Growth of Pd particles in methanol synthesis over Pd/CeO_2

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The metal–support contact structure of Pd–CeO_2 changed with increasing the temperature of reduction. Upon high temperature reduction, severe sintering of Pd particles occurred, while sintering of the ceria support was marginal. The catalytic deactivation of the Pd/CeO_2 catalysts during methanol synthesis was caused by the further structural change in the Pd–CeO_2 contact under reaction conditions. Considerably large Pd particles (about 100 nm) were formed in the catalysts subjected to methanol synthesis, and there was a close correlation between the activity loss and the growth of the Pd particles. It was proposed that the structure of Pd–ceria contact shifted from small Pd clusters supported on ceria to sintered large Pd particles dispersed in a mass of ceria.

KEY WORDS: Pd–CeO_2 catalyst; deactivation; sintering; metal–support contact; methanol synthesis

1. Introduction

Palladium in combination with ceria as a support or promoter has received much attention because of applications in automobile emission control and low-temperature methanol production from syngas [1–4]. The growth of the Pd particles was proved to be one of the most important contributing factors to thermal degradation of the three way catalysts, Pd sintering into large (30–80 nm in diameter) particles after high temperature aging [5–7]. We have recently reported that that the Pd/CeO_2 catalysts prepared by the deposition–precipitation method and the coprecipitation method exhibited much higher activity for methanol synthesis from syngas than the conventional Cu-based catalysts [4,8]. These high catalytic activities were attributed to the presence of cationic Pd species due to the strong contact between Pd and ceria, which significantly depends on the temperature of reduction. We also revealed that the sharp increase in the catalytic activity at the initial stage was due to the further structural changes of Pd–CeO_2 contact [9]. However, significant deactivation was also observed after the induction period during methanol synthesis, implying that the Pd–CeO_2 contact may be further considerably changed under reaction conditions. In this study, we have attempted to find the reason for the deactivation of the Pd/CeO_2 catalyst in order to improve the catalytic stability. HRTEM, FE-SEM and EDX studies proved that Pd clusters grew to form some large particles with a diameter of about 100 nm during methanol synthesis.

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2. Experimental

The Pd/CeO_2 catalyst was prepared by the deposition-precipitation method with a final palladium loading of 2.44 wt%, which was determined by ICP analysis [4]. Methanol synthesis from H_2/CO (molar ratio = 2.0) were performed with a fixed-bed continuous-flow reactor operated at 2 MPa, 523 K and a gas space velocity of 7200 h^{-1}. Prior to the reactions, the catalysts were reduced with 10 vol% H_2 in N_2 at 573 K (low temperature reduction, LTR) and 773 K (high temperature reduction, HTR), respectively.

The extended X-ray absorption fine structure (EXAFS) of the reduced samples was determined at room temperature in the transmission mode for the K-edges of Pd at beam-line BL01B1 of SPring-8, Japan. The Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3–15 Å. Inverse Fourier transformation was obtained within the windows of 1.8–2.8 Å in r space. The analysis was performed with a program of "REX" supplied by Rigaku. The Pd–Pd reference was derived from the EXAFS spectra of Pd foil.

Power X-ray diffraction (XRD) patterns were recorded with a Rigaku Rotaflex 20 diffractometer using nickel-filtered Cu K radiation.

FE-SEM observations were carried out using a Hitachi S-5000 instrument equipped with a LINK (AN 1000) probe for EDX analysis.

HRTEM observations were performed with a Hitachi H-9000NA microscope operating at 300 kV.

3. Results

Figure 1 shows the yields of methanol and methane as a function of time-on-stream over the Pd/CeO_2 catalysts subjected to different pretreatments as well as regenerations during the courses of the reactions. For curves (A) and (B), the

