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Transformation of methane formation sites into methanol formation ones during CO–H_2 reaction over Pd/CeO_2 in its SMSI state

Shuichi Naito*, Toshinori Kasahara, Toshihiro Miyao

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

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Abstract

The phenomena of induction period of methanol formation, observed in CO–H_2 reaction over Pd/CeO_2 catalysts under SMSI state, was investigated in depth. The magnitude of the induction period was dependent on the extent of SMSI, and higher temperature H_2 reduction lengthened it accompanied with the increase of the number of active sites for methane formation. On the contrary, by the pretreatment of SMSI surface with water vapor, this induction period almost disappeared with the drastic decrease of methane formation rate. These results indicate that methane formation sites would be transformed into methanol formation sites by the oxidation of water vapor formed during CO–H_2 reaction. Infrared spectroscopic investigation of adsorbed CO after various pretreatments indicated that during the induction period thin layers of reduced ceria, which preferentially covered Pd(1 1 1) plane under SMSI state, were removed from the Pd(1 1 1) plane by formed water vapor during CO–H_2 reaction. It was concluded that Pd(1 1 1) plane adjacent to ceria would be the efficient active sites for methanol formation.

Keywords: Palladium; Cerium oxide; CO hydrogenation; Methane; Methanol; Strong metal support interaction

1. Introduction

There are many studies concerning the activity and selectivity controlling factors of methane and methanol formation in CO–H_2 reaction over supported Pd catalysts. Many factors have been proposed such as particle sizes of Pd, the composition of supports and the addition of promoters. In the case of methanol formation, two different Pd species have been considered as active sites. The first one is cationic Pd species, which was proposed by Ponec and co-workers [1] many years ago in the stabilization of Pd^+ by Mg^{2+}. Recently, Matsumura et al. [2] have reported that methanol is effectively synthesized in CO–H_2 reaction at lower temperatures as 443 K over Pd/CeO_2, in which the Pd species are cationic.

The other active site is the metallic Pd particles, where the selectivity controlling factors seem to be rather complicating. Hicks and Bell [3] have studied CO hydrogenation over Pd/SiO_2 and Pd/La_2O_3 and concluded that the Pd dispersion has little effect on the methanol turnover frequency over both Pd/SiO_2 and Pd/La_2O_3, for dispersion between 10 and 20%. They also observed that the Pd morphology influences the specific activity of Pd/La_2O_3 for methanol synthesis: Pd(1 0 0) is nearly threefold more active than Pd(1 1 1).

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* Corresponding author. Tel.: +81-45-481-5661x3903; fax: +81-45-491-7915.
E-mail address: naitos01@kanagawa-u.ac.jp (S. Naito).

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For a fixed morphology, the specific methanol synthesis activity of Pd/La_2O_3 is a factor of 7.5 greater than that of Pd/SiO_2. Gotti and Prins [4] and Gusovius et al. [5] have reported the catalytic behavior of Pd catalysts supported on ultrapure silica and promoted with basic metal oxides in the hydrogenation of CO to methanol at high pressures. Addition of small amount of Ca onto Pd/SiO_2 dramatically promotes the formation of methanol and suppresses the formation of other hydrocarbons. From the measurements of TEM, TPR as well as H_2 and CO chemisorption, they concluded that Ca species located on and near the Pd particles give rise to the catalytic activity for methanol. Moreover, infrared spectra of adsorbed CO suggest that Ca is preferentially located on the Pd(1 1 1) sites of Pd/SiO_2 than the Pd(1 0 0) sites.

Recently we have reported that the activity and selectivity of CO–H_2 reaction over Pd/CeO_2 catalysts changed drastically by SMSI effect. Under low temperature reduction condition both methane and methanol were formed on this catalysts, but there was a certain induction period for methanol formation [6,7]. Higher temperature reduction enhanced the rate of methane formation several times without changing the activation energy. At the same time, the induction period of methanol formation was lengthened a few times. These results indicate that methane formation sites may be formed at the vicinity of Pd and reduced CeO_2 when Pd particles were encapsulated into CeO_2 support. As the reaction proceeded, the rate of methane formation was decreased considerably under both conditions, accompanied with the drastic acceleration of methanol formation rate after the induction period.

