

[Research Note]

Determination of Metal Dispersion of Pt/CeO₂ Catalyst by CO-pulse MethodShin'ichi KOMAI^{†1)}, Yoshiteru YAZAWA^{†1)}, Atsushi SATSUMA^{†1)*}, and Tadashi HATTORI^{†2)}^{†1)} Dept. of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, JAPAN^{†2)} Dept. of Applied Chemistry, School of Engineering, Aichi Institute of Technology, Yachigusa, Yagusa, Toyota, Aichi 470-0392, JAPAN

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In order to establish a CO adsorption method for rapid measurement of metal dispersion of catalysts containing CeO₂ that disturbs the measurement due to the adsorption of H₂ or CO, the effect of reduction conditions on CO adsorption over Pt/CeO₂ catalyst was examined on the basis of the standardized manual of CO-pulse method established by the Committee on Reference Catalyst, the Catalysis Society of Japan. Reduction of the catalysts under the standardized condition (673 K, 15 min) showed that Pt catalysts supported on low surface area CeO₂ (12.6 m²·g⁻¹) gave reasonable ratios of adsorbed CO to total Pt. However, the CO/Pt ratio exceeded unity on high surface area CeO₂ support (66.7 m²·g⁻¹), suggesting adsorption of CO on the CeO₂ surface. Reduction of the catalyst under milder conditions at 373 to 573 K for 15 min to 5 h gave constant CO/Pt ratio of 0.40 within a reasonable experimental error. The mean particle diameter estimated from this CO/Pt ratio on the assumption of spherical particles closely agreed with a volume-area mean diameter measured by TEM. It was concluded that the dispersion of Pt supported on CeO₂ can be measured by lowering the reduction temperature to suppress the effect of the CeO₂ support.

Keywords

Metal dispersion, Platinum catalyst, Ceria support, Carbon monoxide adsorption, Reduction condition

1. Introduction

Metal dispersion is one of the most fundamental properties of supported metal catalysts, and determination is essential for the better understanding of metal catalysis and for the development of new catalysts. The chemisorption of probe molecules is the most widely used method for such determinations, and H₂ and CO are the most frequently used probe molecules. The Committee on Reference Catalyst of the Catalysis Society of Japan has established a standardized manual of the rapid determination of the metal surface area of supported metal catalysts using the CO-pulse method^{1),2)}. In the procedure of standardization, Al₂O₃ and SiO₂ were used as the supports for metals such as Pt, Pd and so on.

Precious metal catalysts supported on CeO₂ or containing CeO₂ as an additive have attracted much attention, because CeO₂ is a standard additive of three-way catalysts for automotive emission control due to the ability of oxygen storage and stabilization of metal dispersion. However, it is well known that the presence of CeO₂ causes problems with the determination of

metal dispersion by the chemisorption method³⁾. Using H₂ as the probe, hydrogen spillover easily occurs at room temperature, resulting in large errors in the chemisorption values, so the most reliable dispersion values can only be measured by irreversible adsorption measurement either at saturation or by extrapolation to zero pressure at 195 K, as very low temperature is necessary to suppress the hydrogen spillover⁴⁾. Using CO as the probe, large errors in the adsorption values are caused by the chemisorption of CO on the CeO₂ surface, if the CeO₂ surface is partially reduced³⁾. This problem can be overcome by rather sophisticated methods such as the quantitative FT-IR (fourier transform infrared spectroscopy) method that can differentiate adsorption on metal from that on CeO₂⁵⁾⁻⁷⁾.

The aim of this study is to establish a simple and rapid method for the measurement of metal dispersion on CeO₂-containing catalysts without sophisticated apparatus and techniques. The effect of reduction conditions on CO adsorption over Pt/CeO₂ catalysts was examined using the standardized manual of CO-pulse method^{1),2)}, and the results were compared with the results of TPR (temperature programmed reduction) and TEM (transmission electron microscope) measurement.

