Diffuse reflectance IR spectroscopic study on the role of promoters in the reactivity of carbon monoxide with hydrogen over novel Pd sulfide catalyst

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Introduction

For an industrial methanol synthesis, Cu/Zn-type catalyst is currently employed using $CO/H_2/CO_2$ feed. This type of catalyst is usually operated at 523 K and 5 – 10 MPa and yields above 1000 g/kg-cat/h of methanol. However, due to thermodynamic limitations, a single-pass CO conversion is restricted below 60% (523 K and 5.0 MPa), which requires a gas-recycle system. Besides the Cu/Zn-type catalyst, reduced Pd catalysts are well known to show excellent activities at lower reaction temperatures and pressures. For example, a reduced Pd/CeO_2 yields 300 g/kg-cat/h of methanol from CO/H_2 feed at 443 K and 3.0 MPa, which is comparable with that obtained with the Cu/Zn catalyst at 503 K and 3.0 MPa from $CO/H_2/CO_2$ feed.[1]

Many studies have shown that the methanol synthesis activity and selectivity of the reduced Pd catalyst changes sensitively depending on the natures of the supports[1, 2] and some metal additives such as Ca nitrate and Mg chloride improve a methanol synthesis activity of a reduced Pd/SiO_2.[3-5] It is suggested that they change an electronic property of surface Pd sites and/or a morphology of Pd crystallites. Searching new type of methanol synthesis catalysts, the authors found that Rh sulfide ($Rh_{17}S_{15}$)[6] and Pd sulfide ($Pd_{16}S_7$)[7] yield methanol from CO/H_2 feed at a relatively higher reaction temperature and pressure (613 K and 5.1 MPa). These sulfide catalysts have a quite unique property, a sulfur tolerance. $Pd_{16}S_7$ shows a quite stable activity even in the presence of H_2S 100 ppm in concentration while a commercial Cu/Zn/Al catalyst is irreversibly poisoned by H_2S.[7] In order to make clear the active site of the $Pd_{16}S_7$, we examined effects of supports[8] and metal additives.[9] It was found that a sulfided Pd/SiO_2 promoted with Ca nitrate shows a higher activity than the $Pd_{16}S_7$. STY of methanol obtained with the sulfided $Ca\text{-}Pd/SiO_2$ was 5 times higher than that obtained with the $Pd_{16}S_7$. At 593 K, 5.1 MPa and 30 m^3 (STP)/kg-cat/h, STY of methanol obtained with the sulfided $Ca\text{-}Pd/SiO_2$ reached 730 g/kg-cat/h, which is about 50% of that obtained with the commercial Cu/Zn/Al catalyst from $CO/H_2/CO_2$ feed at the same reaction conditions.

As concerns reactive adsorbed species formed on the sulfided $Ca\text{-}Pd/SiO_2$, the authors found the formation of adsorbed CO species after the methanol synthesis by means of *in-situ* DRIFT spectroscopy.[9] The adsorbed CO species was hydrogenated in a stream of H_2 to yield methanol. In this paper, to make clear the role of the Ca additive in the formation of such the reactive adsorbed species, the nature of adsorbed species formed on sulfided $Ca\text{-}Pd/SiO_2$, sulfided Pd/SiO_2, sulfided Ca/SiO_2 and sulfided SiO_2 were examined by *in-situ* DRIFT spectroscopy as well as CO uptake measurement.

Experimental

CO uptake measurements. CO uptake of the sulfided sample after CO hydrogenation reaction was measured by a pulse method. An oxidized sample was charged in a stainless steel reactor and then the reactor was connected with a gas-line for the sulfiding pretreatment and CO hydrogenation reaction. After sulfiding the sample in a stream of H_2S/H_2 at 673 K, the temperature was reached down to room temperature. A feed composed of CO 33%/H_2 62%/Ar was then continuously fed to the reactor at 5.1 MPa followed by heating of the sulfided sample up to 613 K. This temperature was held for 2 h and then the temperature was reached down to room temperature again. After flushing the syngas in the reactor with a helium flow at 573 K, CO 10%/He pulse was introduced into the reactor at 308 K. The amount of adsorbed CO was determined with a thermal conductivity detector.

DRIFT measurements. To obtain DRIFT spectra of adsorbed species formed on the sulfided sample during and/or after CO hydrogenation reaction, a high-pressure DRIFT chamber equipped with ZnSe window (Spectra-Tech Inc.) was employed here. Details of the procedures for DRIFT measurements can be referred to our preceding paper.[9]

Sample preparations. All the oxidized samples used here were prepared by the impregnation method. Details of the preparation methods can be also referred to our preceding paper.[9]

