

## Research Note

### 溶媒洗浄と焼成による Pt ナノ粒子の PVP 保護ポリマー除去

田口 明, 長岐友介, 米山優紀

富山大学水素同位体科学研究センター

930-8555 富山市五福 3190

### Solvent washing and calcination for effective PVP-cap removal on Pt nanoparticles

Akira Taguchi, Yusuke Nagaki, Yuki Yoneyama

Hydrogen Isotope Research Center, University of Toyama

Gofuku 3190, Toyama 930-8555

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#### Abstract

Repeated washing with ethanol and hexane of polyvinylpyrrolidone (PVP)-capped Pt nanocolloid could generate an uncovered Pt surface. Pt dispersion was significantly improved by this washing as compared to unwashed Pt. IR spectrometry revealed that PVP-free Pt supported on SiO<sub>2</sub> could be obtained by calcination at 200 °C, while unwashed Pt required more than 250 °C.

#### Research note

Polyvinylpyrrolidone (PVP) is one of the most commonly used polymeric capping agents for metal nanoparticle preparation [1,2]. The PVP used during synthesis is usually removed before or after deposition on a catalyst support. While UV-ozone treatment [3] and oxygen

plasma treatment [4] are interesting methods for PVP removal, thermal treatment is the most common method for this purpose. Free PVP starts to decompose at about 280 °C in the presence of O<sub>2</sub> [5]. Metal nanoparticles enhance the combustion of PVP and decrease the PVP decomposition temperature to 180 °C. However, about 380 °C is needed for the full combustion of PVP [5]. Thus, the removal of PVP under mild conditions is still a challenging issue. Recently, washing by ethanol-hexane cycles has been found to remove PVP from Pt surface [6,7]. Although PVP partially remained on metal nanoparticles, the metal even in this condition was effective in catalyzing ethylene hydrogenation [5,6] and the ring opening reaction of benzocyclopentane [8].

We investigated the PVP removal from Pt nanocolloid using ethanol/hexane washing and calcination. Pt nanocolloid with and without PVP washing were supported on SiO<sub>2</sub> by impregnation, followed by calcination at different temperatures. The solvent washing was found to be effective for catalytic combustion of PVP. The changes in infrared spectra and Pt dispersion of the obtained SiO<sub>2</sub> supported Pt nanoparticles are reported.

Commercially available SiO<sub>2</sub> beads (CARiACT Q-50, Fuji Silysia Chemical Ltd.; surface area 76.2 m<sup>2</sup>/g [9]) was ground to powder and used in this study. PVP-capped Pt nanocolloid (Pt diameter of about 2 nm, 0.195 wt% in H<sub>2</sub>O/ethanol) was purchased from Wako Pure Chemical Industries, Ltd. An incipient wetness impregnation method, where the loading amount of Pt was controlled to 2.0 wt%, was carried out for preparation of SiO<sub>2</sub> supported Pt samples as follows. The as-received PVP-capped Pt nanocolloid solution was concentrated by evacuation. Then, the obtained solution was re-dispersed in an adequate amount of methanol (typically, 1.66 mL for 1.00 g of SiO<sub>2</sub>). After impregnation this methanol solution into SiO<sub>2</sub>, the sample was dried under vacuum, and subsequently at 60 °C in an oven overnight. The obtained catalyst was denoted as Pt-PVP (Table 1). Portions of the Pt-PVP were then calcined

at 250 °C or 400 °C for 8 h. These are denoted as Pt-250 and Pt-400, respectively (Table 1).

Solvent washing was carried out as described in literature with a slight modification [6]. An adequate amount of the PVP-capped Pt nanoparticle solution was

diluted with acetone (1/9 in volume) and centrifuged at 5,000 rpm for 10 min. The obtained black oily phase was dispersed into ethanol under ultrasonication (5 min). Then, hexane was added into ethanol solution (1/3 of ethanol/hexane in volume), followed by ultrasonication and centrifugation again. The dispersion and centrifugation were repeated 3 times. Finally, the oily phase was dispersed in methanol and used for impregnation in the same manner as mentioned above. The sample obtained after drying was denoted Pt(wsh) (Table 1). Portions of Pt(wsh) was then calcined at 200 and 400 °C for 8 h and denoted as Pt(wsh)-200 and Pt(wsh)-400, respectively, as summarized in Table 1.

The FT-IR spectra were recorded on a Spectrum 100 instrument (Perkin Elmer). Self-supported wafers were prepared by pressing, and the spectra were obtained with a resolution of 4 cm<sup>-1</sup>. Pt dispersion was measured by CO chemisorption using a pulse-flow reactor system. About 0.1 g of the sample was reduced in advance under an H<sub>2</sub> (50%)/N<sub>2</sub> (balance) gas flow (50 cm<sup>3</sup>/min) at 200 °C for 1 h. A CO (2.0 %)/He (balance) gas mixture in 0.5 cm<sup>3</sup> was injected into the sample at 0 °C. The concentration of CO in the outflow was monitored by an on-lined thermal conductivity detector (TCD) in the gas-chromatograph (GC-8A, Shimadzu). Pt dispersion was calculated using the following equation:

$$\text{Pt dispersion} = \frac{\text{Number of CO molecules adsorbed}}{\text{Number of Pt atoms loaded}} \times 100$$