The induction phenomena in the rate of methanol formation in CO–H_2 reaction have been found for many cases such as Ru/Al_2O_3, $CeCu_2$ and Cu/ZnO catalysts. The magnitude of the induction phenomena was dependent on the type of the catalyst precursors and the nature of the support. Recently Ali and Goodwin [8] investigated the induction phenomenon observed for the rate of methanol synthesis on Pd/SiO_2 by evaluating the surface concentration of the active intermediates leading to methanol and their residence times for the beginning and for the end of the induction period. They concluded that it could best be attributed to an increase in the number of active sites/intermediates forming methanol. In the present work, we have also focused our attention for the induction period of methanol formation over Pd/CeO_2, applying infrared spectroscopic investigations of adsorbed CO under various reaction conditions. We concluded that the methanol formation sites may be created by the transformation of methane formation sites with the formed water during CO–H_2 reaction.

2. Experimental

Ceria (20 m^2/g) supported Pd/CeO_2 catalysts were prepared by a conventional impregnation method, employing $(NH_4)_2PdCl_4$ as a precursor. The reaction was carried out in a closed gas circulation system (CO:H_2 = 1:3, total = 120 Torr). Before each run the catalyst was reduced by hydrogen at 573 K (low temperature reduction: UTR) or 773 K (high temperature reduction: HTR). To gather primary products, a liquid nitrogen cold trap was employed in the circulation system, and the products were analyzed by gas chromatography as well as mass spectroscopy. In the case of infrared spectroscopic experiments for CO adsorption and during CO–H_2 reaction, a catalyst desk was put in an infrared cell, which was connected to the circulation system. Infrared spectra were taken with JEOL Diamond 20 Fourier-transform spectrometer.

The particle sizes and dispersion of Pd/CeO_2 were determined by XRD line width measurements, TEM photograph as well as H_2 and CO adsorption at room temperature. These methods confirmed that LTR and HTR treatments did not affect Pd particle sizes (30–40 nm). But the amount of adsorbed H(a) and CO(a) on the Pd surface decreased drastically by HTR treatment (in the case of H(a): from 8.1×10^{-5} to 3.0×10^{-5} mol/g-cat. and in the case of CO(a): from 8.0×10^{-5} to 1.7×10^{-5} mol/g-cat.), and were restored to their original values by O_2 treatment at 723 K followed by LTR. These results clearly indicate the modification of thin layers of reduced ceria (Ce_2O_3) on the surface of Pd particles (SMSI effect), which could be observed by high resolution TEM and EDX analysis. XPS analysis indicated the existence of reduced Ce^{3+} in the spectra of Ce 3d transition, although no shift was observed for Pd 3d transition from bulk metal.

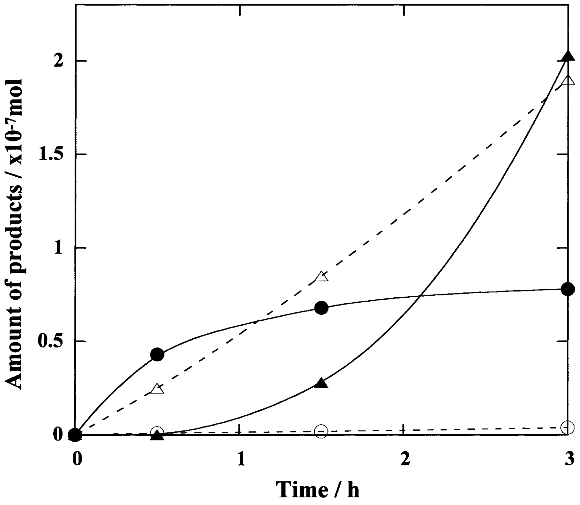

Fig. 1. Time courses of CO–H_2 reaction over 4 wt.% Pd/CeO_2 at 413 K under LTR: LTR (solid lines); H_2O pretreatment after LTR (broken lines); methane (○, ●); methanol (△, ▲).

3. Results and discussion

Figs. 1 and 2 demonstrate the typical time courses of CO–H_2 reaction over 4 wt.% Pd/CeO_2 at 413 K under LTR and HTR conditions, respectively. Under LTR condition, both methane and methanol were formed from the beginning of the reaction, but the rate of methanol formation was very slow and exhibited an induction period of 1 h. After induction period, its formation rate increased drastically and was accompanied by a decrease in the rate of methane formation. On the other hand, the situation was completely different and the selectivity changed drastically under HTR. The rate of methane formation increased several times at the initial stage of the reaction without changing activation energy (85–87 kJ/mol), and the length of the induction period for methanol formation became several times longer, which indicates that active sites are created by HTR treatments. To clarify the phenomena taking place during the induction period for methanol formation, freshly reduced catalysts were pretreated by 10 Torr of water vapor for 2 h, and then CO–H_2 reaction was carried out at 413 K. By this water vapor pretreatment, the induction period for methanol formation almost disappeared and the methane formation was suppressed dramatically (open symbols with broken lines in both figures). These results clearly indicate that methane formation sites are transformed into methanol formation sites by the oxidation of water produced during CO–H_2 reaction.