Results and Discussion

To make clear effects of the Ca additive on the number of adsorption sites for CO of sulfided Pd/SiO_2, CO uptakes of the sulfided $Ca\text{-}Pd/SiO_2$ with different Ca/Pd molar ratios were measured. In **Figure 1**, methanol yields normalized to moles of Pd atom in the sulfided $Ca\text{-}Pd/SiO_2$ with Ca/Pd molar ratios of 0, 0.1, 0.5 and 1.0 are plotted against amount of CO adsorbed on them. Slopes of dashed lines shown in the figure are TOF of each supported sulfide. The addition of small amount of Ca additive to the sulfided Pd/SiO_2 (Ca/Pd molar ratio = 0.1) increases the methanol yield substantially while it has little influence on the amount of adsorbed CO, which results in the increase of TOF from 0.06 sec^{-1} to 0.20 sec^{-1}. It is worthy to note that both sulfided Ca/SiO_2 and sulfided SiO_2 yield no methanol and amount of CO adsorbed on them are negligible. Thus, it is suggested that the irreversible adsorption of CO predominantly occurs on coordinatively unsaturated Pd sites and the addition of the Ca additive significantly enhances a reactivity of the adsorbed CO species for the methanol formation.

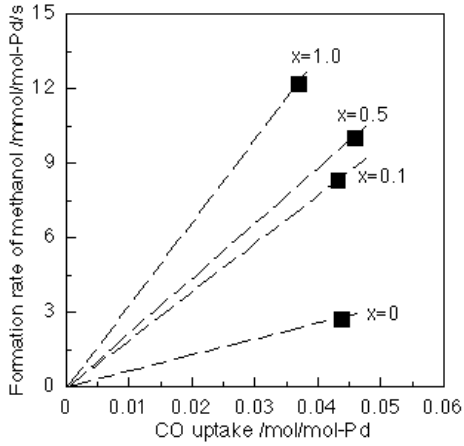
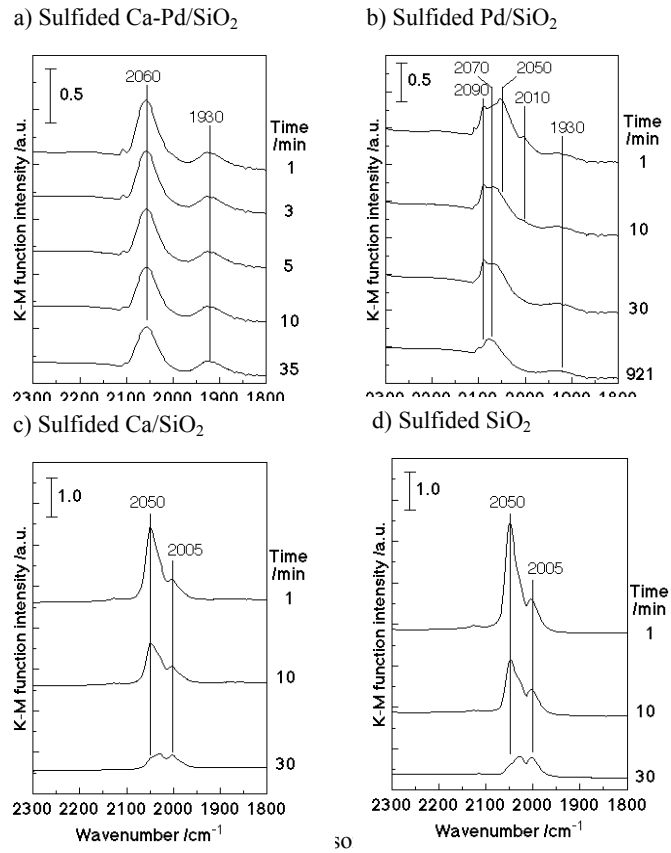


Figure 1 Relationship between yield of methanol normalized to moles of Pd atom in the sulfided $Ca\text{-}Pd/SiO_2$ with different Ca/Pd molar ratios (x; x = 0, 0.1, 0.5, 1.0) and amount of CO adsorbed on them. CO hydrogenation reaction was carried out at 613 K, 5.1 MPa and 20 m^3 (STP)/kg-cat/h using the feed composed of CO 33%/H_2 62%/Ar.

To make clear differences of the nature of adsorbed CO species formed on the sulfided $Ca\text{-}Pd/SiO_2$ and sulfided Pd/SiO_2, DRIFT spectra were measured for both the sulfided samples during and/or

after CO hydrogenation reaction. DRIFT spectra of the sulfided Ca-Pd/SiO_2 (Ca/Pd molar ratio = 0.5) measured during the reaction showed IR bands at 1820, 1600, 1450, 1270, 1110, 1062, 1031, 1007 and 957 cm^{-1}. A shoulder band was also visible at 1304 cm^{-1}. The bands at 1062, 1031 and 1007 are assigned to C-O stretching vibration of the gas-phase methanol while the shoulder band at 1304 cm^{-1} is assigned to C-H bending vibration of the gas-phase methane. On the contrary, very weak bands due to the gas-phase methanol were observed in the spectra of the sulfided Pd/SiO_2 during the reaction. Thus, the promoting effects of the Ca additive were clearly identified by DRIFT measurements. However, the intensity of the band due to the gas-phase CO was too strong to observe the adsorbed CO species.

