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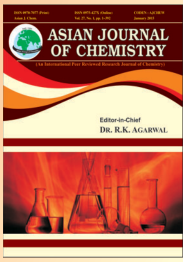

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Preparation and Characterization of Platinum and Rhodium Nanoparticles Stabilized by Functional Polymer Microspheres

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The platinum and rhodium nanoparticles with different sizes were synthesized by *in situ* reduction of the metallic precursor, supported on the highly crosslinked monodisperse poly(DVB-co-AA), poly(EGDMA-co-VPy) and poly(EGDMA-co-HEMA)-SH microspheres with different functional groups on the surface, which were prepared by distillation-precipitation polymerization. The Pt and Rh nanoparticles were characterized by TEM, which show high distribution on the polymer supporters and narrow-dispersed diameters. The interaction between Pt and Rh nanoparticles and the functional groups of polymer supports were investigated by X-Ray photoelectron spectroscopy (XPS). It is found that the sizes of metallic particles have relationship with the interaction of metals and functional groups and electronegativity of metals: with respect to the same metal, the stronger interaction, the smaller diameter of the nanoparticle; for the same polymer supporter, the larger electronegativity of the noble metals, the bigger size of the nanoparticle.

Keywords: Distillation-precipitation polymerization, Platinum nanoparticles, Rhodium nanoparticles.

INTRODUCTION

Due to the quantum size effect, metallic nanoparticles possessed several special physico-chemical properties and have promising prospects in the areas of optics, sensor, catalysis, biomedicine, *etc*[1]. The metals in platinum group were regarded as 'modern gold metal' and have been widely used in fields of aircraft industry, electronics and chemical industry[2]. Most of these metals can be used as effective and stable catalysts in a variety of fields, such as heterogeneous oxidation, fuel cells, sensors and so on[3-6]. Moreover, they had the ability to adsorb several kinds of gases, in which Pt and Rh are very important catalysts in the treatment process of vehicle exhaust. They can effectively participate in the oxidation of CO and reduction of NO[7]. Besides the excellent catalytic properties, rhodium nanoparticles can also be utilized as H_2 storage materials[8].

Crosslinked functional polymer microspheres had the properties of easy separation, diverse functional groups and abundant active sites[9]. Therefore, they had the advantages of being catalytic supporters. For instance, the metallic nanoparticles acting as catalysts and supported on the crosslinked polymers can still keep high activity after multiple recycling. Pal *et al.*[10] utilized anion exchange resin as the supporters for gold nanoparticles catalysts and recovered their catalytic activity using the high-efficiency surfactant. However the recovering process was very complicated and difficult to manipulate. Chen and Chen[11] supported the platinum nanoparticles through *in situ* reduction, using polystyrene microspheres modified by poly(*N*-isopropylacrylamide) as supporters. But the low mechanical stability and the decomposition of microspheres in the good solvent limited their further application. It is also noted that the Pt nanoparticles were asymmetrically supported by the polymer microcapsule and can be used to construct the autonomous motors through H_2O_2 catalytic decomposition[12].

In the present work, we synthesized several crosslinked polymer microspheres with different functional groups by the distillation-precipitation polymerization and then we used them as supporters in the preparation of Pt and Rh nanoparticles by *in situ* reduction of the metallic precursor. The Pt and Rh nanoparticles with different diameters were prepared by using these polymers as supporters and the influence of the polymers to the size of the nanoparticles were discussed in this work.

EXPERIMENTAL

2,2'-Azobisisobutyronitrile (AIBN, analytical grade, Chemical Factory of Nankai University) was recrystallized from methanol. 4-Vinylpyridine (4-VP, 96 %, Aladdin) was distilled under vacuum before being used. Divinylbenzene (DVB, 80 % divinylbenzene isomers, technical grade, Shengli Technical Factory) was washed with 5 % aqueous sodiumhydroxide, water and then dried over anhydrous magnesium sulfate prior to use. Acetonitrile (analytical grade, Tianjin Kangkede Technology Co., Ltd.) was dried with calcium hydride and purified bydistillation before use. Ethylene glycoldimethacrylate (EGDMA), 2-hydroxyethyl methacrylate (HEMA), *N*,*N*-methylenebisacrylamide (MBAAm), sodium sulfide (Na_2S), sodium borohydride ($NaBH_4$), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), rhodium chloride hydrate ($RhCl_3$) and other reagents were of analytical grade received from Aladdin Industrial Inc. and used without further purification.

