Effect of the Promotion of Ceria on Pd/MgO Catalyst for Methanol Synthesis

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The hydrogenation of CO was carried out over Pd supported on MgO. The addition of various lanthanide oxides increased the activity of Pd/MgO to produce methanol. CeO₂ exhibited the highest promoting effect at a temperature as low as 250°C and the optimum molar ratio of Ce/Pd was about unity. TPR experiment showed that CeO₂ on MgO (without Pd) suffered less reduction with hydrogen compared with that supported on Al₂O₃. Thus, the former retained the Ce(IV) state almost completely under the reducing condition, which was ascertained by XAFS measurement. XAFS analysis also indicated that Pd in Pd/MgO suffered reduction extensively while that in Pd/CeO₂/MgO partly retained the oxidized state owing to the reduction-resistant CeO₂ on MgO. The results of CO adsorption XPS, XAFS, and TEM measurement revealed that addition of CeO₂ increased the dispersion of Pd metal particles. It was concluded that the high active of the catalyst resulted from the combination of highly dispersed Pd metal and partly oxidized Pd component with a Pd-O bond.

1. Introduction

Methanol is one of the key substances in the petrochemical industry. It is a raw material to produce various useful chemicals such as acetic acid, methyl methacrylate, methyl amine, and formaldehyde. It can be used as a clean fuel in such future-oriented energy systems such as fuel cells and methanol-fueled vehicles. Cu/ZnO/Al₂O₃ catalyst is used for commercial production of methanol; however, it suffers from such disadvantage as poisoning by S and Cl, and Cu is rather fragile against heat. Thus, the effort to improve its performance is still being made¹¹)-¹⁵).

Methanol synthesis from CO and H₂ is an exothermic reaction with a standard enthalpy (ΔH°₂⁹⁸) of −90.97 kJ mol⁻¹ and the number of molecules decreases with an advance of the reaction¹⁶). Thus, the synthesis favors low temperature and high pressure, and the equilibrium conversion exceeds 90% at 100°C and under a pressure of 1 MPa. Precious metals are well-known hydrogenation catalysts and inherently enhance the activation of CO and H₂. Among the precious metals, Pd seems to be the most promising, and its catalytic action in the hydrogenation of CO as well as CO₂ is investigated by many researchers¹⁷)-²²). In order to obtain oxygen-containing compounds, the C-O bond must not be broken and still the catalysts must maintain high activity. Addition of alkali or alkali-earth metals such as Li or K promotes the formation of methanol, which is produced via formate ion and/or formyl species¹³)-¹⁵). Thus, basic compounds are effective catalyst components. The electronic state of Pd is also important. Driessen et al. and other researchers suggested that oxidized state of Pd (Pd⁴⁺) activates CO without C-O bond scission and metallic Pd activates H₂ to carry out subsequent hydrogenation¹⁸),²³). Palladium has been modified with various oxides of lanthanide¹⁶)-¹⁹). Rieck and Bell reported that an addition of a lanthanide oxides such as La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, and Sm₂O₃ to Pd/SiO₂ generally promotes C-O bond scission producing methane²⁰). On the other hand, Vannice et al. reported that La₂O₃ and Nd₂O₃ are the best supports for Pd to produce methanol because they are basic and assist in producing formyl intermediate, while CeO₂ (the least basic among the lanthanide oxides) accelerates C-O bond scission through Pd-C-O-Ce interaction¹⁸).

