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Preparation of highly dispersed platinum catalysts on various oxides by using polymer-protected nanoparticles☆

Kana Kimura[a], Hisahiro Einaga[b,*], Yasutake Teraoka[b]

[a] *Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*
[b] *Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasuga-kouen, Kasuga, Fukuoka 816-8580, Japan*

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ABSTRACT

Supported Pt catalysts were prepared by a colloidal deposition method including the photochemical preparation of Pt nanoparticles protected by poly(*N*-vinyl-2-pyrrolidone) and their deposition by liquid-phase adsorption on the various kinds of supporting materials, TiO_2, CeO_2, SiO_2, Al_2O_3 and MgO. We investigated the effect of preparation condition on the properties of supported Pt catalysts. The amount of Pt adsorbed and Pt dispersion depended on the kinds of supporting materials. The highest Pt dispersion was obtained when they were deposited on TiO_2 (P25). The Pt dispersion did not depend on the pH value of mother liquor and the amount of Pt used in the liquid adsorption process. Pt/TiO_2 and Pt/CeO_2 showed higher activity for CO oxidation than Pt/Al_2O_3 and Pt/MgO.

1. Introduction

Supported noble metal catalysts are one of the key materials in the various kinds of catalytic reactions. The size of noble metal particles and their dispersions on the supporting materials are important factors in determining the catalytic activity of the supported noble metal catalysts. In conventional impregnation methods for preparation of supported metal catalysts, precursor metal salts are adsorbed onto supporting materials, and then they are oxidized and reduced to form metal particles. One of the drawbacks in these procedures is that the size and shape of the metal particles on the supporting materials are difficult to control.

We have studied alternative techniques for preparation of supported metal catalysts which include the syntheses of colloidal metal particles by chemical reduction in the presence of a protective agent in liquid phase, followed by their deposition on supporting materials (colloidal deposition methods) [1–6]. This technique has advantage over impregnation method in controlling the size and shape of metal nanoparticles by changing the preparation conditions such as reducing agents and protective agents [7,8].

Recently, we have reported the catalytic properties of Pt/TiO_2 catalysts prepared by colloidal deposition methods including photochemical preparation of Pt nanoparticles protected by poly(*N*-vinyl-2-pyrrolidone) (PVP) and their deposition on TiO_2 by liquid phase adsorption [9]. The Pt/TiO_2 catalysts thus prepared have shown high activity for CO oxidation compared with those prepared by impregnation method due to higher Pt dispersion [10]. On the basis of these results, our next target is to apply the colloidal deposition methods to the preparation of various kinds of supported noble metal catalysts. In this paper, we prepared supported Pt catalysts by the colloidal deposition methods including photochemical preparation of PVP-protected Pt particles and their deposition on supporting materials by liquid phase adsorption to discuss the applicability of this method. We also investigate the effect of preparation condition on the properties of supported Pt catalysts and optimize the condition to obtain the catalysts with high Pt dispersion.

2. Experimental

The synthesis of PVP-protected Pt nanoparticles by photochemical reduction in ethanol–water solution and their deposition on oxide supports were carried out according to the previous paper [9]. $H_2PtCl_6{\cdot}6H_2O$ (6.6×10^{-5} mol) and PVP (K-30, 2.63×10^{-3} mol) were dissolved in an ethanol (50 mL)–water (50 mL) solution. After the solution was photoirradiated to form PVP-protected Pt colloidal particles with average particle size of 2 nm, 1.29 g of supporting material was put into the colloidal solution. TiO_2 (JRC-TIO-4, P25), TiO_2 (anatase-type structure, Wako Pure Chem. Ind., Ltd.), Al_2O_3 (JRC-ALO-8), CeO_2 (JRC-CEO-3), SiO_2 (JRC-SIO-6), and MgO (JRC-MGO-3-1000A) were used as supporting materials. Rutile-type TiO_2 support was obtained by calcining TiO_2 (P25) at 800 °C for 5 h. The mixture was ultrasonicated for 10 min, and stirred at room temperature for 24 h. Then the oxide-supported Pt catalysts were obtained by filtration, washing with pure water and drying at

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[*] Corresponding author. Tel.: +81 92 583 7525; fax: +81 92 583 8853.
E-mail address: einaga@mm.kyushu-u.ac.jp (H. Einaga).

