Thermal Decomposition Behaviors of PVP Coated on Platinum Nanoparticles

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ABSTRACT: TG-DTA, TEM, and IR were used to investigate the thermal decomposition behavior of poly(*N*-vinyl-2-pyrrolidone) (PVP). The TG-DTA results show that the thermal decomposition behavior of PVP on platinum (Pt) is quite different from that of pure PVP. For pure PVP, 95.25% is decomposed when the temperature is increased up to 500°C; while under the same experimental condition, PVP coated on the Pt nanoparticles is only 66.7% decomposed. This is further supported by IR measurement. TEM results exhibited that the partially decomposed PVP still plays a role in stabilizing Pt nanoparticles: after heating treatment at 500°C for half an hour, the platinum nanoparticles did not aggregate heavily. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 23–26, 2006

Key words: platinum nanoparticles; PVP decomposition; thermogravimetric analysis (TGA); TEM; catalysts

INTRODUCTION

Nanostructured polymer–metal hybrid complexes have gained much attention for their peculiar physical and chemical properties in the field of catalysis. Metal nanoclusters, formed through bridges between metal atoms and bulk metals, are expected to show novel catalytic performance.[1–3] Poly(*N*-vinyl-2-pyrrolidone) (PVP) is widely used as stabilizers in preparation of metal and bimetal nanoparticles, such as platinum,[4] copper,[5] palladium,[6] copper/palladium,[7] gold/palladium,[8] cobalt/platinum.[9] PVP plays a very important role in the formation of metal nanoparticles. The interaction between each unit of PVP and metal nanoparticles is very weak, but the collective interaction occurs simultaneously at a whole PVP molecular frame with a lot of active groups. This is the advantage of PVP, by which many kinds of metal nanoparticles can be stabilized. Taking the advantage of PVP, good-quality metal colloids with high catalytic activities are easily prepared by wet chemistry. For the actual application, however, many metal colloids are further modified because of the difficulty in separation of the metal colloids from their products.

In recent years, considerable interest has been devoted to supported metal clusters both in the laboratory and in industry.[10] As catalysts, supported metal clusters allow easy separation from the reaction products as well as repetitive recycling.[11] Heating treatments are always employed to change metal colloids into supported catalysts. Therefore, the thermal decomposition behaviors of PVP on metal nanoparticles are essential to investigating the activity and longevity of catalyst. In this work, platinum (Pt) is selected as a representative of the metal nanoparticles, and the behavior of PVP in the heating process is investigated by TEM, TG-DTA, and IR methods.

EXPERIMENTAL

Materials

Hexachloroplatinic (IV) acid, $NaBH_4$ and PVP (KT-30, average molecular weight 40,000) were purchased from Shanghai, China, and used without further purification.

Preparation of PVP-protected platinum nanoparticles

An amount of 8.60 mL $6.09 \times 10^{-3} M$ H_2PtCl_6 was first added into 51.40 mL doubly-distilled water. Then, 86 mg PVP (0.78 mmol of monomeric units) was added to the mixture as a protective reagent (the molar ratio between PVP and Pt is 15 : 1). Subsequently, 1 mL of fresh 1% $NaBH_4$ was slowly added to the mixture under stirring (the molar ratio between $NaBH_4$ and Pt is $\approx$20 : 1 so as to reduce the metal ions completely).

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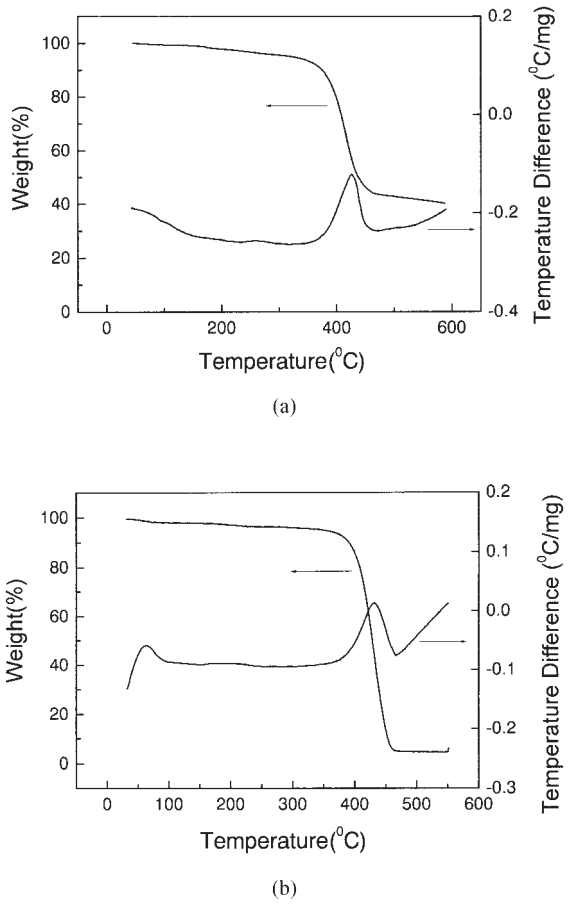


Figure 1 (a) The TG-DTA curves of PVP-Pt nanoparticles. (b) The TG-DTA curves of pure PVP.