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Table 1 Amount of Adsorbed CO on Pt/CeO₂ Catalysts and CeO₂ Supports

Entry	Pt loading [wt%]	CeO ₂ surface area [m ² ·g ⁻¹]	Reduction		CO adsorbed [mmol·g ⁻¹]	CO/Pt [—]
			temperature [K]	time [min]		
1	0.5	12.6	673	15	0.0115	0.45
2	5.0	12.6	673	15	0.0563	0.22
3	0.5	66.7	673	15	0.0353	1.38
4	0.5	66.7	673	300	0.0501	1.96
5	0	66.7	673	15	none	—
6	0	66.7	823	15	trace	—
7	0	66.7	823	180	0.0085	—
8	0.5	66.7	373	30	0.0115	0.45
9	0.5	66.7	373	60	0.0087	0.34
10	0.5	66.7	573	15	0.0092	0.36
11	0.5	66.7	573	30	0.0090	0.35

2. Experimental Section

Two samples of CeO₂ were prepared by calcining cerium nitrate in an air flow for 3 h at 773 and 1023 K. The formation of CeO₂ was confirmed by XRD (X-ray diffraction), and the BET surface area was measured by N₂ adsorption at liquid nitrogen temperature as 66.7 and 12.6 m²·g⁻¹ for the samples obtained by calcination at 773 and 1023 K, respectively. The supports were named CeO₂(12.6) and CeO₂(66.7), where the numerals in parentheses indicate the BET surface area. Pt/CeO₂ catalysts were prepared by impregnating the CeO₂ with an aqueous solution of Pt(NO₂)₂(NH₃)₂, followed by drying at 383 K for 16 h and calcination in flowing air at 673 K for 3 h. The samples were then reduced in flowing H₂ at 623 K for 3 h.

The amount of adsorbed CO was measured by the CO-pulse method. The standardized manual of the rapid determination of metal surface area of supported metal catalysts is as follows^{1),2)}: the catalyst is first treated in an air flow at 673 K for 15 min followed by purge with He for 15 min, and then reduced in a flow of H₂ at 673 K for 15 min followed by purge with He for 15 min, then the catalyst is cooled down to room temperature in a flow of He, and a series of CO pulses are injected with an interval of 2 to 3 min until the amount of exit CO pulses reaches a steady state value. Pulse size of 50 to 200 mm³ is preferred for catalyst of 100 to 200 mg with a metal loading of about 0.5%. In the present study, the reduction temperature and time were varied in the ranges of 373-823 K and 15-300 min, respectively, to examine the effect of the reduction conditions, and five pulses of 100 mm³ were injected onto 100 mg catalyst with an interval of 2 min. The mean particle diameter, d_{VA} , was estimated from the ratio of adsorbed CO to total Pt, referred to as CO/Pt, by the following equation⁸⁾ on the assumption of the adsorption stoichiometry of CO/Pt_s = 1:

$$d_{VA} = \alpha(M_w/a_m\rho N_o) \cdot (\text{CO/Pt})^{-1} \quad (1)$$

where α is a geometrical parameter, M_w is the atomic

weight of Pt, a_m is the effective area occupied by a Pt atom in the surface, ρ is the density, and N_o is Avogadro's number. The mean diameter that can be estimated from the gas adsorption data is the volume-area mean diameter, defined as $\alpha \sum V_i / \sum S_i$ where V_i and S_i are the volume and the surface area of the i th particle, respectively⁸⁾. In the present study, α was taken as 6 on the assumption of the spherical particle, and a_m was taken as 12.5 nm⁻² according to the literature⁹⁾.

The reduction behaviors of CeO₂ supports and Pt/CeO₂ catalysts were examined through TPR (temperature programmed reduction) by monitoring the consumption of H₂ with TCD (thermal conductivity detector) and the weight loss with TG (Rigaku, TG 8120). The catalyst (100 mg) was calcined in flowing O₂/He or O₂ at 673 K for 2 h followed by purge with N₂ for 30 min. Then, the TPR profile was recorded in a flow of 7% H₂ and Ar at a heating rate of 10 K/min.

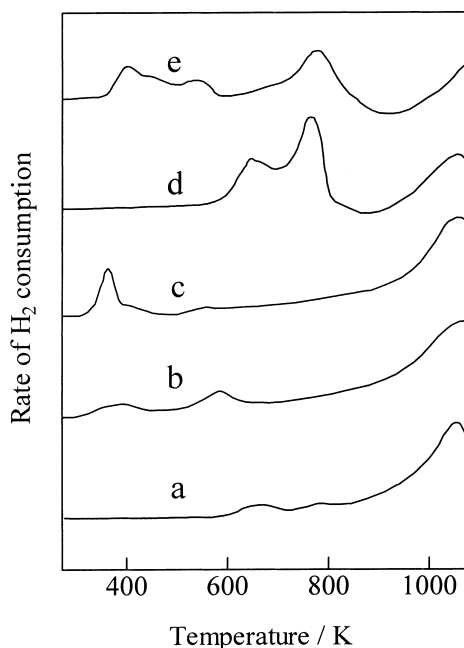
Transmission electron micrographs were taken by using a JEOL JEM-2010 with acceleration voltage of 200 kV. Reduced catalyst particles were dispersed in resin, and after solidification of the resin, thinly sliced specimens for TEM measurement were prepared with a microtome. The volume-area mean diameter was calculated from the particle size distribution by the following equation^{8),10)}:

$$d_{VA} = \sum n_i d_i^3 / \sum n_i d_i^2 \quad (2)$$

where n_i is the number of particles of diameter d_i .