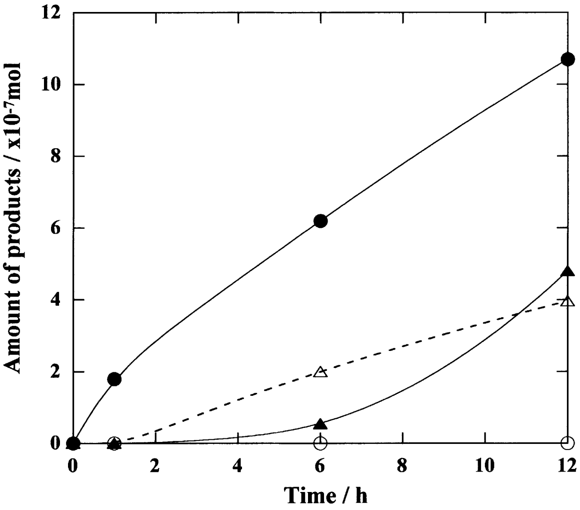

Fig. 2. Time courses of CO–H_2 reaction over 4 wt.% Pd/CeO_2 at 413 K under HTR: HTR (solid lines); H_2O pretreatment after HTR (broken lines); methane (○, ●); methanol (△, ▲).

We have already reported that $^{12}C^{18}O$–$^{13}C^{16}O$ isotopic exchange reaction took place at around 240–270 K over Pd/CeO_2 (LTR) with the activation energy of 20 kJ/mol, and was enhanced for several times by HTR treatment without changing the activation energy [7]. This situation was quite similar to the enhancement effect of methane formation by SMSI as mentioned above. The extremely high activity with low activation energy in this exchange reaction strongly suggests that this process did not proceed through dissociative adsorption of CO, but through a geminal dicarbonyl adsorbed species, $(CO)_2$(a), as proposed by Bossi et al. [9] in the case of Ru/Al_2O_3. It is worth noticing that the exchange reaction was strongly retarded by the presence of H_2, suggesting the formation of $(HCO)_2$(a) type intermediates, which inhibits the reverse reaction to dicarbonyl species. Moreover, the exchange reaction did not proceed at all over the surface after the induction period of methanol formation in CO–H_2 reaction. From these experimental results we have already proposed a new reaction mechanism for methane formation through dicarbonyl adsorbed species at the interface of Pd and reduced ceria (probably Ce_2O_3), and methane

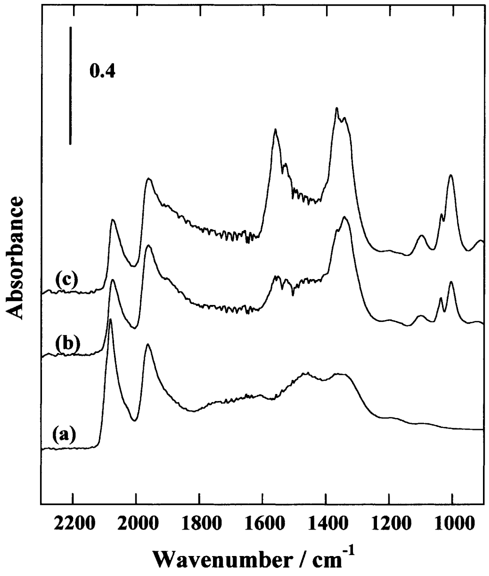

Fig. 3. FT-IR spectra of adsorbed CO and adsorbed species during CO–H_2 reaction over 4 wt.% Pd/CeO_2 at 413 K under LTR: (a) adsorbed CO at room temperature; (b) CO–H_2 reaction for 2 h; (c) CO–H_2 reaction for 6 h.