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Table 1
Deposition of Pt colloid during liquid-phase adsorption process and Pt dispersion on various oxide supports.

Support		Deposition of Pt colloid[a]/%	BET surface area/$m^2\ g^{-1}$	CO chemisorbed[b]/$cm^3\ g^{-1}$	Pt dispersion[c]/%
TiO_2	P25	>99[d]	54	0.60	52
	Rutile	97	7	0.45	39
	Anatase	97	9	0.31	27
Al_2O_3 (JRC-ALO-8)		>99[d]	159	0.20	17
MgO (JRC-MGO-3-1000A)		>99[d]	15	0.56	49
CeO_2 (JRC-CEO-3)		79	86	0.46	50
SiO_2 (JRC-SIO-6)		40±1	104	0.14	18

[a] The percentage of the amount of Pt adsorbed on support.
[b] The amount of CO chemisorbed on oxide-supported Pt catalyst at 323 K.
[c] Pt dispersion estimated from the amount of CO chemisorbed.
[d] The Pt concentration in the filtrate was lower than detection limit.

383 K. The supported Pt catalysts were heated at 673 K in air for 2 h to remove polymers.

In order to determine the Pt loading on the supported catalysts thus prepared, the amount of Pt in the filtrate was measured using ICP Spectrometer SPS1700 (Seiko Instruments Inc.). The sample for ICP measurement was prepared by evaporation of the filtrate at ca. 623 K, followed by the addition of 15 mL of aqua regia and stirring overnight to oxidize Pt metals to Pt^{4+} ions. The amount of Pt^{4+} ion in the solution was determined using standard curve.

X-ray diffraction patterns of supported Pt catalysts were obtained using RINT2200 (Rigaku). BET surface areas of the supports were measured by N_2 adsorption at 77 K using BELSORP-mini (BEL JAPAN Inc.). The zeta potential of the oxide in ethanol–water solution was measured using zeta potential and particle size analyzer ELS-8000 (Otsuka Elestrons) by electrophoresis. The amount of CO chemisorbed on supported Pt catalysts was measured using BEL-CAT (BEL JAPAN Inc.) by pulse method to determine Pt dispersion on supporting materials. All measurements were carried out with at 323 K with He-balanced CO (1.0%) gas. The catalysts were pretreated by reduction at 473 K in N_2-balanced H_2 (5.0%) to prevent SMSI effect and adsorption of CO on CeO_2 support [11]. Catalytic CO oxidation was carried out with a fixed-bed flow reactor by feeding He-balanced CO (0.5%)–O_2 (5.0%) with W/F of 1×10^{-3} g min mL^{-1}. After the catalyst bed was heated at 573 K in He, it was cooled down to the reaction temperature (313–473 K). CO and CO_2 were analyzed by gas chromatography using a Shimadzu GC-14B gas chromatograph equipped with a thermal conductivity detector (GC-TCD) and MS13X and Porapak Q columns.

3. Results and discussion

3.1. Effect of supporting materials

Table 1 summarizes the results of liquid phase adsorption study for PVP-protected Pt nanoparticles on various kinds of supporting materials. The amounts of Pt adsorbed and Pt dispersions on catalyst support are the indexes for evaluating the adsorption properties of catalyst supports. Pt nanoparticles were completely deposited on TiO_2, Al_2O_3 and MgO, whereas they were partially deposited on SiO_2 and CeO_2. Especially, Pt nanoparticles (6.6×10^{-5} mol) can be mostly adsorbed on the TiO_2 supports with low surface area (7–9 m^2/g). These findings indicate that adsorption capacity for Pt deposition, defined as the amount of Pt adsorbed per the surface area of supporting materials, depended on the kinds of supporting materials. The adsorption capacity was larger for TiO_2 than other supporting materials.