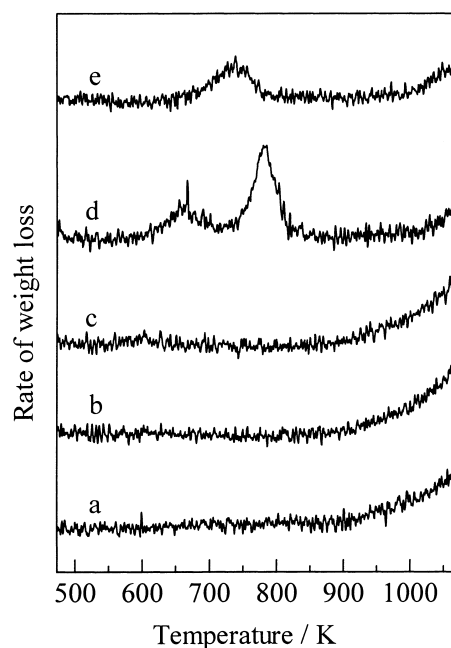
3. Results and Discussion

Entries 1-3 in **Table 1** show the amounts of adsorbed CO on Pt/CeO₂ catalysts measured according to the standard CO-pulse method^{1),2)}. Using CeO₂(12.6) with low surface area, the Pt dispersion, defined as the CO/Pt ratio, was 0.45 and 0.22 for Pt loading of 0.5 and 5.0%, respectively. Using CeO₂(66.7) with high surface area, the amount of adsorbed CO exceeded the amount of total Pt. The CO adsorption was also enhanced, if the catalyst was reduced for prolonged



a: CeO₂(12.6), b: 0.5%Pt/CeO₂(12.6), c: 5.0%Pt/CeO₂(12.6), d: CeO₂(66.7), e: 0.5%Pt/CeO₂(66.7).

Fig. 1 TPR Profiles of H₂ Consumption on CeO₂ Supports and Pt/CeO₂ Catalysts



a: CeO₂(12.6), b: 0.5%Pt/CeO₂(12.6), c: 5.0%Pt/CeO₂(12.6), d: CeO₂(66.7), e: 0.5%Pt/CeO₂(66.7).

Fig. 2 TPR Profiles of Weight Loss of CeO₂ Supports and Pt/CeO₂ Catalysts

times (entry 4). These results suggest that CO was adsorbed not only on the Pt surface but also on the CeO₂ surface, because it is known that the reduced CeO₂ chemisorbs large amounts of CO³. The CO-pulse method was then applied to the confirmation of CO adsorption on the CeO₂ surface (entries 5 to 7). No CO adsorption was observed on CeO₂(66.7) pretreated according to the standard method. Even if the CeO₂ sample was reduced at 823 K for 15 min, only a trace amount of CO was adsorbed. On the other hand, when the sample was reduced at 823 K for 3 h, adsorption of detectable amounts of CO was confirmed. Higher reduction temperature and longer reduction time than the standard conditions were necessary to confirm the adsorption of CO on the CeO₂ surface. However, these results do not mean that CO is not adsorbed on the CeO₂ surface of Pt/CeO₂ catalyst reduced at 673 K, because the presence of metal promotes the adsorption of CO on the CeO₂ surface⁶.

Figure 1 shows the TPR profiles of the rate of H₂ consumption on CeO₂ supports and Pt/CeO₂ catalysts. In the case of CeO₂(12.6), two reduction peaks were observed at about 670 and 790 K, in addition to a large peak above 900 K probably due to the reduction of bulk CeO₂. In the cases of 0.5%Pt/CeO₂(12.6) and 5%Pt/CeO₂(12.6), the reduction peaks at about 670 and 790 K disappeared and new peaks appeared at about 400 and 580 K. The new peaks may be attributed not only to the reduction of CeO₂, which was accelerated

under the effect of Pt, but also to the reduction of Pt oxide. The sharp peak at 360 K in the case of 5%Pt/CeO₂(12.6), may be assigned to the reduction of Pt oxide, because Pt oxide can be reduced more easily than CeO₂. CeO₂(66.7) also showed two reduction peaks at about 650 and 770 K. In the case of supported Pt, the peak at 650 K diminished and new peaks appeared below 600 K, which suggests that the reduction of CeO₂ was accelerated by Pt in this case, too.