We have been investigating the catalytic action of precious metals supported on ceria (CeO₂), and found that CeO₂ highly activates precious metals in various reactions such as N₂O decomposition on Rh/CeO₂²⁶),²⁷), oxidation of formaldehyde on Ru/CeO₂²⁶),²⁷), and decomposition of methanol on Rh/CeO₂ or Pt/CeO₂²⁸),²⁹). Our previous work revealed that CeO₂ helped activate CO on Pd but La₂O₃, Pr₂O₃, and Dy₂O₃ were better supports for methanol production³⁰). In the course of
2. Experimental

2.1. Catalyst Preparation

Ultra-fine particle size γ-Alumina (BET surface area: 260 m²/g) was obtained from Taihei Co., silica gel (surface area: 273 m²/g) from Nippon Aerosil Co., and MgO from Nacalai Tesque Co. (surface area: 9.5 m²/g). MgO and other supports were dispersed in an aqueous solution containing the desired amounts of Pd(NO₃)₂ and nitrate salts of lanthanides (typically, Ce(NO₃)₃). The amount of Pd as metal loaded was 5 wt%. After stirring the solution for 1 h at room temperature, it was evaporated to dryness using a rotary evaporator. The solid portion was dried at 80°C overnight, followed by calcination at 550°C in air for 3 h. An alternate method of preparation was applied to Pd/Ce/MgO catalyst, in which Ce(NO₃)₃ was impregnated on MgO first and the Ce-loaded MgO was calcined at 550°C in air for 3 h, followed by Pd(NO₃)₂ impregnation and calcination under the same conditions. This preparation method is referred to as Method-A, and the catalyst thus prepared is designated as Pd/CeO₂/MgO-A. Unless otherwise stated, the amount of lanthanides added was equimolar to Pd.

2.2. Apparatus and Procedure

The reaction was carried out with a high pressure flow reactor. A portion of 0.5 mL of the catalyst was charged in the reaction tube and was reduced with hydrogen at 320°C for 1 h before reaction. A total of 2 MPa of a mixture of CO (22.2 vol%) and H₂ (77.8 vol%) was fed from a cylinder with a space velocity of 2400 h⁻¹. The temperature of the catalyst bed was increased at a rate of 5°C/min, and the amount of H₂ consumed was monitored with a Shimadzu 4CPT gas chromatograph equipped with a TCD detector.

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Adsorption of CO on Pd was measured with an ordinary vacuum line. Samples were reduced with 13 kPa of hydrogen at 320°C for 20 min followed by evacuation at that temperature for another 20 min. After the samples were cooled down to room temperature, CO was introduced.

3. Result

3.1. Hydrogenation of CO on Pd/MgO Promoted by CeO₂ and Other Lanthanide Oxides

Figure 1 shows the effect of the addition of some lanthanide oxides (Pd/lanthanide molar ratio of 1) on methanol production. The maximum rate methanol production was observed at 300°C on Pd/MgO without lanthanides. Lanthanum (La), praseodymium (Pr), neodymium (Nd), samarium (Sm), and dysprosium (Dy) all exhibited an accelerating action although the effects were not profound. The maximum production rate was also attained around 300°C on the catalysts with these lanthanides. In the case of Ce, however, the maximum rate was attained around 250°C, and its effect was much more remarkable.

Effects of the supports (MgO, SiO₂, and Al₂O₃) were investigated in the reaction at 250°C with Ce as an additive (Table 1). The Ce/K edge spectra were obtained at the BL01BL station of Japan Synchrotron Radiation Research Institute (JASRI). XPS spectra were obtained with a Shimadzu ESCA 750 spectrophotometer. Ce 3d, Pd 3d, and Mg 2s lines were employed to determine the surface concentration of Ce, Pd, and Mg, respectively. XRD data were obtained with a Rigaku Denki Geigerflex 2012 X-ray analyzer and TEM images with a Hitachi H-9000 transmission electron microscope.
be due to the production of Dimethyl ether (DME).

The addition of CeO₂ improved the activity of all catalysts, and its effect on methanol production was the largest for Pd/MgO. Thus, hereafter we focused our attention on Pd/CeO₂/MgO catalysts. A minor effect of CeO₂ was found for Pd/CeO₂/MgO-A, and this point will be addressed later.

**Figure 2** shows the effect of the amount of CeO₂ loaded on the activity of Pd/MgO. As the amount of Pd loaded (as metal) was 5 wt%, Pd/lanthanide = 1 molar ratio, H₂ = 77.8 vol%, CO = 22.2 vol%, SV = 2400 h⁻¹ (2 MPa).