The amount of Pt nanoparticles adsorbed on SiO_2 with higher surface area was much lower than that on TiO_2 and therefore the adsorption capacity of SiO_2 was very much lower. One may point out that the difference in these adsorption capacities originated from the electrostatic interaction between the PVP-protected Pt and supporting materials. Fig. 1 shows the pH dependence of zeta potential for various oxides measured by electrophoresis in ethanol–water solution. The pH dependency of zeta potential and the isoelectric points were quite similar to those obtained in aqueous solution reported in the literature [12–14]. In this study, the adsorption of the Pt nanoparticles on supporting materials was performed under acidic condition (ca. pH 2). Under the pH condition, the surfaces of TiO_2 (P25) and Al_2O_3 supports were positively charged, whereas SiO_2 support was negatively charged or electroneutral. Because surface charge of PVP-protected Pt nanoparticles was slightly negative, they can be attracted to positively charged materials. Therefore, we cannot exclude the possibility that electrostatic force of attraction operate between Pt particles and the TiO_2 supports. However, Pt cannot be completely adsorbed on CeO_2 supports even though their surface area (86 m^2/g) was higher than TiO_2 and the CeO_2 surface was positively charged at pH 2, implying that other factors than zeta potential were also important for adsorption of Pt particles on the supporting materials.

Pt dispersion also depended on the supporting materials, and the highest Pt dispersion was obtained for TiO_2 (P25) among the supports tested in this study. The average size of Pt particle prepared by our method was approximately 2 nm. The Pt dispersion should be around 60% when they were highly dispersed on supporting material. The Pt dispersion for Pt/TiO_2 (P25) was close to this value and decreased with the decrease in TiO_2 surface area. On the other hand, Pt dispersion was much lower on Al_2O_3 support, although all of Pt nanoparticles (6.6×10^{-5} mol of Pt) used in the liquid phase adsorption process was adsorbed on the Al_2O_3 support. This indicates that Pt nanoparticles were greatly aggregated during their deposition on Al_2O_3 and/or the Pt particle growth

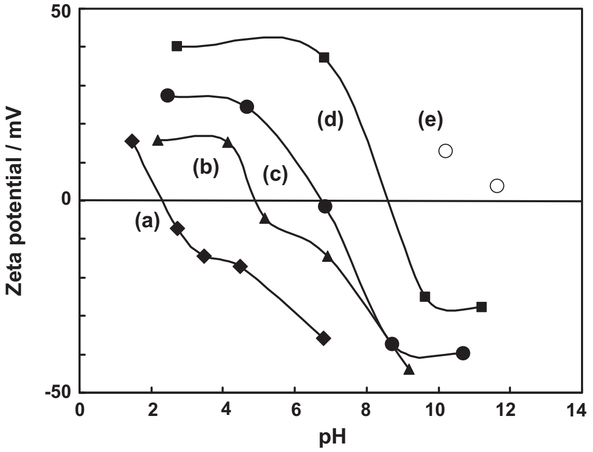

Fig. 1. The pH dependence of the zeta potential of SiO_2 (a), CeO_2 (b), TiO_2 (c), Al_2O_3 (d), and MgO (e) in ethanol–water solution. The pH of mixed solution was adjusted by addition of HNO_3 or NH_3 aqueous solution.

Table 2
Effect of pH of mother liquor used for the adsorption process on Pt dispersion.

pH	Base	Zeta potential[a]/mV		CO chemisorbed[b]/cm^3 g^{-1}	Pt dispersion[c]/%
		PVP-Pt	Pt[d]		
2	–	0.37		0.60	52
6–7	NH_3	−0.60		0.63	55
10	NH_3	−0.35		0.57	50
	NaOH	−1.92		0.72	63
2	–	–	−21.2	0.42	36

[a] The zeta potential determined by electrophoresis in ethanol–water (1:1) solution.
[b] The amount of CO chemisorbed on Pt/TiO_2 at 323 K.
[c] Pt dispersion estimated from the amount of CO chemisorbed.
[d] The sample was prepared by photochemical reduction in the absence of PVP.

occurred in the subsequent oxidation–reduction processes. These findings show that the interaction between Pt and Al_2O_3 was much weaker than that between Pt and TiO_2. From the standpoint of the amount of Pt adsorbed and Pt dispersion on catalyst support, TiO_2 support is the most suitable supports for the colloidal deposition method used in this study. However, Pt dispersion on CeO_2 was close to that on TiO_2, although the amount of Pt adsorbed on CeO_2 was lower than that on TiO_2. CeO_2 is also promising support when Pt nanoparticles can be completely adsorbed on the support.

