[Research Note]

Promotion Effect of CeO₂ on Pd/SiO₂ Catalyst for Methanol DecompositionSeiichiro IMAMURA^{†1)*}, Hideyuki YAMANE^{†1)}, Hiroyoshi KANAI^{†1)},
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The effects of CeO₂ addition to supported Pd catalysts were investigated in the decomposition of MeOH to H₂ and CO. The catalytic activity of SiO₂-supported Pd was lower than those of Al₂O₃-, MgO- and ZrO₂-supported Pd catalysts. Carbon dioxide and methane were produced in a temperature region higher than 350°C over Pd/Al₂O₃, Pd/MgO, and Pd/ZrO₂ but not over Pd/SiO₂. Addition of CeO₂ promoted the reaction for all catalysts. The activity of Pd-CeO₂/SiO₂ was high as that of Pd-CeO₂/ZrO₂ without losing the high selectivity for CO and H₂. XAFS analysis indicated that most of the Pd is metallic particles which are highly dispersed on CeO₂/SiO₂ and a small part of the Pd is in the oxidized state.

Keywords

Methanol decomposition, Ceria, Palladium, Silica, XAFS

1. Introduction

Decomposition of MeOH to CO and H₂ is an important reaction because CO and H₂ are key raw materials for producing various chemicals. Advantages in energy transportation are also expected: as liquids are more easily transported over long distances than gases, so MeOH can be conveyed to process sites for conversion into CO and H₂ for various purposes. Various catalysts have been developed for MeOH decomposition^{1)–16)}. Ni and precious metals such as Pt or Pd are effective as catalysts mainly based on Al₂O₃, SiO₂, and ZrO₂ supports, whereas the effectiveness of CeO₂-supported catalysts is unclear^{17),18)}. CeO₂ which is a ubiquitous component in automobile catalysts because of its unique functions including stabilization of the alumina support and maintaining the high surface area^{19),20)}, prevention of sintering of precious metals, and consequent stabilization of the dispersed state^{21),22)}, promotion of CO oxidation^{23)–25)} and the water-gas shift reaction^{26)–28)}, and action as an oxygen reservoir^{29)–38)}.

Previously, we found that Pt supported on CeO₂ has high catalytic activity for the decomposition of MeOH³⁹⁾. Pt could be highly dispersed on CeO₂ and Pt–O–Ce interaction was possibly a factor. We also found that CeO₂ promotes the hydrogenation of CO

over Pd catalyst. Although Pd supported on pure CeO₂ causes extremely high activation of CO, the main product was CH₄, the C–O bond scission product. In contrast, Pd supported on MgO with added CeO₂ showed high selectivity for MeOH^{40),41)}. Therefore, CeO₂ has great potential for modifying catalysis of the reactions involving CO, H₂, and MeOH.

The present study investigated the action of CeO₂ in the decomposition of MeOH over Pd catalyst on different supports, in particular Pd supported on SiO₂.

2. Experimental**2.1. Catalysts**

MgO was obtained from Nacalai Tesque Co. (surface area: 9.5 m²/g), ultra-fine γ -Al₂O₃ (surface area: 260 m²/g) from Taimei Co., silica gel (surface area: 273 m²/g) from Nippon Aerosil Co., and ZrO₂ (surface area 23.1 m²/g) from Nacalai Tesque Co. The supports were dispersed in an aqueous solution containing known amounts of Pd(NO₃)₂ and Ce(NO₃)₃. The amount of Pd loaded was 5 wt% as metal. The solution was stirred for 1 h at room temperature, then 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. Unless otherwise stated, the amount of Ce used was equimolar to that of Pd.

2.2. Apparatus and Procedure

The reaction was carried out in an ordinary flow

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reactor under atmospheric pressure. The catalyst (0.5 ml) was charged in a tubular reactor and reduced under hydrogen at 320°C for 1 h before the reaction. Argon containing 3.8 vol% of MeOH was introduced into the reactor and the temperature was increased at 5°C/min until the prescribed temperature was attained. The products were analyzed 10 min later. Hydrogen, CO, CH₄, and CO₂ were analyzed with a Shimadzu GC-3BT gas chromatograph (Unibeads C column (3 m) at 140°C), and H₂O, DME (dimethyl ether), and MeOH with a Shimadzu GC-4BTP gas chromatograph (Porapak T column (3 m) at 140°C).

