm^{-1} were assigned to symmetric O–C–O stretching of the adsorbed formate, the absorption at 1574 cm^{-1} corresponded to the asymmetric O–C–O stretching of the adsorbed formate, and the bands at 2336 and 2360 cm^{-1} corresponded to gaseous CO_2. The weak peak at 1062 cm^{-1} was assigned to the C–O stretching vibration of methanol or methoxy species. The peaks at 2074, 2114, and 2179 cm^{-1} were assigned to gaseous CO. The intensities of CO_2, formate and methoxy species increased with increasing the reaction time, and reached a steady state after 60 min. This results suggested that the methanol synthesis for CO hydrogenation involved the surface formate and methoxy species. The formation of the surface formate species next proceeded to a gaseous CO_2 and H_2, where CO_2 was formed by a water gas-shift reaction. That is, the methanol was synthesized from only CO_2 and H_2 over the Pd/Ga_2O_3 catalyst. Because CO_2 formation by the water gas-shift reaction proceeded significantly more slowly, the methanol synthesis activity of CO hydrogenation was very

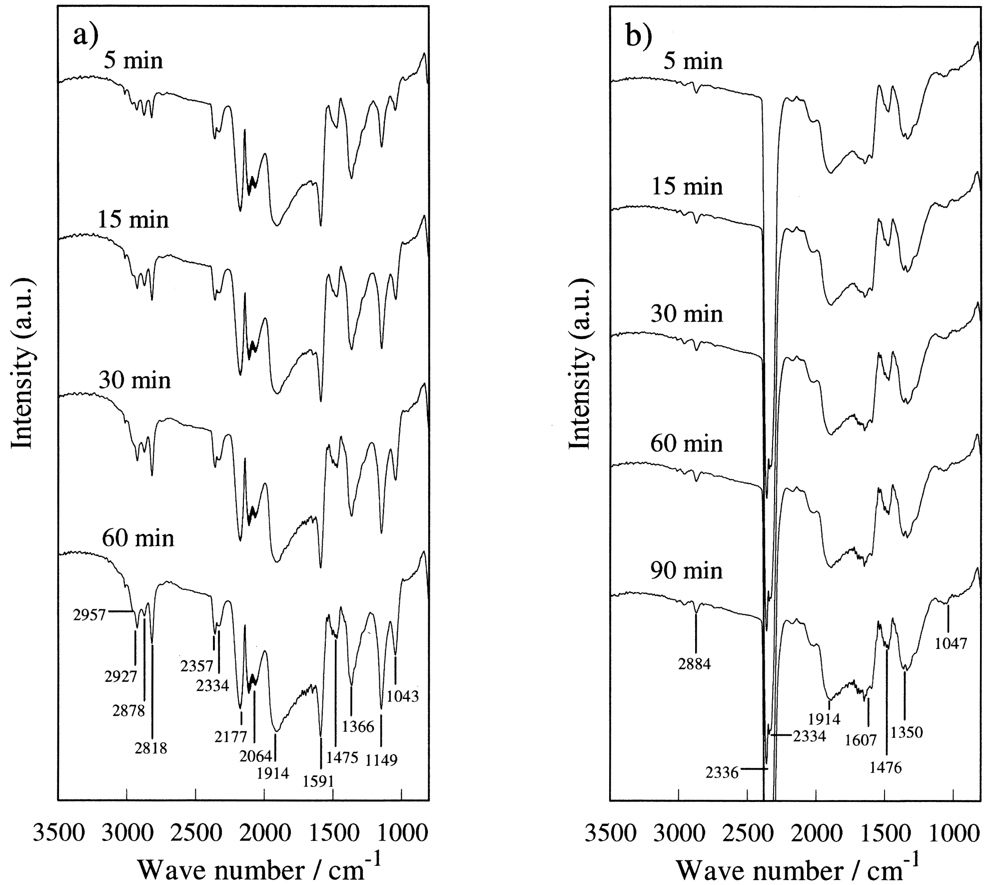

Fig. 2. FT-IR spectra of CO (a) and CO_2 (b) hydrogenations over a Pd/ZrO_2 catalyst.
(a): the sample was exposed to a H_2/CO flow (2:1), (b): the sample was exposed to a H_2/CO_2 flow (3:1), The spectra were recorded at a reaction temperature of 523 K and a pressure of 1 atm.

low.