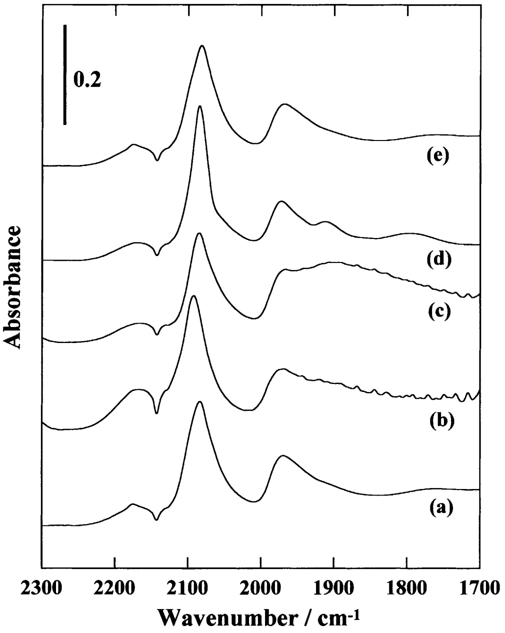

Fig. 4. FT-IR spectra of adsorbed CO after various pretreatments: (a) LTR; (b) 1 Torr of H_2O vapor pretreatment at 413 K after LTR; (c)10 Torr of H_2O vapor pretreatment at 413 K after LTR; (d) H_2 reduction at 413 K; (e) LTR.

would be formed through these intermediates by the disproportionation and hydrogenation.

Fig. 3 shows the infrared spectra of adsorbed CO (spectrum (a)) as well as adsorbed species during CO–H_2 reaction at 413 K over Pd/CeO_2 under LTR condition. When the mixed gas of CO and H_2 was introduced onto the freshly reduced (LTR) surface at 413 K, two strong bands at 2076 and 1958 cm^{-1} were observed, which can be attributed to the linear CO(a) on top of smaller Pd particles and the bridged CO(a) on Pd(1 0 0) plane of larger Pd particles [3,10,11]. In addition, broad peaks emerged at around 1650–1350 cm^{-1}, which may be assigned to formate and carbonate species formed at the interface of Pd and ceria [12]. Spectra (b) and (c) were taken after induction period of methanol formation, where a new broad shoulder peak emerged gradually at around 1900 cm^{-1}, which can be assigned to bridged CO(a) on Pd(1 1 1) plane of larger Pd particles. Binet and co-workers [13] have investigated CO adsorption on Pd particles supported on ceria and found that decoration of Pd crystallites by ceria was observed for temperatures as low as 673 K in the case of less dispersed Pd/CeO_2 catalysts. Reversibility of the decoration upon reoxidation at 883 K was found to depend on the Pd faces, CO adsorption on (1 1 1) faces being more easily recovered than CO adsorption on (1 0 0) faces. Similar decoration and recovery phenomena are taking place in our case, and thin layers of reduced ceria, which preferentially covered Pd(1 1 1) plane under SMSI state, are removed from the Pd(1 1 1) plane by water vapor formed during CO–H_2 reaction, generating methanol formation sites. Resultantly exposed Pd(1 1 1) plane adjacent to ceria would be the efficient active sites for methanol formation.

To confirm this consideration, freshly reduced Pd/CeO_2 (LTR) was pretreated with 1 Torr of H_2O vapor at 413 K. As shown in Fig. 4 introduction of CO at room temperature gave a similar broad peak at around 1900 cm^{-1}, whose intensity increased considerably when the pretreatment pressure of H_2O was increased to 10 Torr (spectra (b) and (c)). These results suggest that the (1 1 1) plane of Pd particles was already covered with thin layers of reduced ceria under LTR

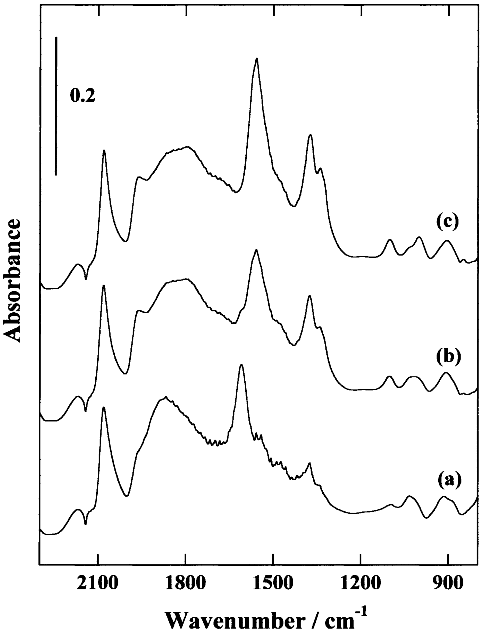

Fig. 5. FT-IR spectra of adsorbed species during CO–H_2 reaction over H_2O pretreated Pd/CeO_2 at 413 K: (a) 0 min; (b) 30 min; (c) 120 min.