Synthesis of polymer microspheres with various functional groups: Herein, we synthesised several kinds of monodisperse crosslinked microspheres with different functional groups, including carboxylic acid, pyridyl and mercapto groups. Monodispersed poly(DVB-co-AA) microspheres with carboxylic acid groups and 70 % crosslinking degree were prepared by distillation-precipitation polymerization of DVB and AA (with the volume ratio of 7 to 3) according to our previous paper[13]. Monodisperd poly(EGDMA-co-4-VP) microspheres with pyridyl groups and 70 % crosslinking degree was synthesised by distillation-precipitation polymerization of EGDMA and 4-VP as the monomer following another paper[14]. Monodispersed polymer microspheres with functional mercapto groups (poly(EGDMA-co-HEMA)-SH) were prepared from poly(EGDMA-co-HEMA) microspheres (70 % crosslinking degree) modified by carbon-carbon double bonds through esterification reaction by acryloyl chloride and successively modified by mercapto groups through the addition of hydrogen sulfide to the double bond[15].

Pt and Rh nanoparticles supported by functional polymer microsphere: A series of Pt and Rh nanoparticles with various diameters were synthesized by *in situ* reduction of the metallic precursor ($H_2PtCl_6 \cdot 6H_2O$ or $RhCl_3$) with $NaBH_4$ as reductant in the presence of polymer supporters with different functional groups, such as poly(DVB-co-AA), poly(EGDMA-co-HEMA)-SH or poly(EGDMA-co-4-VP) microspheres. The functional groups on the supporters can interact with metal atoms to stabilize the nanoparticles. All metallic nanoparticles supported on the functional polymer microspheres were prepared by altering the polymer microsphere-supporters while maintaining all the other conditions, with the ratios of the functional group to metal and the reductant ($NaBH_4$) to metal keeping at 50/1 and 40/1, respectively. A typical procedure for the preparation of the Pt nanoparticles supported on the poly(DVB-co-AA) microspheres (Pt NPs@poly(DVB-co-AA)) is as follows: poly(DVB-co-AA) microspheres (0.045 g, with 0.065 mmol carboxylic acid group) were suspended in 7.5 mL of dry tetrahydrofuran in a 25 mL round-bottom flask. Then 0.26 mL of 4.95 m MH_2PtCl_6 aqueous solution (COOH/Pt = 50/1 in molar ratio) was added into the suspension. After mixture was stirred at room temperature for 24 h, 3.3 mL of 0.14 M fresh $NaBH_4$ solution ($NaBH_4$/Pt = 40/1) was rapidly added into the reaction system. The mixture immediately turned dark brown, indicating the formation of the Pt nanoparticles and then the reaction system was aging for another 12 h at room temperature under constant stirring. The resulting PtNPs@poly(DVB-co-AA) were separated by vacuum filtration over a G-6 sintered glass filter and successively washed by THF and acetone each for three times, then dried in a vacuum oven over night to yield the final product.

The blank samples for XPS characterization were prepared by the same procedure as those above without the addition of metallic precursor.

The morphologies of Pt and Rh nanoparticles supported by functional polymer microsphere were determined by transmission electron microscope (TEM, FEI TECNAI-20, Germany) at an acceleration voltage of 200 kV. All of the data of particle sizes reflect the average about 50 particles each, which are calculated by the following formula:

$$U = D_w/D_n,\ D_n = \sum_{i=1}^{k} n_i D_i \Big/ \sum_{i=1}^{k} n_i,\ D_w = \sum_{i=1}^{k} n_i D_i^4 \Big/ \sum_{i=1}^{k} n_i D_i^3 \quad (1)$$

where U is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, N is the total number of the measured particles, D_i is the particle diameters of the determined nanoparticles.