The solution turned immediately from light yellow to brown and much bleb appeared, thus resulting in a transparent colloid. After stirring for several hours and storing at room temperature for more than 24 h, the colloid was dialyzed against doubly-distilled water several times to get rid of excess $NaBH_4$ and other ions. The obtained colloid was dried by vacuum evaporation of solvent from the nanocluster dispersion and by drying the residual solvent under vacuum for a day. Evaporation and drying were carried out at a temperature as low as possible (45°C) to prevent any structural change of the nanoparticles.

Measurements

The thermal decomposition of PVP coated on platinum nanoclusters and pure PVP were characterized by TG-DTA with SDT2960. Under nitrogen flow at 100 mL/min, the TG-DTA experiments were carried out from room temperature to 600°C at a heating rate of 10°C/min. TEM photographs were taken by using a Hitachi H6000-II electron microscope. Samples were prepared by placing a drop of the colloid solution upon a copper grid covered with a perforate carbon film and dried in air.

RESULTS AND DISCUSSION

TG-DTA and elemental analysis

The TG-DTA curves of as-synthesized PVP coated on Pt nanoparticles are shown in Figure 1(a). The residue weight is 40.06%. According to the precursor component, all the hexachloroplatinic(IV) acid is reduced. The platinum content is 10.61%, and the weight of platinum will not change in the TG-DTA experimental process. The percentage of decomposed PVP is thereby derived to be 67.05%, and 32.95 wt % of PVP remained in the TG-DTA experiment. This is very different from the situation of pure PVP. As seen from Figure 1(b), under the same experimental conditions, the residue weight of PVP is only 4.75%, and the percentage of decomposed PVP is 95.25%. In addition, the starting decomposition temperature is also different. For pure PVP, it starts to decompose at about 380°C, whereas for PVP coated on Pt nanoparticles, the decomposition happens at 350°C, 30° lower than that for pure PVP.

To confirm the results stated above, the elemental analysis of the as-synthesized PVP on Pt nanoparticles was performed by ICP and EA-1110 autoelement analysis meters. The results are summarized in Table I. They are consistent with what is inferred from precursor components. The PVP coated on Pt sample was heated at 500°C for half an hour under a high pure nitrogen drought and then cooled down under nitrogen ambience. The obtained residue sample was weighted and the percentage was calculated to be 39.80%. This is close to the TG-DTA experimental result, 40.06%. The element components of the obtained residue sample were also analyzed, as listed in Table I.

Decomposed percentage of different elements, W_{dp}, can be calculated by

TABLE I
Weight Percent of all Component Elements of PVP Coated Platinum Nanoparticles Before and After Heating Treatment at 500°C Under Nitrogen for 0.5 h

Component elements	Before heating treatment (wt %)	After heating treatment (wt %)	Lost weight percent of different elements during the heating process (wt %)
C	57.44	55.07	61.84
H	7.60	2.47	87.07
N	11.88	7.13	76.11
O	12.60	9.49	70.07
Pt	10.48	25.83	1.91

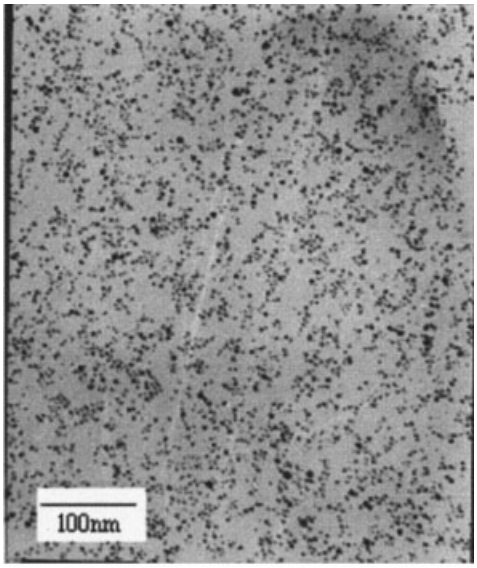
$$W_{dh} = \frac{W_{bh} - W_{ah} \times 39.80\%}{W_{bh}}$$

where W_{bh} is the percentage of different elements before heating, and W_{ah} is the percentage of different elements after heating. The decomposed percentage of different elements was calculated, and the results are listed in Table I. The decomposed percentage of PVP on platinum nanoparticles is 67.24%. As seen from Table I, the decomposed percentage of carbon element is 61.84%. It is less than the average value, 67.24%. The decomposed percentages of other elements are higher than that value, especially for the hydrogen element, which is 87.07%, 19.83% higher than the total decomposed percentage, but still lower than the pure PVP decomposed percentage.