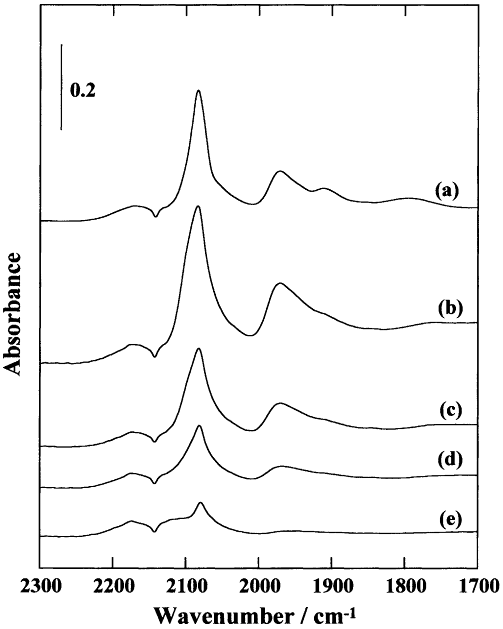

Fig. 6. Dependence of the FT-IR spectra of adsorbed CO over Pd/CeO_2 at room temperature upon the H_2 pretreatment temperatures after oxidation at 623 K: (a) 413 K; (b) LTR (573 K); (c) 673 K; (d) 723 K; (e) HTR (773 K).

treatment (spectrum (a)), which were removed by formed H_2O during CO–H_2 reaction or H_2O pretreatment. As shown spectra (d) and (e), these phenomena were reversible and by H_2 reduction of H_2O pretreated catalysts at 413 K, the intensity of 1900 cm^{-1} peak decreased and disappeared at LTR condition. These results strongly support the above consideration that the appearance of Pd(1 1 1) plane during CO–H_2 reaction or H_2O pretreatment would be closely related to the transformation of methane formation active site into methanol formation sites. Fig. 5 shows the infrared spectra of adsorbed species during CO–H_2 reaction at 413 K after H_2O pretreatment at the same temperature. The adsorbed CO peak at 1880 cm^{-1} stayed almost unchanged during the reaction. Under this condition, no induction period was observed and high activity and selectivity for methanol formation was obtained as shown in Fig. 1. It is interesting to note that strong adsorbed H_2O peak at 1640 cm^{-1}, which was formed by H_2O pretreatment, transformed quickly to formate peaks at 1580 and 1380 cm^{-1}, suggesting the formation of adsorbed formate intermediate by the reaction of CO(a) and H_2O(a). From these experimental results, we like to propose that Pd(1 1 1) plane next to ceria would be the active sites for methanol formation.

To investigate these phenomena more deeply, we studied the changes of FT-IR spectra of adsorbed CO at room temperature, by raising the pretreatment temperatures of H_2 reduction after the oxidation of Pd/CeO_2 at 673 K. As shown in Fig. 6(a), when the oxidized surface was reduced at 413 K, we could observe three peaks at 2078, 1960 and 1900 cm^{-1} on smaller Pd crystallites, (1 0 0) and (1 1 1) planes of larger Pd crystallites, respectively, as mentioned already. No induction period for methanol formation was observed under these conditions. However, when the oxidized surface was reduced at 573 K (LTR), the 1900 cm^{-1} peak, assignable to adsorbed CO on Pd(1 1 1) plane, almost disappeared (spectrum (b)). This phenomenon strongly suggests that Pd(1 1 1) plane is preferentially covered with thin layers of reduced ceria by SMSI effect even under LTR condition. Since no methanol was formed in the absence of (1 1 1) plane, the surface structure of Pd(1 1 1) next to ceria support would be important for methanol formation. By raising the reduction temperature from 573 to 723 K, the intensities of 1960 and 2080 cm^{-1} peaks were decreased gradually, and under HTR condition (773 K), only a weak peak of 2080 cm^{-1} remained as shown in Fig. 6(e). During these processes, the activity for methane formation was increased drastically, indicating that the surface structure of Pd covered with thin layers of reduced ceria is important for methane formation.

4. Conclusion

Infrared spectroscopic investigation of adsorbed CO over Pd/CeO_2 after LTR pretreatment suggests that Pd(1 1 1) plane is completely covered by thin layers of reduced ceria, which brings about the induction period of methanol formation in CO–H_2 reaction. As the reaction proceeds, formed water vapor oxidizes the reduced ceria and removes the thin layers of ceria from Pd(1 1 1) surface. Resultant surface structure of Pd(1 1 1) adjacent to ceria is the efficient active site for methanol formation. It is also concluded that there exists a tendency of SMSI occurrence with reduced ceria, whose feasibility order is as follows: (1 1 1) plane $>$ (1 0 0) plane $>$ smaller Pd particles. Accompanied with the progress of SMSI state, the activity for methane formation is increased drastically, indicating that the surface structure of Pd covered with thin layers of reduced ceria is important for methane formation.

Acknowledgements

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