**Table 1** CO Hydrogenation over Pd Catalyst at 250°C—Effect of Supports and CeO₂ Addition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conv. [%]</th>
<th>MeOH select. [%]</th>
<th>MeOH yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/SiO₂</td>
<td>1.9</td>
<td>64.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Pd/CeO₂/SiO₂</td>
<td>3.2</td>
<td>86.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Pd/Al₂O₃a</td>
<td>2.8</td>
<td>15.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Pd/CeO₂/Al₂O₃b</td>
<td>9.3</td>
<td>8.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Pd/MgO</td>
<td>0.6</td>
<td>100</td>
<td>0.6</td>
</tr>
<tr>
<td>Pd/CeO₂/MgO</td>
<td>6.8</td>
<td>83.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Pd/CeO₂/MgO-Ac</td>
<td>2.2</td>
<td>87.0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Reaction conditions are shown in Fig. 1.

Table 1 CO Hydrogenation over Pd Catalyst at 250°C—Effect of Supports and CeO₂ Addition

- **a)** DME selectivity of 69.1%.
- **b)** DME selectivity of 68.3%.
- **c)** Prepared by method-A (see experimental section).

Although the conversion of CO was high, methane was found to be the main product on the catalysts with a large amount of CeO₂, showing that the cleavage of C-O bond had occurred. Thus, the optimum Pd/Ce molar ratio of 1 was employed hereafter (Pd: 5 wt%, CeO₂: 8.1 wt%).

### 3.2. Characterization of Pd/CeO₂/MgO in Comparison with Other Catalysts

The result of the TPR profiles for CeO₂ is shown in **Fig. 3**. Although a noticeable reduction occurred for
CeO₂ supported on Al₂O₃ in the temperature range from 500 to 700 °C, the CeO₂ supported on MgO or SiO₂ was scarcely reduced. The effect of the supports on the reduction of CeO₂ will also be discussed later based on the XAFS result.

Figure 4 shows the result of the reduction of Pd catalysts which were calcined at 550 °C in air for 3 h. The consumption of hydrogen in the low temperature region is due to the reduction of Pd from PdO (analyzed by XRD technique). A standard sample, PdO, or Pd on SiO₂ and Al₂O₃ was reduced even at room temperature, while that on MgO was reduced at a higher temperature. The negative peaks found in the profiles for the former three samples (in Fig. 4) are probably attributed to the desorption of bulk-phase hydrogen (β-hydrogen)33). Addition of CeO₂ shifted the reduction peak to a slightly higher temperature region for Pd/CeO₂/Al₂O₃ and Pd/CeO₂/MgO, while it had no effect for Pd/CeO₂/SiO₂. This implies that Pd and CeO₂ are present separately on SiO₂ or exert scarce effect to one another if they are in close proximity.

Figure 5 shows the Ce K-edge XANES of CeO₂ supported on MgO, Al₂O₃, and SiO₂ together with those of the standard samples. The peak for Ce⁺⁺ (CeO₂) is placed at a higher level than the peaks for Ce⁺⁺⁺ [Ce(NO₃)₆·6H₂O and Ce₂O₃]. We can see a small shift of the peaks of the three catalysts to lower energy level after H₂ reduction indicating the possibility of a slight reduction of Ce⁺⁺⁺. However, the low resolution in the Ce K-edge region did not give a conclusive evidence. Thus Ce La-edge XANES were observed (Fig. 6). It is shown that Ce⁺⁺⁺ is characterized by a doublet in the near edge region (CeO₂), whereas Ce⁺⁺⁺ by a strong white line [Ce(NO₃)₆·6H₂O]33). The spectra of the samples before reduction are shown in Fig. 6 (A). The spectrum of CeO₂ on
MgO before reduction was almost exactly the same as that of pure CeO2, and that of CeO2/SiO2 has a stronger second peak at a higher energy level. The peak at a lower energy level is stronger for CeO2/Al2O3, that may indicate that the Ce is in a lower valence state than that of CeO2 even with calcination at 550°C. All samples except standard samples (CeO2 and Ce(NO3)3·6H2O) were reduced with hydrogen at 320°C (pre-treatment temperature) for 1 h and their spectra are shown in Fig. 6 (B). The CeO2 on MgO scarcely suffered reduction, but that on SiO2 was assumed to be reduced slightly. Al2O3 seems to accelerate the reduction of CeO2 remarkably judging from the marked increase in the intensity of the lower energy peak. Thus, CeO2 on MgO is robust against reduction compared with that on Al2O3 or SiO2.