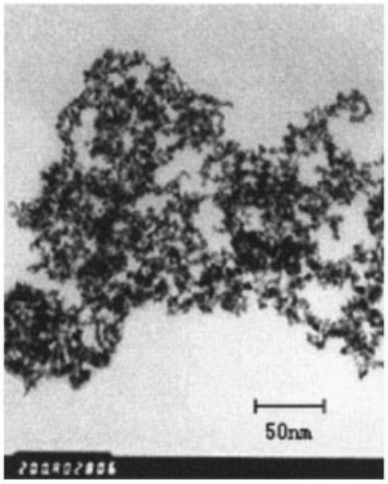
As analyzed above, in comparison with pure PVP, three different thermal decomposition features for the polymer on the platinum nanoparticle surface are observed: (1) the starting decomposition temperature is lower; (2) the decomposition rate is slower; and (3) the relative decomposition amount is smaller.

TEM

TEM was used to characterize the as-synthesized platinum nanoparticles and the heating-treatment PVP-protected platinum nanoparticles. As shown in Figure 2(a), the particles are fairly well-dispersed and the average diameter is about 2.5 nm. The TEM photograph of heating treatment sample is shown in Figure 2(b). The particle size is $\approx$ 5 nm. As the temperature increased, part of PVP melted and decomposed. The platinum nanoparticles may contact easily and combine with each other; they aggregated together somehow, and PVP decomposed partly. A large quantity of residue of PVP remained between the platinum nanoparticles, and the particles still retained nanoscale dimension, indicating that the residue of PVP still plays a stabilization role, although the structure of PVP changed.



(a)



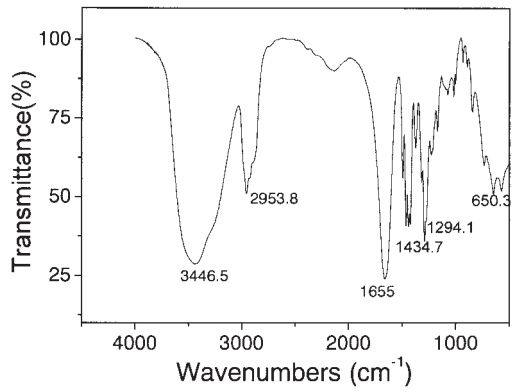
(b)

Figure 2 (a) TEM image of PVP-Pt nanoparticles. (b) TEM image of PVP-Pt nanoparticles heated at 500°C under nitrogen atmosphere for 0.5 h.

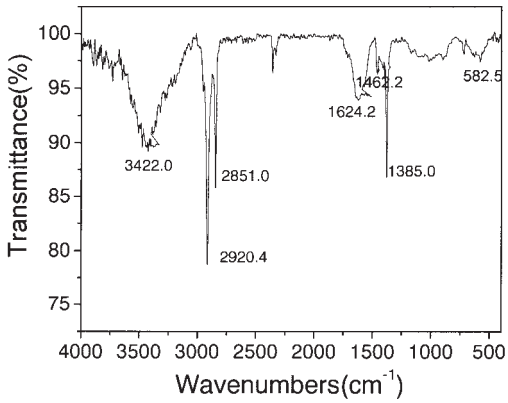
IR spectra

Transmission FTIR is employed to further characterize the residue of decomposition. For PVP coated on Pt without being heated, a strong absorption band appears at 2954 cm^{-1}, which is attributed to the band of CH_2, and a stronger absorption band appears at 1655 cm^{-1}, which is assigned to the band of CO [Fig. 3(a)]. After heating treatment, as shown in Figure 3(b), the absorption band at 2954 cm^{-1} is much changed in intensity, whereas the absorption band at 1624 cm^{-1} gets weak but still exists. This indicates that the chain of carbon was broken during the heating treatment.

In the whole decomposition process, platinum nanoparticles act as a catalyst, leading the decomposition behavior of PVP to be different from its counterpart, pure PVP. With increasing temperature, PVP is gradually melted, and the adjacent two or three particles become more mobile and very possibly unite together to form one particle (see Scheme 1). Meanwhile, because of the substrate effect by platinum particles, which act like a catalyst, instead of being decomposed into simple compounds such as carbon dioxide, PVP is decomposed into some new organic molecule and they stick to the particles. As seen from Figure 2(b), these particles were linked together as a net.



(a)

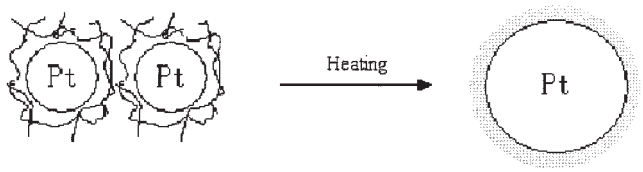


(b)

Figure 3 (a) IR spectrum of PVP-Pt nanoparticles before heating treatment. (b) IR spectrum of PVP-Pt nanoparticles after heating treatment.

CONCLUSION

The decomposition behavior of PVP on platinum is quite different from pure PVP. Pt nanoparticles may play a role as the catalyst for the decomposition of adsorbed PVP. Among all four elements of PVP on Pt, the carbon element has the lowest decomposition, whereas hydrogen has the highest decomposition. The decomposed hydrogen is 87.07%, which is still lower than the decomposition of pure PVP.



Scheme 1 Conformation change of PVP coated on Pt nanoparticles caused by heating treatment.

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