The nature of interaction between metallic nanoparticles and functional groups on the microspheres is determined by X-Ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD multitechnique X-Ray photoelectron spectrometer) with a standard AlK_α excitation source ($h\nu = 1486.6$ eV). The binding energy (BE) was calibrated by measuring C1s peak of alkyl carbon (BE = 284.6 eV) and the peak fitting used the freely available XPS Peak 4.1 program.

RESULTS AND DISCUSSION

Functional polymer microspheres supported Pt and Rh nanoparticles: Distillation-precipitation polymerization has been proved to be a useful and facile technique for the preparation of monodisperse polymer microspheres with various functional groups with high accessibility on their gel layer and surface. Poly(DVB-co-AA), poly(EGDMA-co-4-VP) and poly(EGDMA-co-HEMA)-SH microspheres were successfully synthesized by distillation-precipitation polymerization, with carboxylic acid, pyridine and mercapto as the functional groups, respectively. The crosslinking degree of these three polymer microspheres was controlled at about 70 % by add 70 % crosslinking monomer at the beginning of the polymerization. Because the functional groups didn't exist in the crosslinking agents, the amount of the functional groups was determined absolutely by the other functional monomers, such as AA, 4-VP and HEMA (successfully modified by mercapto group). Thus, for certain amount of polymer microspheres, the amount of the functional groups were the same.

Here, polymer microspheres with various functional groups were utilized as supporters to stabilize Pt and Rh nanoparticles, respectively. Platinum and rhodium nanoparticles with different diameters were successfully synthesized by altering the metallic precursors or the polymer supporters and fixing other conditions, such as the temperature, pressure, the ratio of functional groups to metal and the ratio of $NaBH_4$ to metal. The morphology and dimension of the obtained Pt and Rh nanoparticles were determined by TEM as shown in Fig. 1. It is obvious that the diameters of the polymer-supported metallic nanoparticles were narrow-dispersed for every supporter. As is known that nanoparticles have high surface energies, which is the reason of aggregation of the small particles. The gel layers with functional groups on the surface of polymer supporters can stabilize the nanoparticles and prevent the coalescence.

According to Fig. 1, the size of the Pt (a) poly(DVB-co-AA)@Pt; (b) poly(EGDMA-co-VPy)@Pt; c) poly(EGDMA-co-HEMA)-SH@Pt) and Rh (c) poly(EGDMA-co-HEMA)-SH@Pt; (d) poly(DVB-co-AA)@Rh; (e) poly(EGDMA-co-VPy)@Rh; (f) poly(EGDMA-co-HEMA)-SH@Rh) nanoparticles varied as the change of the polymer supporters. The diameters of Pt and Rh nanoparticles were calculated by formula 1 and summarized in Table-1, which were compared with the data of the Au nanoparticles synthesized previously[16] (Table-1). The data in Table-1 were discussed in terms of rows and columns. Each column in Table-1 illustrated that for the same metal (*e.g.*, Rh, Pt or Au), metallic nanoparticles with different diameters can be obtained by utilizing different polymers as supporters. The average size diameter and the size distribution of the functional polymer microspheres supported metallic nanoparticles were: 4.39 nm and 1.13 for poly(DVB-co-AA)@Pt, 3.06 nm and 1.14 for poly(EGDMA-co-VPy)@Pt, 1.34 nm and 1.09 for poly(EGDMA-co-HEMA)-SH@Pt, 1.65 nm and 1.10 for poly(DVB-co-AA)@Rh, 1.40 nm and 1.08 for poly(EGDMA-co-VPy)@Rh, 0.98 nm and 1.10 for poly(EGDMA-co-HEMA)-SH@Rh, respectively. The diameters of metallic nanoparticles for each metal were decreased in order of polymer supporters: poly(DVB-co-AA)>Poly(EGDMA-co-VPy) > poly(EGDMA-co-HEMA)-SH, as from up to bottom in the table. In a previous paper, it has demonstrated that the changing of diameters of the Au nanoparticles as a result of the varying of the interaction of Au atoms and functional groups on the polymer supporters[16]. The mercapto group has the strongest interaction with Au, showing the smallest size of particles; while the carboxylic acid has the weakest interaction, giving the biggest size. In the present paper, the Pt and Rh nanoparticles exhibited the similar results to the Au nanoparticles, as discussed above in order of poly(DVB-co-AA), poly(EGDMA-co-VPy) and poly(EGDMA-co-HEMA)-SH. The results further confirmed that the diameters of the metallic nanoparticles decreased along with the raising of interaction of metal and functional groups, corresponding to the ability of electron donation of functional groups on the supporters, in the order of carboxylic acid, pyridyl group and mercapto group. Thus, as to the same metal, the sizes of polymer-supported nanoparticles consisted with the interaction between the metal atoms and functional groups on the polymers.