For CO_2 hydrogenation, the formate species and gaseous CO_2 were observed. Intensive formate bands immediately appeared, indicating that the rate of formate synthesis is very fast from CO_2 and H_2. The weak peak of the methanol or methoxy species appeared at around 1062 cm^{-1}, and then increased with increasing reaction time. These results suggested that methanol synthesis proceeds via formate and methoxy intermediates. It was thus considered that the methanol synthesis had the same reaction mechanism between the CO and CO_2 hydrogenations over the Pd/Ga_2O_3 catalyst. Furthermore, this mechanism was in good agreement with that reported over the Cu/ZnO catalyst.[16]

Pd/ZrO_2 Catalyst. Figures 2 (a) and (b) show the in situ FT-IR spectra of CO and CO_2 hydrogenations at 523 K and 1 atm over the Pd/ZrO_2 catalyst. The peaks appeared at 1043, 1149, 1366, 1475, 1591, 1914, 2064, 2177, 2334, 2357, 2818, 2878, 2927 and 2957 cm^{-1} in flowing CO/H_2. The peaks at 1043, 2818 and 2927 cm^{-1} are assigned to C–O stretching and C–H stretching of the adsorbed methoxy species. The bands centered at 1366, 1591, 2878 and 2957 cm^{-1} were due to the surface formate species. The 1149 cm^{-1} band was assigned to an adsorbed formaldehyde species. The adsorbed and gaseous CO were observed at between 1900 and 2200 cm^{-1}. The weak signals at 2334 and 2357 cm^{-1} were due to gaseous CO_2. It was found that the formate, methoxy and formaldehyde species were formed by CO hydrogenation over the Pd/ZrO_2 catalyst. Baiker et al. also identified the surface species during the hydrogenation of CO and CO_2 reactions over the Pd/ZrO_2 catalyst using in situ FT-IR spectroscopy.[8] The surface species observed in this study were in good agreement with the literature data. Furthermore, it was reported that the mechanism of methanol synthesis proceeded via formaldehyde and methoxy species by CO hydrogenation over the Pd/ZrO_2 catalyst because there is no apparent correlation between methanol formation and a decrease in the surface formate.[9] That is, the formaldehyde and methoxy species are the pivotal intermediates on the route to methanol, while the formate species is not a direct precursor of methanol production.

The formate species (around 1350, 1607 and 2884 cm^{-1}), the methoxy species (1047 cm^{-1}), and carbonate species (1476 cm^{-1}) were observed for CO_2 hydrogenation. The peaks at 2334 and 2360 cm^{-1} corresponded to gaseous CO_2. No formaldehyde species was observed by CO_2 hydrogenation, indicating that the reaction pathway was clearly different between the CO and CO_2 hydrogenation reactions. Baiker et al. reported[9] that the surface carbonate does not necessarily act as an intermediate during the formation of surface formate; rather, a direct pathway from CO_2 and H_2 appears to dominate. The methanol was thus produced via surface formate and methoxy

Table 3. Catalytic Activity of Methanol Synthesis for CO Hydrogenation over Pd/ZrO_2, ZrO_2, and the Physically Mixed Pd/SiO_2 and ZrO_2 Catalysts

Catalysts[a)]	CO uptake	Metal surface area	Activity[b)]	TOF
	ml/g-cat	m^2/g-cat	mol/kg-cat h	h^{-1}
Pd/ZrO_2	0.68	2.16	8.88	164.5
ZrO_2	—	—	—	—
Pd/SiO_2	2.26	7.22	0.35	2.0
$Pd/SiO_2 + ZrO_2$	1.15	3.68	0.14	1.5

a) Pd content = 5 wt%, $Pd/SiO_2:ZrO_2 = 1:1$ (weight ratio).

b) Reaction conditions: Reaction temperature = 523 K, $H_2/CO = 2$, Total pressure = 50 atm.

species. Because the formate hydrogenation to methoxy species is very slow, the rate of methanol formation by CO_2 hydrogenation proceeded more slowly as compared to that by CO hydrogenation.

The Effect of a ZrO_2 Support on the Pd/ZrO_2 Catalyst. In order to clarify the effect of a ZrO_2 support on the Pd/ZrO_2 catalyst, we examined the catalytic activity and the surface species during the hydrogenation of CO over Pd/SiO_2, ZrO_2, and the physically mixed Pd/SiO_2 and ZrO_2. Table 3 shows the catalytic activity for CO hydrogenation at 50 atm and 523 K. In spite of the surface area of Pd being very large, the methanol synthesis activity of the Pd/SiO_2 catalyst was very low. This means that the Pd metal does not operate the active site for methanol synthesis. Furthermore, ZrO_2 exhibited no catalytic activity. The activity of the physically mixed Pd/SiO_2 and ZrO_2 catalyst was the same as that of the Pd/SiO_2 catalyst, suggesting that the formation of an active site was necessary for a strong interaction between Pd and ZrO_2.