3.2. *Effect of pH in liquid adsorption process*

It has been reported that the electrostatic interaction between metal precursor and catalyst support affects the metal dispersion of the resulting supported metal catalysts when they are prepared by conventional impregnation technique [14,15]. Accordingly, the pH value of the mother liquor is one of the important factors for obtaining highly dispersed supported metal catalysts in the liquid phase adsorption process. In the present study, the effect of pH of the mother liquor in the liquid phase adsorption process on the Pt dispersion for Pt/TiO_2 catalysts was investigated to clarify the relationship between the Pt dispersion and surface charge of TiO_2, as shown in Table 2. Here, the pH value was controlled by the addition of aqueous NaOH or NH_3 solution. Pt particles were completely adsorbed on TiO_2, independent of pH. The Pt dispersion was almost unchanged when the pH value was adjusted to the conditions under which TiO_2 surface was practically electroneutral (pH 6) and negatively charged (pH 10). In addition, Pt nanoparticles that had been supported on TiO_2 at pH 2 were not desorbed from the TiO_2 surface after Pt/TiO_2 was redispersed into aqueous solution at pH 11. These findings show that the adsorption behavior of PVP-Pt on TiO_2 was independent of pH value of the mother liquor of colloidal dispersion and the strong interaction between Pt and TiO_2 cannot be explained in terms of zeta potential of Pt and TiO_2. It is worth to note that the Pt dispersion did not depend on the kinds of alkaline reagents used to control the pH value. Thus, the adsorption behavior was not affected by the cation species contained in the mother liquor.

3.3. *The role of PVP in Pt deposition on TiO_2*

The effect of the presence of PVP was also investigated by using the same preparation method for supported Pt catalysts. Pt nanoparticles synthesized in the absence of PVP were unstable and precipitated in the colloidal dispersion within a few days on standing at room temperature. Although they were completely adsorbed on TiO_2 by the same liquid adsorption process, the Pt dispersion for the Pt/TiO_2 catalysts prepared in the absence of PVP was lower than those prepared in the presence of PVP (Table 2). This result indicates that the presence of PVP prevents the Pt aggregation in colloidal dispersion and is thus useful for obtaining the Pt/TiO_2 catalysts with high Pt dispersion.

3.4. *Effect of Pt loading*

The effect of Pt loading on the Pt dispersion was investigated to optimize Pt loading of Pt/TiO_2 catalysts. In this process, TiO_2 (P25) was dispersed into the Pt colloidal solution at Pt loading of 1–10 wt%. All the filtrates were transparent and the absence of Pt in the filtrate was confirmed by ICP analysis: the amount of Pt^{4+} ion was lower than detection limit. Thus, Pt particles were completely adsorbed on to TiO_2 up to the Pt loading of 10 wt% of Pt. Fig. 2 shows the results of CO chemisorption measurements and Pt dispersion for the Pt/TiO_2 catalysts prepared at different Pt loading. Pt dispersion strongly depended on the Pt loading. Pt dispersion was evaluated to be 51–54% in the Pt range of 1–3 wt%. However, Pt dispersion decreased with increase in Pt loading when Pt loading was changed from 4 wt% to 10 wt%. This indicates that Pt particle of 2 nm diameter can be deposited up to 3 wt% and aggregation or sintering of Pt particle occurred on TiO_2 at the Pt loading higher than 4 wt%. However, the peak assignable to Pt was not observed in XRD pattern of 10 wt%-Pt/TiO_2, revealing that the lowering of Pt dispersion was not ascribed to the increase of particle size of Pt, but to the aggregation of Pt particle on TiO_2.