Then, attentions were paid to the nature of adsorbed CO species remaining on the surface of sulfided samples after the reaction. The temperature was reached down to 298 K under the high-pressure syngas flow and then the pressure of the syngas flow was reached down to 0.3 MPa followed by the flushing with helium. DRIFT spectra of adsorbed CO species were recorded during the flushing as a function of time (**Figure 2**). DRIFT spectra of the sulfided Ca-Pd/SiO_2 show IR bands at 2060 and 1930 cm^{-1}. A weak band is also visible at around 2100 cm^{-1}. In a spectrum of the sulfided Pd/SiO_2, bands are visible at 2090, 2070, 2050, 2010 and 1930 cm^{-1} at the beginning of the flushing while the bands at 2050 and 2010 cm^{-1} disappear quickly. To assign these bands, DRIFT spectra of sulfided Ca/SiO_2 and sulfided SiO_2 were also measured. Both the spectra show bands at 2050 and 2005 cm^{-1} at the beginning of the flushing. The intensities of these bands decrease quickly during the flushing. A weak band is also visible at 2030 cm^{-1} in the both spectra of the sulfided Ca/SiO_2 and sulfided SiO_2 after the flushing of 30 min. These bands are assigned to CO species weakly interacted with SiO_2 surface (possible surface hydroxyl groups). From these spectra, we can assign the bands at 2050 and 2010 cm^{-1} appeared in the spectrum of the sulfided Pd/SiO_2 to CO species interacted with SiO_2 surface. In other words, the bands at 2060 and 1930 cm^{-1} in the spectra of the sulfided Ca-Pd/SiO_2, and those at 2090, 2070 and 1930 cm^{-1} in the spectra of the sulfided Pd/SiO_2 can be assigned to CO species adsorbed on Pd sites (2090, 2070 and 2060 cm^{-1}: linear-type adsorbed species, 2030 cm^{-1}: bridge-type adsorbed species). Since the IR band positions of CO species adsorbed on Pd sites linearly in the spectra of the sulfided Pd/SiO_2 is higher than that of the sulfided Ca-Pd/SiO_2, surface Pd sites formed on sulfided Pd/SiO_2 are in a slightly electron deficient state compared with those on the sulfided Ca-Pd/SiO_2. As reported previously,[9] the intensities of the bands of adsorbed CO species remaining on the surface of the sulfided Ca-Pd/SiO_2 after the methanol synthesis decreases during the heating of the sample in a stream of H_2. The decrease of the intensities of these bands is accompanied with the appearance of the bands due to the gas-phase methanol. On the contrary, no bands due to the gas-phase methanol were observed during the heating of the sulfided Pd/SiO_2 in the stream of H_2 while the intensities of the bands due to the adsorbed CO species decreases with increasing the temperature. Thus, the reactivity of adsorbed CO species remaining on the surface of sulfided Ca-Pd/SiO_2 for the methanol formation is much higher than that on the sulfided Pd/SiO_2. This is quite consistent with the notion suggested by the CO uptake measurements. Thus, it is concluded that the addition of the Ca additive to the sulfided Pd/SiO_2 slightly increase the electron density of the surface Pd sites, which results in the increase of the reactivity for the methanol formation of CO species adsorbed on them.



(a; Ca/Pd molar ratio = 0.5), sulfided Pd/SiO_2 (b), sulfided Ca/SiO_2 (c) and sulfided SiO_2 (d) after CO hydrogenation reaction at 613 K and 5.1 MPa using the feed composed of CO 33%/H_2 62%/Ar. All the spectra shown here were measured during the helium flushing at 298 K and 0.3 MPa as a function of time.

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References

1) Matsumura, Y.; Shen, W.-J.; Ichihashi, Y.; and Okumura, M., *J. Catal.,* **2001**, 197, 267.
2) Ichikawa, M. ; and Shikakura, K., *Shokubai*, **1979**, 21, 253.
3) Kikuzono, Y.; Kagami, S.; Naito, S.; Onishi, T.; and Tamaru, K., *Chem. Lett.*, **1981**, p. 1249.
4) Gotti , A.; and Prins, R., *J. Catal.*, **1998**, 175, 302.
5) Gusovius, A. F.; Walting, T. C.; and Prins, R., *Appl. Catal. A; General*, **1999**, 188, 187.
6) Yamada, M.; Koizumi, N.; Miyazawa, A.; and Furukawa, T., *Catal. Lett.,* in print
7) Koizumi, N.; Miyazawa, A.; Furukawa, T.; and Yamada, M., *Chem. Lett.*, **2001**, p. 1282.
8) Koizumi, N.; Murai, K.; Takasaki, S.; and Yamada, M., Pap. - *Am. Chem. Soc., Div. Fuel Chem.*, **2001**, 46 (2), 437-438.
9) Koizumi, N.; Murai, K.; Takasaki, S.; Yamada, M. Prepr. Pap. - *Am. Chem. Soc., Div. Fuel Chem.*, **2002**, 47 (1), in-print