For each row in Table-1, the data exhibited the diameters of different metallic nanoparticles with the same functional polymer microspheres as supporters. Here, the second row was selected as the representative to discuss. In this row, the Au, Pt and Rh nanoparticles with different diameters were stabilized by the same polymer-supporter, poly(EGDMA-co-VPy) with pyridyl as the functional groups. The diameters of

TABLE-1
SIZE AND SIZE DISTRIBUTION OF THE METALLIC NANOPARTICLES

Polymer substrates	Functional groups	Au[16]	Pt	Rh
Poly(DVB-co-AA)	-COOH	10.7 (1.07)	4.39 (1.13)	1.65 (1.10)
Poly(EGDMA-co-VPy)	-pyridine	7.36 (1.08)	3.06 (1.14)	1.40 (1.08)
Poly(EGDMA-co-HEMA)-SH	-SH	5.2 (1.2)	1.34 (1.09)	0.98 (1.10)

In parentheses is U: monodispersity index

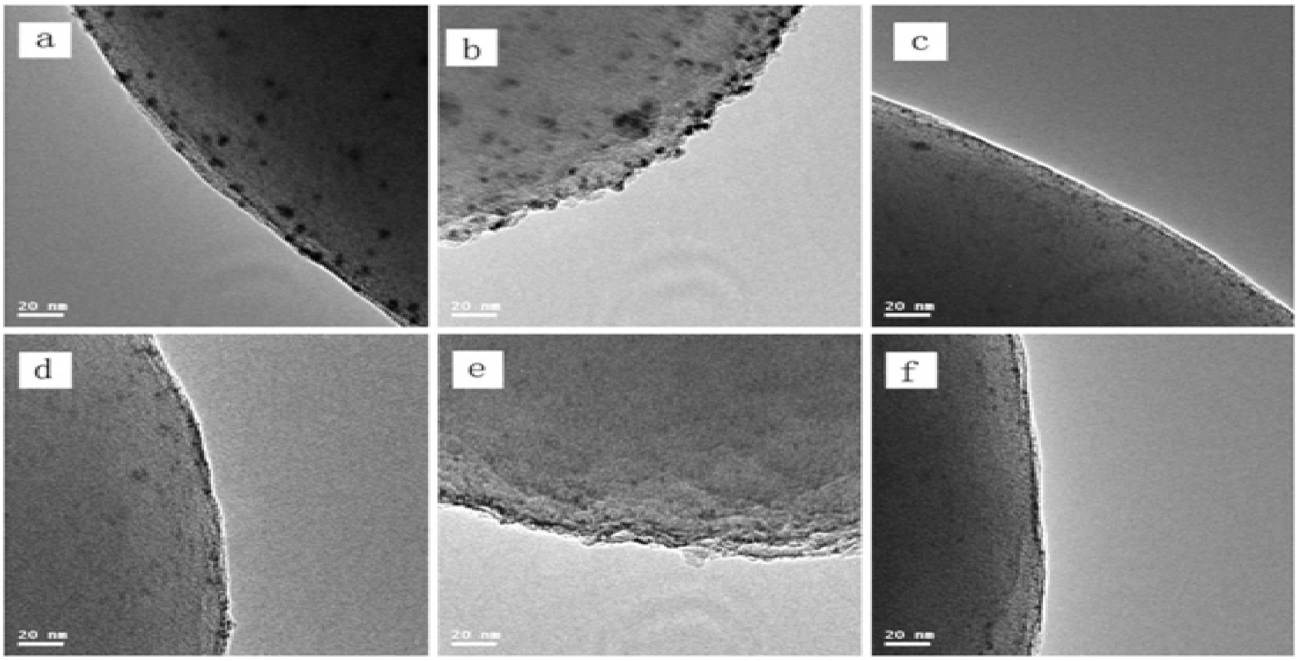

Fig. 1. TEM photographs of the functional polymer microspheres with Pt and Rh nanoparticles (a) poly(DVB-co-AA)@Pt; (b) poly(EGDMA-co-VPy)@Pt; (c) poly(EGDMA-co-HEMA)-SH@Pt; (d) poly(DVB-co-AA)@Rh; (e) poly(EGDMA-co-VPy)@Rh; (f) poly(EGDMA-co-HEMA)-SH@Rh

the Au, Pt and Rh nanoparticles decreased with the order: Au > Pt > Rh. As for the other two rows, the diameters of the metallic nanoparticles were in the same order as the second row. So, it was apparent that Au(0) atoms had the greatest tendency to aggregate, then form the biggest particles. On the other hand the Rh(0) atoms were not easy to aggregate and so easy to make up relatively small particles. These results can be explained by the different electric electronegativity of the three metals: they are 2.54, 2.28 and 2.20 for Au, Pt and Rh, respectively. The metallicity of these metals increased in order of Au, Pt and Rh, opposite to that of electronegativity, so the electron acceptability decreased from Au to Pt and to Rh. Among the three metals, Au(0) atoms had the greatest tendency to attract electrons from surrounding atoms, consequently formed the biggest particles when the metallic salt was reduced by $NaBH_4$. At the beginning of the reaction, the Au^{3+} was reduced to Au^0 in a short time, interacted among one another and then these atoms constructed relatively stable nanoclusters by the strong attraction of Au atoms, followed by growing to the final nanoparticles stabilized by polymers, which interacted with the surface-atoms of the nanoparticles. Thus the particles size was determined by the