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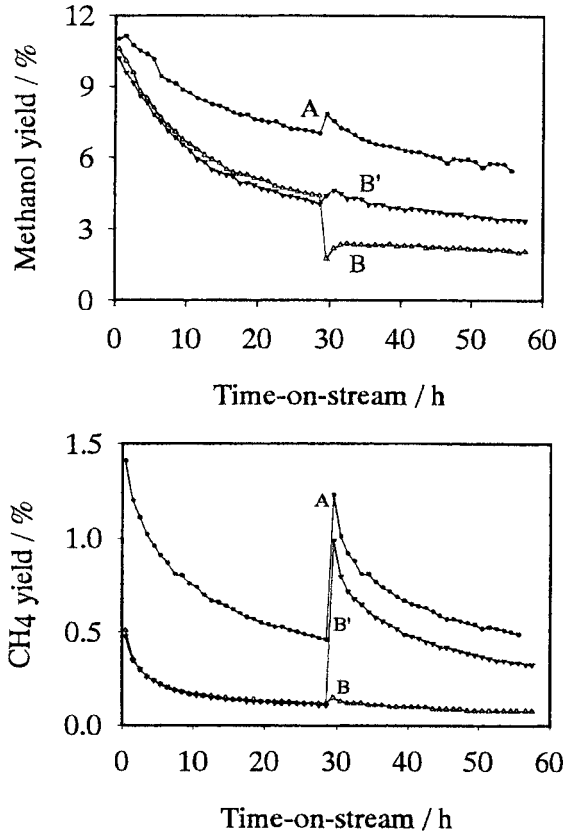


Figure 1. Methanol yields as a function of TOS during CO hydrogenation at 523 K. Curve (A) initially reduced at 573 K, followed by reoxidation and reduction at 573 K after 28.5 h on stream; curve (B) initially reduced at 773 K, reoxidation and reduction at 773 K after 28.5 h on stream; curve (B′) the same procedure as curve (B), but finally reduction at 573 K during the regeneration.

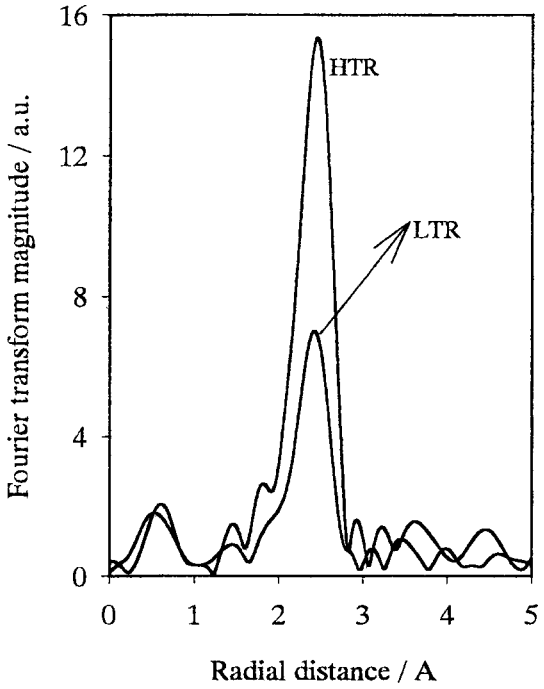


Figure 2. Fourier transforms of the Pd/CeO_2 catalysts.

catalysts were initially pretreated by LTR and HTR, respectively. The HTR catalyst results in lower methanol yield and much less methane formation than that of the LTR catalyst. Consequently, rather low total CO conversions are observed over the catalysts pretreated by HTR.

When the LTR catalyst (curve (A)) used for CO hydrogenation for 28.5 h is reoxidized and reduced at 573 K again, the methanol yield only slightly increases and soon decreases with time-on-stream. However, the corresponding methane yield is almost recovered to its initial level, followed by a similar TOS pattern as that of the freshly reduced catalyst. A comparison between the reduction temperatures of the regeneration process has been made for the initially HTR-treated catalyst. After 28.5 h operation, the catalyst in curve (B) is reoxidized and further reduced with hydrogen at 773 K. The methanol yield drastically decreases and there is even a short induction period before the final stable production. The methane yield has not been affected by this regeneration. The catalyst in curve (B′) was also initially reduced at 773 K and exposed to CO hydrogenation for 28.5 h. When it was subjected to reoxidation at 773 K and then reduction at 573 K, the methanol yield is only slightly recovered, but the methane yield jumps to a close level of curve (A).