Figure 2 shows TPR profiles measured by monitoring weight loss in a flow of H₂-Ar mixture. The reduction peaks were not obvious below 900 K for CeO₂(12.6), 0.5%Pt/CeO₂ and 5%Pt/CeO₂, possibly due to the low signal-to-noise ratio. In the case of CeO₂(66.7), two reduction peaks were observed at about 650 and 770 K in addition to the high temperature peaks in the same way as **Fig. 1**. The weight loss in these reduction peaks was estimated to correspond to the removal of half an oxygen atom per surface cerium cation, assuming that the surface cerium concentration was equal to that on the (100) face of CeO₂. In the case of 0.5%Pt/CeO₂(66.7), the peak at 650 K was diminished and a very weak and broad peak, or very weak peaks, newly appeared at about 520 K. The disappearance of the peak at 650 K and the appearance of the peak at about 520 K agreed qualitatively with the H₂ consumption profile shown in **Fig. 1**, although the peak at about 520 K was much weaker than those in **Fig. 1**. This disagreement may be explained by con-

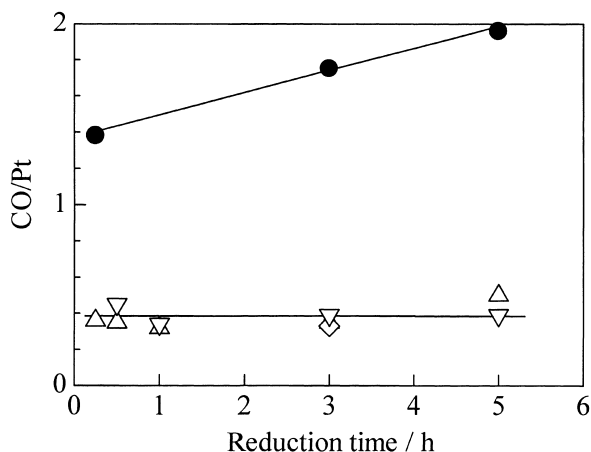


Fig. 3 Dispersion of Pt of 0.5%Pt/CeO₂(66.7) Catalysts as a Function of Reduction Temperature (●: 673 K, ∇: 573 K, ◇: 473 K, △: 373 K) and Reduction Time

sidering the difference between H₂ consumption and weight loss. If the adsorption of hydrogen or the conversion of O²⁻ into OH⁻ is fast and the subsequent dehydroxylation is slow, the H₂ consumption will appear as a sharp peak and the weight loss as a weak and broad peak.

Since TPR experiments indicated that the CeO₂ surface of 0.5%Pt/CeO₂(66.7) catalyst was reduced at 673 K and below, the effect of reduction conditions on CO adsorption over 0.5%Pt/CeO₂(66.7) was examined by the CO-pulse method. The experimental procedure was the same as that prescribed for the standard method^(1,2) except for the reduction temperature and time. **Figure 3** shows that, at the reduction temperature of 673 K, the amount of CO adsorbed was larger than the amount of total Pt even at the reduction time of 15 min. The adsorption amount further increased with reduction time, to almost twice as large as the total Pt after reduction for 5 h, as mentioned earlier (entries 3 and 4 in **Table 1**). This result is in accordance with the above-mentioned TPR results indicating that the CeO₂ surface of 0.5%Pt/CeO₂(66.7) catalyst can be reduced at 673 K. When the catalyst was reduced at 573 K and below, on the other hand, the adsorption amount was less than the total Pt, and essentially independent of the reduction temperature and time, as shown by open symbols in **Fig. 3** and in entries 8-11 of **Table 1**. It may be tentatively concluded from these results that the dispersion of Pt supported on CeO₂ can be measured by the CO-pulse method after reduction below 573 K. It should be added that the mean CO/Pt ratio at the reduction temperature of 573 K and below was 0.38, and the mean particle diameter, calculated from this value by the Eq. (1), was 3.0 nm.