Figure 7 and Table 2 show the result of the TPR of Pd/Ce/MgO catalysts with varying amount of CeO2 calcined at 550°C in air for 3 h. The H2 absorption peak for Pd/MgO is very broad, but the peaks have a tendency to become sharper with an addition of CeO2. This shows that the Pd is more uniformly distributed in the presence of CeO2. As the molar ratio of H2 adsorbed below 150°C to the charged Pd was always larger than unity except for Pd/MgO, reduction of CeO2 also seemed to occur.

The results of XRD and TEM analyses are shown in Figs. 8 and 9, respectively. Although the XRD peak of metallic Pd was observed on the Pd/MgO catalyst, the addition of CeO2 (Ce/Pd = 1) decreased its intensity and no Pd peak was observed when the amount of CeO2 was further increased (Ce/Pd = 3). This phenomenon coincides very well with the result of TEM observation. Although many Pd particles are observed on Pd/MgO (Fig. 9 (A)), its number decreases with the addition of equimolar amount of CeO2 to Pd (Fig. 9 (B)); Pd particles are scarcely present on Pd/CeO2/MgO (Ce/Pd = 3) (Fig. 9 (C)). The mean particle size of Pd on Pd/MgO was 87 Å and 79 Å as determined by XRD technique (Scherrer equation) and TEM observation, respectively. The TEM image of Pd/Ce/MgO with Ce/Pd ratio of unity indicated that the particle size of Pd decreased to 52 Å. The particle size of Pd determined by separate CO chemisorption experiment was found to be 167 Å (Pd/MgO), 111 Å (Pd/Ce/MgO : Ce/Pd = 1), and 116 Å (Pd/Ce/MgO : Ce/Pd = 3). Although discrepancies exists among these data, it is clear that the addition of CeO2 results in the decrease in the crystallite size of Pd, suggesting that a strong inter-

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**Table 2: H2 Consumed during the TPR Procedure for Pd/Ce/MgO up to 150°C**

<table>
<thead>
<tr>
<th>Ce/Pd molar ratio</th>
<th>Peak temp. [°C]</th>
<th>H2 consumed [mol/mol-Pd]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>53, 87</td>
<td>1.01</td>
</tr>
<tr>
<td>0.25</td>
<td>65, 71</td>
<td>1.14</td>
</tr>
<tr>
<td>0.5</td>
<td>59, 76</td>
<td>1.31</td>
</tr>
<tr>
<td>1</td>
<td>88</td>
<td>1.57</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>1.57</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>1.53</td>
</tr>
</tbody>
</table>

a) Experimental conditions are shown in Fig. 7.
action exists between Pd and CeO$_2$.

Table 3 shows the result of ESCA analysis of the surface Pd concentration. The Pd/(Pd + Ce + Mg) molar ratio was calculated on the basis of the ratio of the peak intensity of 3d$^{3/2}$ plus 3d$^{5/2}$, 4d$^{3/2}$ plus 4d$^{5/2}$, and 2s$^{1/2}$ electrons for Pd, Ce, Mg, respectively. The surface molar ratio of Pd in the absence of Ce is 0.109 compared with the initially loaded ratio of 0.020. This is natural because Pd is localized on the surface. When CeO$_2$ was added, the surface Pd concentration decreased remarkably and, with the addition of 1 to 3 molar equivalent of CeO$_2$, surface Pd/(Pd + Ce + Mg) molar ratio was almost the same as the loaded value, which indicates that Pd interacted with CeO$_2$ and part of it might have penetrated into CeO$_2$ as in the case of Rh/CeO$_2$ catalysts$^{28,29}$.