The small Pd particles in the reduced catalysts were measured by EXAFS. The XANES (X-ray absorption near-edge structure) spectra of the LTR and HTR samples are similar to that of palladium foil, indicating that no significant structural changes occurred during the reduction processes. As shown in figure 2, the Fourier transforms of the spectra show the presence of Pd–Pd bonding at 2.4 Å. The peak assigned to Pd–Pd bonding is considerably intensified in the HTR catalyst. The roughly calculated coordination number of Pd–Pd is 8.0, which is significantly larger than that of the LTR catalyst with a coordination number of 4.0. The mean diameters of the Pd clusters are estimated to be 0.5 and 1.3 nm in the LTR and HTR catalysts, by utilizing a procedure proposed for predicting Pd particle size from EXAFS data [10,11].

Figure 3 compares the FE-SEM images of the Pd/CeO_2 catalysts after reduction (samples (a) and (c)) and after methanol synthesis for 28.5 h (samples (b) and (d)). For the catalysts just after reduction, no clear palladium particles could be distinguished because they are too small, in consistency with the EXAFS observations. EDX analysis indicates the homogeneous distribution of rather small palladium clusters on ceria. While for the catalysts subjected to methanol synthesis, large palladium crystals were observed. These large Pd crystals are attached on the well-crystallized platelets of ceria with sharp boundaries. The morphological forms of these large palladium particles seem to be related to the previous reduction temperatures. Spherical polyhedra are mainly observed in the LTR catalyst, and elongate polyhedra are dominant in the HTR-treated sample. Figure 4 shows the HRTEM micrographs of the Pd/CeO_2 catalysts subjected to CO hydrogenation for 28.5 h, that is, samples (b) and (d) in figure 3. These HRTEM images clearly

show the presence of larger crystallites with two distinctive morphologies growing in these Pd/CeO_2 catalysts. The mean crystallite size of typical palladium particles examined is 90–100 nm. These values are very close to those of the particle sizes determined by XRD measurements. Meanwhile, the particle sizes of the ceria support are only slightly increased from 7–9 nm after reduction to 10–15 nm after reaction. Hence, it can be said that the Pd–ceria contact was structurally shifted from small Pd particles supported on CeO_2 to few sintered large Pd particles dispersed in a mass of ceria during the reaction processes.

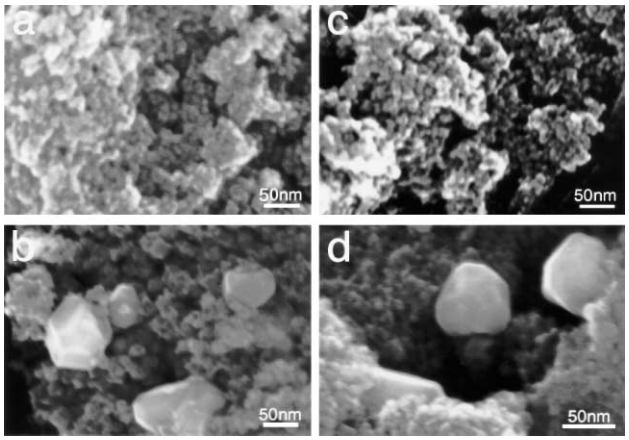
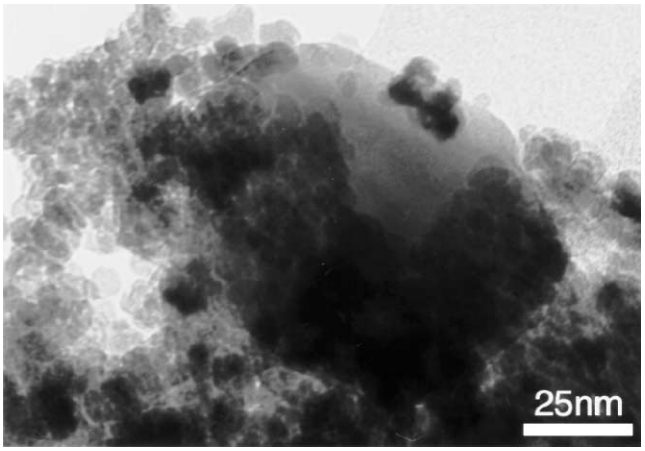
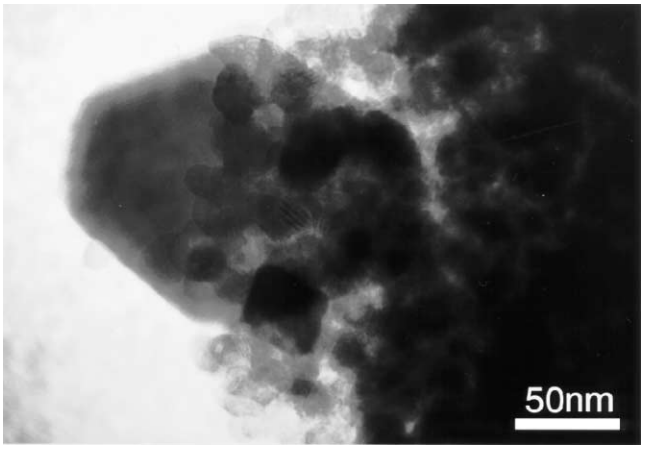