In order to confirm this conclusion, the particle size distribution was measured by TEM and the result was compared with that of the CO-pulse method. Pt parti-

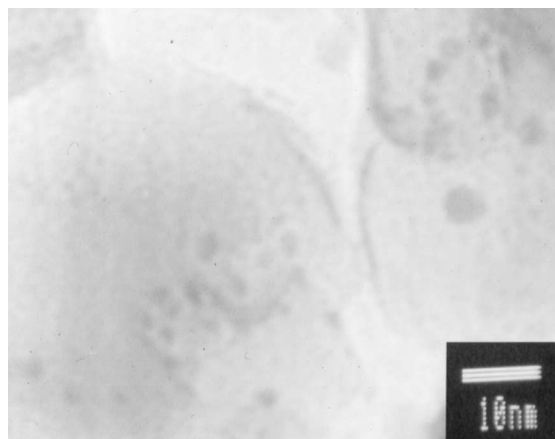


Fig. 4 Representative TEM Photograph of 0.5%Pt/CeO₂(66.7) Catalyst

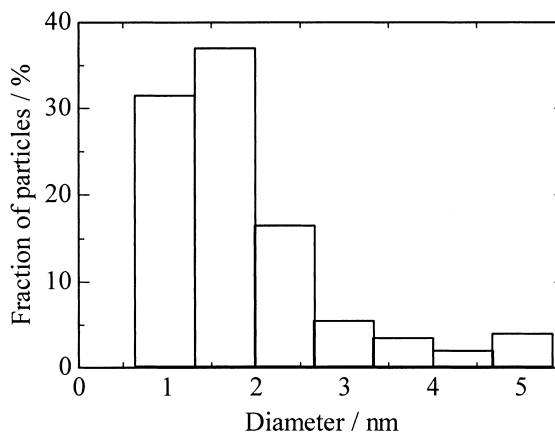


Fig. 5 Particle Size Distribution of 0.5%Pt/CeO₂(66.7) Catalyst

cles less than 5 nm were observed on the TEM photographs of 0.5%Pt/CeO₂(66.7), as shown in **Fig. 4**. **Figure 5** shows the particle size distribution obtained from the TEM photographs. The highest peak of the histogram was observed in the range of 1.3-2.0 nm. However, since the distribution was rather wide and asymmetric, the volume-area mean diameter, which corresponds to the mean diameter obtained from the chemisorption data^(8,11), was significantly larger than the peak. The volume-area mean diameter calculated by the Eq. (2) was 3.1 nm, which closely agreed with the mean particle diameter calculated from the CO/Pt ratio. This close agreement confirms the conclusion that the dispersion of Pt supported on CeO₂ can be determined by the CO adsorption, when the catalyst is reduced at low temperature, *i.e.*, at 573 K and below in this case.

The H₂ consumption peak was observed below 573 K, but the weight loss peak was not. These results suggest that H₂ may be adsorbed rapidly, probably to convert O²⁻ into OH⁻, but OH⁻ may be only slowly

dehydroxylated below 573 K, and that the active sites to adsorb CO may be generated on CeO₂ surface only after the dehydroxylation. Further, not every type of dehydroxylation may result in the adsorption of CO on the CeO₂ surface, because CeO₂(66.7) lost weight below 673 K as shown in **Fig. 1**, but did not adsorb appreciable amounts of CO after reduction at 673 K as shown in **Table 1**. Further studies are necessary to confirm these hypotheses.

4. Conclusions

The effect of reduction conditions on CO adsorption over Pt/CeO₂ catalyst was examined to establish a CO adsorption method for the rapid measurement of metal dispersion of catalysts containing CeO₂. The CO pulse method closely agreed with TEM measurements if the catalyst was reduced at 573 K. It was concluded that the metal dispersion can be determined by CO adsorption, if the catalyst is reduced at such low temperature that the CeO₂ surface is not seriously dehydroxylated.

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要 旨

COパルス法によるPt/CeO₂触媒の金属分散度の測定

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CeO₂を含む触媒では、還元CeO₂表面にH₂やCOが吸着するので、吸着法による金属分散度の測定が困難であると言われていた。そこで、Pt/CeO₂触媒を用い、触媒学会参照触媒委員会による金属表面積のCOパルス迅速測定法の標準化マニュアルを基礎としてCO吸着量に対する前処理条件の影響を検討した。標準化マニュアル指定の条件(673 K, 15分)で還元した場合、低表面積CeO₂ (12.6 m²·g⁻¹)担体では吸着CO量と担持Pt量の比は妥当な値であったが、高表面積のCeO₂ (66.7

m²·g⁻¹)に担持したPt触媒ではCO吸着量は担持Pt量を上回った。還元温度を373~573 Kに下げたところ、還元時間15分から5時間の範囲で、CO/Pt比は約0.40とほぼ一定となった。この値から球形粒子を仮定して推算した平均粒子径は、TEMで観察した体面積平均粒子径とよく一致した。以上より、還元温度を下げれば、CeO₂の還元効果が抑制されて吸着法による金属分散度測定が可能であることが示された。