Pd K-edge XANES spectra of the catalysts are shown in Fig. 10 together with those of the standard samples. Pd metal and oxidized state of Pd (PdO) are clearly distinguishable from their spectra; the spectrum of the former has a set of three peaks and that of the latter two peaks of which the peak at a lower energy level

Table 3 Surface Pd Concentration Determined by ESCA Analysis$^{a)$

<table>
<thead>
<tr>
<th>Ce/Pd molar ratio</th>
<th>Charged Pd/(Pd + Ce + Mg) molar ratio</th>
<th>Surface Pd/(Pd + Ce + Mg) molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.020</td>
<td>0.109</td>
</tr>
<tr>
<td>0.5</td>
<td>0.020</td>
<td>0.040</td>
</tr>
<tr>
<td>1</td>
<td>0.021</td>
<td>0.028</td>
</tr>
<tr>
<td>2</td>
<td>0.022</td>
<td>0.025</td>
</tr>
<tr>
<td>3</td>
<td>0.023</td>
<td>0.023</td>
</tr>
</tbody>
</table>

$^a)$ Catalysts were reduced in H$_2$ at 320°C for 1 h.

Fig. 9 TEM Images of Pd/Ce/MgO

Fig. 10 Pd K-Edge XANES Spectra of the Catalysts before Reduction (A) and after Reduction (B)
is sharp. Before reduction, Pd in all catalysts is in the form of PdO, and the Pd in Pd/MgO is nearly in the metallic state after the reduction because its spectrum is exactly the same as that of Pd foil. The addition of CeO₂, however, changes the situation; the peak at the lowest energy level became remarkable relative to the other two. Thus, it is deduced that the reduction of Pd in Pd/CeO₂/MgO was suppressed by the addition of CeO₂ and the Pd has the character intermediate between Pd⁰ and Pd²⁺.

Figure 11 shows the Fourier transforms (FT) of the EXAFS of Pd K-edge spectra before reduction. As phase shift correction was not applied, the peaks are observed at distances shorter than those of the real position. Pd foil shows only Pd-Pd interaction at 2.5 Å, and PdO shows Pd-O bond at 1.6 Å and Pd-Pd bond (Pd-O-Pd bond) at about 3 Å. Pd/MgO exhibits almost the same spectrum as that of PdO, indicating that the Pd is aggregated on MgO in the form of PdO. Pd/CeO₂/MgO catalysts show strong Pd-O bond, but their Pd-Pd interaction is weak, especially for the catalyst with the Ce/Pd ratio of 3. Pd is present also in the form of PdO but in a more dispersed state than that on MgO. Fourier transforms of the EXAFS of Pd K-edge spectra after reduction treatment are shown in Fig. 12. Pd in Pd/MgO has only a peak of metallic Pd-Pd bond in accordance with the XANES result. Addition of CeO₂ decreases the metallic Pd-Pd interaction and enhances the Pd-O interaction, that implies that PdO is not completely reduced.

The result of the curve fitting for the FT data of reduced catalysts is set out in Table 4. The curve fitting was carried out by using empirical parameters: the empirical phase shift and the back-scattering amplitude functions were derived from the reference compound [Pd foil: CN (coordination number) of 12 and Pd-Pd distance of 2.75 Å]. Coordination number of Pd for Pd/MgO is as large as 9.3, showing that the Pd is in an aggregated state. CN drastically decreased on addition of CeO₂; the dispersion of aggregated Pd metal occurred. A further increase in CeO₂ led to a small additional CN decrease. These results coincided with those of Pd K-edge XANES observation that the addition of CeO₂ retarded the reduction and, hence, aggregation of Pd.