Figure 3. FE-TEM pictures of Pd/CeO_2 catalysts: (a) LTR, (b) LTR + TOS 28.5 h, (c) HTR and (d) HTR + TOS 28.5 h.



(a)



(b)

Figure 4. HRTEM images of Pd/CeO_2 catalysts: (a) LTR + TOS 28.5 h and (b) HTR + TOS 28.5 h.

4. Discussion

Examination of the methanol yield in terms of the reduction temperature confirms that the LTR catalyst gives higher methanol yields than that of the HTR catalyst. This can be understood by assuming a reaction model with a synergistic effect between the ceria support and the Pd particles. The main task of the palladium is to produce atomic hydrogen that is spilled over to the Pd–CeO_2 interface, where the subsequent hydrogenation of adsorbed CO or the potential intermediates of methanol takes place. For the catalysts just after reduction, the particle sizes of palladium were estimated to be 0.5 nm for LTR and 1.3 nm for HTR. The corresponding particle sizes of ceria were determined to be 7 nm after LTR and 9 nm after HTR. Based on the actual loading of Pd and the specific weights of Pd (12.03 g cm^{-3}) and CeO_2 (7.13 g cm^{-3}), it can be calculated that one ceria particle is covered by about 40 small Pd clusters after LTR and only 5 Pd clusters after HTR. This reduction temperature dependence of the Pd–CeO_2 contact is schematically demonstrated in figure 5. Clearly, the Pd–CeO_2 interfacial contact area is significantly large and the Pd particles are relatively small in the LTR catalyst. Therefore, larger CO adsorption and faster H_2 spillover rate in the LTR catalyst would give higher methanol production.

According to the above reaction model, the significant deactivation with TOS, particularly for methanol production, can be correlated with the drastic sintering of Pd under reaction conditions. The catalysts, which have experienced CO hydrogenation for 28.5 h, present a totally different morphology of their metal–support interface from their corresponding reduction states. These catalysts consist of large Pd particles of about 90–100 nm in size surrounded by small ceria particles of about 10–15 nm, as demonstrated in figure 6. The drastic growth of palladium particles would considerably decrease the Pd–CeO_2 interfacial contact area for CO adsorption and inhibit hydrogen spillover for the hydrogenation of adsorbed CO, and accordingly the methanol production would decrease.

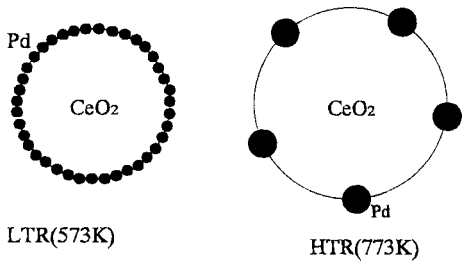


Figure 5. Dependence of Pd–CeO_2 contacts on reduction temperature.

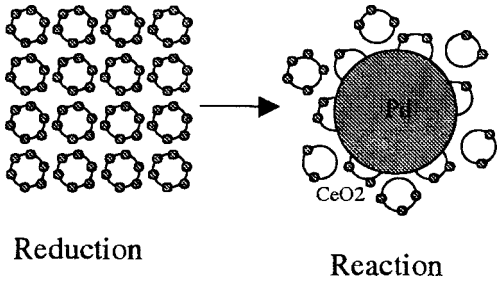


Figure 6. Drastic growth of Pd particles during methanol synthesis.