3.5. *CO oxidation activity*

Fig. 3 shows the results for CO oxidation activities of Pt/TiO_2, Pt/Al_2O_3, Pt/MgO and Pt/CeO_2 catalysts prepared by the colloidal deposition method. Pt/TiO_2 and Pt/CeO_2 exhibited fairly higher activity than Pt/Al_2O_3 and Pt/MgO at any reaction temperature. It is noteworthy that Pt/CeO_2 exhibited the activity comparable to Pt/TiO_2, although Pt loading on CeO_2 was lower than that on TiO_2 (Table 1). On the other hand, Pt/MgO showed lower activity than Pt/TiO_2 and Pt/CeO_2 while Pt dispersion on MgO was close to that on TiO_2 and CeO_2. These indicated that the catalytic properties of supported Pt catalysts for CO oxidation depended not only on Pt

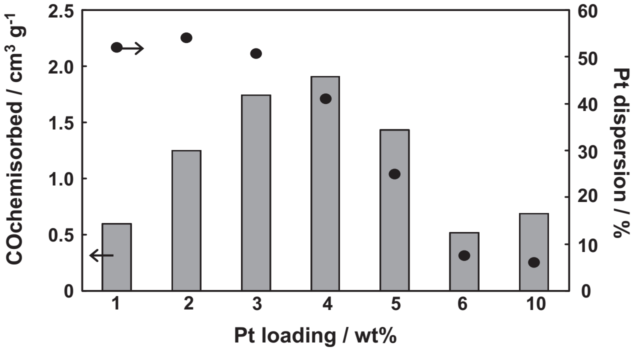

Fig. 2. CO chemisorption at 323 K and estimated Pt dispersion for Pt/TiO_2 (P25) with different Pt loading.

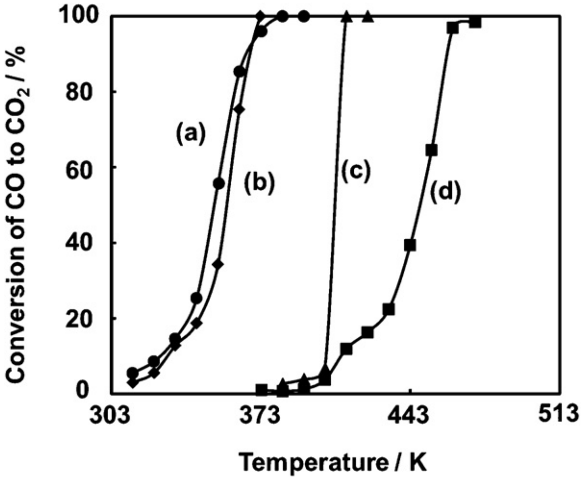

Fig. 3. Oxidation of CO over 1 wt% -Pt/TiO_2 (a), 0.79 wt%-Pt/CeO_2 (b), 1 wt%-Pt/MgO (c) and 1 wt%-Pt/Al_2O_3 (d) prepared by colloidal deposition. Catalyst 0.1 g, He-balanced CO (0.5%)–O_2 (5%), flow rate 100 mL min^{-1} (W/F 1 × 10^{-3} g min mL^{-1}).

dispersion but also on the kinds of support materials when they were prepared by the colloidal deposition method.

4. Conclusions

In this study, we investigated the supported Pt catalysts prepared by the colloidal deposition method which included photochemical reduction of H_2PtCl_6 to Pt nanoparticles in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) in ethanol–water solution and their deposition on supporting materials by using liquid phase adsorption process. The amount of Pt adsorbed and Pt dispersion depended on the kinds of supporting materials, TiO_2, CeO_2, SiO_2, Al_2O_3 and MgO. From the standpoint of these properties, TiO_2 (P25) was the most suitable supports among TiO_2, CeO_2, SiO_2, Al_2O_3 and MgO tested in this study.

We also investigated the effect of preparation condition on the properties of TiO_2-supported Pt catalysts and optimize the condition to obtain the catalysts with high Pt dispersion. For the Pt/TiO_2 catalysts, the Pt dispersion did not depend on the pH value of mother liquor in liquid adsorption process. The Pt loading can be increased up to 10 wt% without Pt desorption in the filtrate. The Pt dispersion was unchanged in the Pt loading level of 1–3 wt% and decreased with the increase in Pt loading due to the Pt agglomeration.

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