Figure 13 shows the Pd K-edge XANES spectra of Pd/CeO₂/MgO and Pd/CeO₂/MgO-A: molar ratio of Pd
300 to CeO₂ is unity in both catalysts. Before reduction, Pd on both catalysts is in the form of PdO. After the reduction, Pd approached a metallic state. However, Pd on Pd/CeO₂/MgO-A seems to be slightly more in the reduced state than that on Pd/CeO₂/MgO. Fourier transforms of the Pd K-edge EXAFS give a clearer difference (Fig. 14). The Pd-O-Pd interaction is stronger for Pd/CeO₂/MgO-A than for Pd/CeO₂/MgO before reduction (Fig. 14 (A)); PdO is in the more aggregated state in the former catalyst. The Pd-Pd interaction (metal) is stronger for Pd/CeO₂/MgO-A after reduction than for Pd/CeO₂/MgO (Fig. 14 (B)), and the curve fitting analysis revealed that CN of Pd for the former catalyst was 6.7 and, in the latter, it was 5.5. These results indicate that the Pd on Pd/CeO₂/MgO-A is more aggregated and in a state more reduced than that on Pd/CeO₂/MgO, and this seems to be the reason for the lower activity of Pd/CeO₂/MgO-A as will be discussed later.

4. Discussion

Although MgO is not an effective support for Pd catalyst in methanol synthesis, the addition of CeO₂ to Pd/MgO exhibits remarkable effect and the activity of Pd/CeO₂/MgO overwhelms that of Pd/CeO₂/SiO₂ and Pd/CeO₂/Al₂O₃ (Table 1). TPR experiments showed that the amount of hydrogen consumed by Pd/CeO₂/MgO exceeded the content of PdO (Table 2), indicating the reduction of cerium oxide. The presence of palladium promotes reduction of cerium oxide, while the reduction of CeO₂ hardly occurs below 100°C in the absence of Pd (Figs. 3)²². This indicates that Pd and CeO₂ interact strongly on the surface of MgO. It is reported that the catalytic activity of Pd supported on CeO₂ for methanol synthesis is high when both components interact strongly²⁹. TPR profiles for Pd/CeO₂/SiO₂ and Pd/CeO₂/Al₂O₃ are also different from those for Pd/SiO₂ and Pd/Al₂O₃ (Fig. 4); interaction between palladium and cerium oxide also exists on these supports. However, the interaction is probably weaker than in the case of Pd/CeO₂/MgO because the reduction temperatures of Pd/CeO₂/SiO₂ and Pd/CeO₂/Al₂O₃ are lower than those for Pd/CeO₂/MgO. Thus, although the increase in the activity of Pd/Al₂O₃ and Pd/SiO₂ by addition of CeO₂ is similarly caused by the interaction between Pd and CeO₂, their lower activity is probably due to the weaker interaction between these components.

The coordination number (CN) of Pd-Pd interaction decreases with the addition of CeO₂ to Pd/MgO (Table 4), indicating a decrease in particle size of Pd⁰⁶. This is also evidenced by the XRD profiles in which the peak at ca. 40° attributed to metallic Pd decreased with the addition of CeO₂ (Fig. 8). The TEM images of the catalysts also agree with the above observation (Fig. 9). In the Fourier transforms of the EXAFS for Pd/CeO₂/MgO without reduction, the intensity of the peak corresponding to Pd-O at 1.6 Å is almost the same as that of PdO; however, the intensity of the peak around 3 Å decreases with the increase in the ratio of Ce/Pd, showing that the Pd-Pd interaction becomes small (Fig. 11). This suggests that the particle size of PdO on the surface of the catalysts becomes small in the presence of CeO₂. For the reduced catalysts, the addition of CeO₂ also decreased the intensity of Pd-Pd interaction and, in addition, helped Pd to maintain its oxidized state. The CeO₂ on MgO is especially resistant against reduction compared with CeO₂ on SiO₂ and Al₂O₃ (Fig. 6). Therefore, CeO₂ on MgO can provide its abundant oxygen to Pd and maintains the
oxidized state of Pd. This is probably the reason why MgO is the support superior to SiO₂ or Al₂O₃. Thus, the high activity is due to the combination of highly dispersed metallic Pd and partially oxidized Pd species. Highly dispersed state of Pd means the presence of abundant active sites. Ponec et al. suggested that cationic Pd species is effective for methanol synthesis. Carbon monoxide is assumed to be adsorbed on Pd in the first step of hydrogenation through a bonding—back bonding interaction. If back bonding is extensive, C-O bond scission would occur leading to methane formation. If Pd is partly present in a cationic state, back bonding interaction is not so strong for causing C-O bond rupture. This seems to be the reason for the high performance of the present Pd/ CeO₂/MgO catalyst for methanol synthesis.