The regeneration operations in figure 1 provide further evidence for this deactivation model. A possible cause for the catalytic deactivation involving CO is the Boudouard reaction, which can lead to loss of activity through coke deposition on the catalyst surface [12]. However, our studies showed that the reoxidation and reduction treatments for the catalysts during the courses of the reactions do not improve methanol production, indicating that carbon deposition was not significant in this system. The difference in methanol yield over the regenerated catalysts in curves (B) and (B′) suggest that further growth of Pd particles occurred during the regeneration of curve (B), in which high temperature reduction was applied again after the reoxidation. Thus, migration of palladium to form larger particles results in decreasing the number of palladium atoms exposed to the surface as well as the interfacial contact area between palladium and ceria. In this sense, it can be said that the sintering of Pd particles is a detrimental factor both for H_2 dissociation to produce atomic hydrogen and for the Pd–ceria interface which provides CO adsorption sites. These features of this Pd/CeO_2 catalyst suggest to us to investigate the detailed bonding of Pd clusters with ceria by controlling the preparation conditions and to find suitable additives to prevent Pd clusters from coagulation.

Additionally, the regeneration operations in figure 1 also suggest that the minor methane be produced through an independent reaction route, which may be less related to Pd particle size. The methane yield recovered almost to its initial levels after the reoxidation and reduction at 573 K over the catalyst of curve (A). Similar feature is also observed in curve (B′), where the methane yield sharply jumps to the close level as that of curve (A) after the final reduction at 573 K. However, the final reduction at 773 K during the regeneration of curve (B) does not give any promotion effect in methane formation. Since these treatments cause alternative oxidation and reduction behaviors of the ceria support, it seems true that the formation of methane is mainly determined by the redox properties of ceria. Higher CH_4 yield is always obtained over the catalysts that are finally reduced at 573 K, regardless of their histories. While the catalysts, which were finally reduced at 773 K, always give much lower methane yields. The decrease in methane yield with TOS may be attributed to the further reduction of ceria under the reaction conditions. This conclusion is somewhat in contradiction with other observations, which suggested that reduced ceria species (Ce^{3+}) be active sites for methanation of CO based on a series of studies in which the CO hydrogenation was conducted over CeO_2 or partially reduced ceria [13–15].

These features also allow us to exclude the significant role of Pd in methane formation. It is well-known that CO dissociation is favored on small Pd particles, and methane formation through Boudouard reaction would be significant on small Pd particles accordingly [16–18]. This seems to be true for the initially reduced catalysts. Higher CH_4 yield is observed over the LTR catalyst because its Pd particles are seen by EXAFS to be smaller than that of the HTR catalyst. However, the regeneration operations during the courses of the reactions clearly demonstrate that the methane production is less affected by the size of Pd particles. The regeneration processes can only change the redox properties of ceria, and any existing large Pd particle cannot be changed, but the methane yield was recovered to its initial levels when finally reduced at low temperatures (573 K). Thus, it is reasonable to say that methane production is mainly controlled by the redox properties of the ceria support and is less affected by the size of Pd particles.

5. Conclusions

The metal–support contact structure of a Pd–CeO_2 catalyst was studied during pretreatment reduction and subsequent methanol synthesis from CO hydrogenation. Upon high temperature reduction with hydrogen at 773 K, severe sintering of Pd particles occurred, while sintering of the ceria support was less significant. The catalytic deactivation of the Pd/CeO_2 catalysts during methanol synthesis was caused by the further structural change in the Pd–CeO_2 contact under reaction conditions. A massive sintering of Pd particles from 0.5–1.3 nm to about 100 nm occurred during methanol synthesis, and this drastic growth of Pd particles can be closely correlated with the decrease in methanol yield with time-on-stream. However, the formation of methane as a by-product was not remarkably affected by the growth of Pd particles, and it is mainly controlled by the redox properties of the ceria support.

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