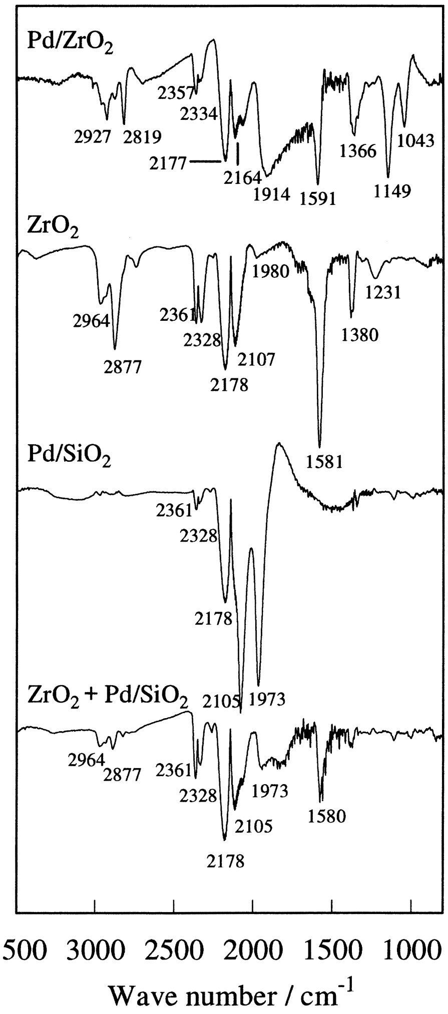

Fig. 3. FT-IR spectra of CO hydrogenation over a Pd/SiO_2, ZrO_2, and the physically mixed Pd/SiO_2 and ZrO_2 catalyst. All spectra were recorded 90 min after the H_2/CO (2:1) flow at a reaction temperature of 523 K and a pressure of 1 atm.

The in situ IR spectra also indicated that a strong interaction between Pd and ZrO_2 was present in the Pd/ZrO_2 catalyst. Figure 3 shows the IR spectra obtained while exposing CO/H_2 at 523 K and a total pressure of 1 atm on Pd/SiO_2, ZrO_2, and the physically mixed Pd/SiO_2 and ZrO_2. Spectra were collected after 90 min at each catalyst. The surface formate (1380, 1581, 2877 and 2964 cm^{-1}) and carbonate (1231 cm^{-1}) were observed over ZrO_2 in flowing CO/H_2 hydrogenation. The adsorbed and gaseous CO were detected at between 1980 and 2178 cm^{-1}. In addition, gaseous CO_2 (2328 and 2361 cm^{-1}) was formed over the entire temperature range on ZrO_2. In contrast, only a very weak gaseous CO_2 was detected during CO hydrogenation over the Pd/SiO_2 catalyst, except that both adsorbed and gaseous CO were observed. It was found that CO_2 formation by the water-gas shift reaction mainly occurred over ZrO_2. For physically mixed Pd/SiO_2 and ZrO_2, the spectrum comprised features attributed to the surface species of Pd/SiO_2 and ZrO_2. No surface formaldehyde and methoxy species were detected over the physically mixed catalyst, suggesting that the active centers of the Pd/ZrO_2 catalyst were attributed to intimate contact between the ZrO_2 and Pd particles. Baiker et al. have reported that the mechanism of CO hydrogenation depended on the structure of the zirconia and the palladium-zirconia interface.[8,9] In a catalyst prepared by wet impregnation, the crystalline palladium particles are in relatively loose contact with the support and, consequently, form a comparatively small interfacial area with the crystalline and stoichiometric zirconia. In contrast, in the palladium/zirconia catalyst derived from the amorphous Pd–Zr alloy, the small palladium particles are intermeshed in the surrounding amorphous zirconia phase, forming an extremely large interfacial area. Furthermore, Guo et al. have reported[17] that stoichiometric ZrO_2 films on Pd(110) were found to decompose at temperatures above 840 K under vacuum conditions. The decomposition of

ZrO_2 on Pd was initiated at the oxide-metal interface through the formation of the Zr–Pd alloy and the release of oxygen. Qin et al. also reported[18] that the intermetallic phase of $PdZr_2O_x$ was formed at the interface of Pd and zirconia after a high- temperature heat treatment. In our FT-IR measurements, the surface formaldehyde and methoxy species, which were intermediates of the methanol synthesis by the hydrogenation of CO, were observed only for the Pd/ZrO_2 catalyst prepared by the coprecipitation method. It was considered that the Pd particles in the catalysts prepared by coprecipitation were in intimate contact with ZrO_2 and that the interface plays an important role in the hydrogenation of CO. Further work on the structural and chemical properties of the Pd–ZrO_2 interface is now being carried out using surface- science techniques.

Conclusion

(1) It is clear that the Pd/ZnO and Pd/Ga_2O_3 catalysts show high methanol formation rates from CO_2 and H_2. On the other hand, the Pd/ZrO_2 catalyst shows a high methanol synthesis activity from CO hydrogenation.

(2) From in situ FT-IR measurements, the formate and methoxy species observed on the Pd/Ga_2O_3 catalyst during CO_2 hydrogenation, indicating that the methanol synthesis proceeds via formate and methoxy intermediates. In contrast, the reaction pathway was clearly different between the CO and CO_2 hydrogenation reactions over the Pd/ZrO_2 catalyst. That is, surface formaldehyde and methoxy species were observed as intermediates during CO hydrogenation, while the surface formate and methoxy species were detected during CO_2 hydrogenation. It was thus determined that the reaction mechanisms of the methanol synthesis form the CO and CO_2 hydrogenation reactions were strongly dependent on the types of supports over the Pd catalysts.

(3) It was considered that the Pd particles in the catalysts prepared by coprecipitation were in intimate contact with the ZrO_2, and that the interface plays an important role in the hydrogenation of CO.

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