The amount of hydrogen consumed increases with the increase in the Ce/Pd molar ratio, but it is almost saturated at the Ce/Pd molar ratio of unity (Table 2) where the maximum activity can be attained (Fig. 2). This suggests that the surface concentration of Pd is also an important factor, and excessive addition of CeO₂ decreases the surface Pd (Table 3), and the decreased activity of Pd/CeO₂/MgO in the region of Ce/Pd > 1 can be explained by the decrease in the surface Pd concentration. That is, excessive CeO₂ is considered to cover the surface of Pd and the effective surface area of Pd is reduced, although Pd itself is highly dispersed.

The fact that the activity of Pd/CeO₂/MgO-A is lower than that of Pd/CeO₂/MgO can be explained by the difference in the state of Pd in both catalysts. The Pd in the former catalyst is present in a more reduced and in a less dispersed state than in the latter catalyst (Figs. 13 and 14).

5. Conclusion

Pd/CeO₂/MgO catalyst is highly active in the formation of methanol from CO and H₂, while Pd/CeO₂/ Al₂O₃ produces mainly DME and the activity of Pd/CeO₂/SiO₂ is low. TPR experiment and XAFS analysis revealed that CeO₂ was reduced relatively easily on Al₂O₃ but not on MgO or SiO₂. The CeO₂ supported on MgO (without Pd) was scarcely reduced with hydrogen and retained Ce(IV) state almost completely.

The oxidation state of Pd is determined by the Ce/Pd ratio, but the increase in the Ce/Pd ratio, but it is almost saturated at the Ce/Pd molar ratio of unity (Table 2) where the maximum activity can be attained (Fig. 2). This suggests that the surface concentration of Pd is also an important factor, and excessive addition of CeO₂ decreases the surface Pd (Table 3), and the decreased activity of Pd/CeO₂/MgO in the region of Ce/Pd > 1 can be explained by the decrease in the surface Pd concentration. That is, excessive CeO₂ is considered to cover the surface of Pd and the effective surface area of Pd is reduced, although Pd itself is highly dispersed.

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Acknowledgments

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References

要旨

Pd/MgO 触媒を用いたメタノール合成におけるセリアの促進効果

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MgO を担体として Pd 触媒を用い, CO の水素化を行った。種々の希土類酸化物の添加により触媒活性はいずれも増大したが, セリアが最も低温で活性向上をもたらした。最適セリア添加量は Pd に対して等モルであった。昇温還元実験の結果, MgO 上のセリアは Al2O3 上のそれと比べるとほとんどの還元を受せず, ほぼ Ce4+ 状態を保つことが認められた。XAFS 解析の結果, 単に MgO 上に担持された PdO は容易に還元を受けるのに対して, セリアを添加するとその還元が抑えられ, 反応条件下で Pd は部分的に酸化された状態にあることがわかった。これは MgO 上でのセリアが還元性であるために, その豊富な酸素を Pd へ与えるためである。また, セリアの添加は Pd 金属の高分散化を促進した。これらの結果より, 高活性化は高度に分散した金属 Pd とセリアの作用のために部分的に酸化された Pd-O 種との組合せにより発現すると推定した。

Keywords

Methanol synthesis, Palladium, Magnesium oxide, Ceria, Promotion effect, XAFS analysis