Table 1 Sample designations and Pt dispersion

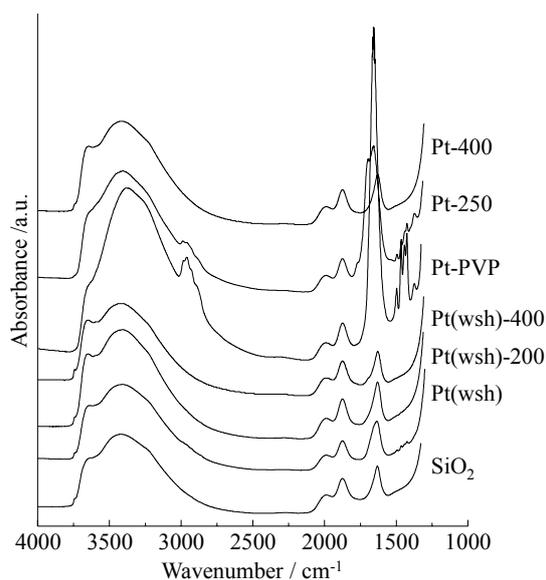
Sample	Calcination temperature	Pt dispersion
Pt-PVP	–	0.23
Pt-250	250 °C	1.92
Pt-400	400 °C	8.13
Pt(wsh)	–	0.98
Pt(wsh)-200	200 °C	4.83
Pt(wsh)-400	400 °C	9.36
SiO <sub>2</sub>	–	n.d.

The CO sorption into SiO<sub>2</sub> was below the TCD detection limit, and hence was neglected.

The IR spectrum of SiO<sub>2</sub> is shown in Fig. 1. A broad absorption band around 3750–3000 cm<sup>-1</sup> is in the hydroxyl-group region, possibly assignable to the asymmetric OH stretching ( $\nu$ ) vibration (abbreviated to  $\nu$ OH) of  $\nu$ Si-OH, adsorbed H<sub>2</sub>O and structural hydrogen-bonded OH [10]. The signals around 1990 and 1874 cm<sup>-1</sup> are  $\nu$ Si-O-Si. A signal around 1635 cm<sup>-1</sup> is attributed to the OH bending ( $\delta$ ) band ( $\delta$ OH). A steep increase around 1250 cm<sup>-1</sup> is due to the  $\nu$ Si-O-Si framework. Impregnation with PVP-capped Pt gave the IR spectrum labeled Pt-PVP in Fig. 1, which had new bands around 3000–2800, 1525–1360 and 1660 cm<sup>-1</sup> attributable to the stretching bands of the PVP framework ( $\nu$ PVP), the bending bands of the PVP framework ( $\delta$ PVP), and the strong carbonyl group ( $\nu$ C=O) band, respectively. Also, an enlargement of the  $\nu$ OH band was observed in the Pt-PVP spectrum, reflecting the hydrophilic nature of PVP.

Calcination at 250 °C (Fig. 1, Pt-250) lowered the signal intensities of  $\nu$ PVP,  $\delta$ PVP and  $\nu$ C=O in the IR spectrum. CO chemisorption study revealed that the active Pt surface on nanoparticles was 1.92 (Table 1). Further calcination at 400 °C (Fig. 1, Pt-400) resulted in the disappearance of PVP framework bands, suggesting a full combustion of PVP. This increased Pt dispersion to 8.13.

In contrast, when ethanol/hexane-washed Pt was loaded onto SiO<sub>2</sub> (Fig. 1, Pt(wsh)) , the IR spectrum showed significantly smaller absorption bands of  $\nu$ PVP,  $\delta$ PVP and  $\nu$ C=O, suggesting virtually complete removal of PVP. Actually, the Pt



**Fig. 1** FT-IR spectra of SiO<sub>2</sub>-supported Pt calcined at different temperatures after preparation from washed and unwashed PVP-capped Pt nanocolloid.

dispersion was evaluated to be 0.98, a value larger than that obtained with Pt-PVP (Table 1). This indicates that ethanol/hexane washing generated uncovered Pt surfaces. Furthermore, subsequent calcination at 200 °C (Fig. 1, Pt(wsh)-200) led to a completely PVP-free IR spectrum. The Pt dispersion of Pt(wsh)-200 increased to 4.83, showing remarkable improvement over Pt-250. The attainment of this large Pt dispersion at a lower calcination temperature suggests enhanced catalytic decomposition of PVP, since the ethanol/hexane-washed Pt nanoparticles had PVP-uncapped Pt on their surfaces.

Also, as expected, Pt(wsh)-400 showed an IR spectrum similar to those of Pt-400 and SiO<sub>2</sub>. The Pt dispersion was evaluated to be 9.36, which was comparable to that of Pt-400. The Pt dispersion considerably smaller than the expected level of more than 50 based on the particle diameter of 2 nm was probably attributable to the aggregation of nanoparticles during impregnation or thermal treatment. Indeed, Pt dispersion of Pt(wsh)-400 after H<sub>2</sub> pretreatment at 400 °C was of 8.59. Therefore, another impregnation method other than the incipient wetness method would be required to prevent the aggregation. On the other hand, the low Pt dispersion on Pt(wsh)-200 as compared to Pt(wsh)-400 is not ignorable. This low Pt dispersion of Pt(wsh)-200 suggests the presence of some IR invisible species, such as partially decomposed PVP [5,6]. However, the Pt nanoparticles prepared in the same washing and thermal conditions with Pt(wsh)-200 showed good activities in hydrogen oxidation and hydrogen isotope exchange reactions [11], indicating that not fully cleaned Pt was required in these catalyses. The details of these catalyses will be reported elsewhere.

In conclusion, our experiments demonstrated the removal of PVP from Pt nanocolloid supported on SiO<sub>2</sub> by direct combustion and the effect of solvent washing. As evidenced by IR spectroscopic and CO chemisorption studies, the ethanol/hexane washing prior to impregnation effectively decreased the burn out temperature of PVP to as low as 200 °C, while 250 °C was

insufficient for the conventionally impregnated sample. This lowering of calcination temperature is expected to expand the application of PVP-capped Pt for catalysts with relatively low thermal resistance [11].

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