Temperature programmed reduction (TPR) was carried out in a flow reactor. Hydrogen (1.9 vol% in Ar) was introduced into the reaction tube containing the catalyst under atmospheric pressure (30 ml/min). The tube was heated in an electric furnace at 5°C/min, and the amount of H₂ consumed was monitored with a Shimadzu 4CPT gas chromatograph equipped with a TCD detector.

2. 3. Analyses

XAFS measurement was carried out in the transmission mode at the BL-10B station for Pd K-edge spectra (ring energy: 2.5 GeV, ring current: 313-441 mA) and at the BL-7C station for Ce L_{III}-edge spectra (ring energy: 2.5 GeV, ring current: 264-445 mA) of the Photon Factory in the High Energy Accelerator Research Organization (Tsukuba, Japan). The catalysts were pre-reduced with hydrogen at 320°C for 1 h and were sealed in a Q-pack pouch under nitrogen. The method of data analysis is described elsewhere^{42),43)}.

3. Results and Discussion

Figure 1 shows that the catalytic activity of Pd without CeO₂ decreased in the order, Al₂O₃ > ZrO₂ ≈ MgO ≫ SiO₂. As expected, the main products were CO and H₂. At higher temperature, CH₄ and CO₂ were produced over Al₂O₃, ZrO₂, and MgO, probably through the following methanation (Eq. (1)) and shift reactions (Eq. (2))³⁹⁾.

Only Pd/SiO₂ did not produce CO₂ and CH₄, probably because this catalyst does not activate CO to form CH₄ via C-O bond rupture in this temperature range. Dimethyl ether (DME) was formed over Pd/Al₂O₃ at low temperature, which indicates that dehydration of MeOH occurs at the acid site of Al₂O₃⁴⁴⁾.

The effect of CeO₂ on the activity of these catalysts is shown in **Fig. 2**. Little effect was seen on MeOH decomposition and products distribution for Pd/Al₂O₃. MeOH decomposition was accelerated a little for Pd/MgO and Pd/ZrO₂. MeOH decomposition for Pd/SiO₂ catalyst was greatly increased to levels similar to those of Pd/CeO₂/MgO and Pd/CeO₂/ZrO₂. In addi-

○ H₂, △ CO, ▽ CH₄, □ CO₂, ◆ DME. Catalyst: 0.5 ml, Pd loading: 5 wt%. Catalysts were reduced with H₂ at 320°C for 1 h before reaction.

Fig. 1 Decomposition of MeOH over Pd Catalysts

tion, high selectivity to CO and H₂ was stably maintained up to 450°C, at which a large amount of by-products were formed on other catalysts. The activity of Pd/SiO₂ for MeOH decomposition was increased, maintaining the inherent low activity for C-O bond scission. Therefore, we further investigated the properties of Pd/CeO₂/SiO₂.

Figure 3 shows the results of the TPR experiment for Pd/CeO₂/SiO₂. The peak below 100°C was due to the reaction, PdO + H₂ → Pd⁰ + H₂O, and the amount of consumed H₂ exactly corresponded to the above stoichiometry for Pd/SiO₂. Addition of CeO₂ caused the peak to shift to a higher temperature region, and the extent of the shift was greater for a molar ratio of CeO₂ to Pd of 3 than equimolar CeO₂. This observation indicates that CeO₂ prevents the reduction of Pd. When the amount of added CeO₂ is large (Ce/Pd molar ratio = 3), the amount of consumed H₂ exceeded the above stoichiometric value. Therefore, reduction with H₂ also involved the oxygen in CeO₂.

The XANES and Fourier transform (FT) EXAFS

○ H₂, △ CO, ▽ CH₄, □ CO₂, ◆ DME. The reaction conditions are shown in Fig. 1.

Fig. 2 Effect of CeO₂ on the Activity of Pd Catalysts for MeOH Decomposition

Catalyst: 0.1 g, Pd loading: 5 wt%, Temperature increase rate: 5°C/min.

Fig. 3 TPR Profiles of Pd/SiO₂ (A), Pd/CeO₂/SiO₂[Ce/Pd = 1] (B) and Pd/CeO₂/SiO₂[Ce/Pd = 3] (C)

(A) XANES of Pd/SiO₂ and Pd/CeO₂/SiO₂, (B) FTs of Pd/SiO₂ and Pd/CeO₂/SiO₂, (C) XANES of PdO and Pd foil (standard samples), and (D) FTs of PdO and Pd foil.

Fig. 4 XAFS Analysis (Pd K-edge)

spectra of Pd/SiO₂ and Pd/CeO₂/SiO₂ pretreated in hydrogen are shown in Fig. 4. The position of the absorption edge of the XANES spectrum of Pd on SiO₂ is almost the same as that of Pd foil (standard sample), showing that Pd on SiO₂ is in the zero valent state. On addition of CeO₂, the shape of the spectrum of Pd slightly changed and the absorption edge shifted to a slightly higher energy. This observation coincides with the fact that CeO₂ prevents the reduction of Pd as suggested by the TPR result. The FT of the EXAFS spectra gives some information about the state of the Pd particles. The peak around 2.4 Å is due to Pd-Pd interaction in metallic Pd. On addition of CeO₂ to Pd/SiO₂, the intensity of this peak decreased and the decrease was greater with larger amounts of CeO₂. Therefore, CeO₂ probably increases the dispersion of the metallic Pd particles. Table 1 shows the result of curve fitting of the FT-EXAFS spectra. The coordination number (CN) around Pd clearly decreases with addition of CeO₂.

The addition of CeO₂ remarkably increased the activity of relatively inert Pd/SiO₂ for MeOH decomposition without affecting the high selectivity for CO and H₂. This high activity is partly due to the increased dispersion of Pd metal particles. CeO₂ maintains small amounts of Pd in the oxidized state, perhaps in the

Table 1 Result of the Curve-fitting of Pd K-edge FT EXAFS

Catalyst	CN	R [Å]	$\Delta\sigma^2$ [10^{-3} Å ²]	R-factor [%]
Pd foil	12	2.75	—	—
Pd/SiO ₂	11.5	2.74	0.62	8.81
Pd/CeO ₂ /SiO ₂ (Ce/Pd = 1)	10.1	2.75	0.15	8.72
Pd/CeO ₂ /SiO ₂ (Ce/Pd = 3)	8.7	2.75	0.50	2.50

Pd loading: 5 wt%.

Catalysts were reduced with H₂ at 320°C for 1 h. Curve-fitting was carried out by an empirical method using a Pd-Pd parameter of the reference Pd foil.

interface region between Pd and CeO₂, which also causes the high activity of Pd/CeO₂/SiO₂ as in the case of Pt/CeO₂ catalyst³⁹. Therefore, the highly active state of Pd is considered to be finely dispersed metallic Pd with oxidized Pd in the periphery in contact with CeO₂.

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要 旨

Pd/SiO₂ 触媒を用いたメタノール分解におけるセリアの促進効果

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担持 Pd 触媒によるメタノールの分解反応においてセリア添加の影響を検討した。SiO₂ 担持 Pd 触媒の活性は Al₂O₃, MgO および ZrO₂ 担持 Pd の活性より低かった。しかし、後者の触媒系では CO₂ やメタンが 350℃ 以上の温度で生成するのに対して、SiO₂ 担持 Pd 触媒上では CO と H₂ への高い選択性が保たれた。セリアを添加するといずれの触媒系でも活性が増大し

たが、その効果は特に SiO₂ 担持 Pd 触媒で著しく、高温における CO と H₂ の高い選択性も損なわれなかった。XAFS 分析の結果、SiO₂ 担持触媒にセリアを添加した場合、Pd の分散度が向上すること、Pd の大部分は金属状態であるが一部は酸化状態を保っていることがわかった。

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