electronegativity of metal, which end of electron acceptability and affect the attraction between atoms composing the metallic nanoparticles and interaction between metallic atoms and polymer supporters. Of course, the particles size was also in relation to the lattice constant, which were 0.420, 0.402 and 0.387 for Au, Pt and Rh, respectively and determined primarily by the metallic species. The lattice constant coordinated with the sizes of particle diameters, which constituted another reason for the change of particles sizes, but not the primary one due to small differences in their values. It cannot match the big change in diameters.In a word, the size of the metallic particles was changed according to the metallic species mainly in terms of electronegativity for the same polymer supporters.

Nature of the interaction between metallic nanoparticles and polymer supporters: It is clear that the metallic particles in the nano-dimension have the tendency to aggregate, so stabilizer is necessary to synthesize the Pt and Rh nanoparticles. Here the functional polymer microspheres with the carboxylic acid, pyridyl group and mercapto group on the surface were used as the stabilizer interacting with the metal atoms. Here, we took poly(EGDMA-co-VPy) as an example to investigate the nature of the interaction between the metallic nanoparticles and functional groups (herein, pyridyl) and utilizing X-Ray photoelectron spectroscopy (XPS) to determine the interaction at the interface. In the present work, the interaction between N atoms of pyridyl groups and the Au, Pt or Rh atoms was analyzed by XPS. In this system, the polymer supporters were constituted by the O, C and N elements, so these elements were specifically investigated through XPS. The results showed that there were no change on the spectra of the XPS for O1s and C1s, a new peak appeared in the region of N1s for the polymer-metal system comparing to the blank polymer. The XPS analysis of N1s was demonstrated in Fig. 2. Curve a is the XPS spectrum of pure poly(EGDMA-co-VPy), (blank sample) with a peak of the binding energy (BE) at 298.57 eV, corresponding to the N atom of pryridyl. The single peak illustrated that there is only one kind of N atoms in the sample and no interaction of these N atoms with other materials. Curve b, c and d represented the N1s electron energy spectra of poly(EGDMA-co-VPy)@Au, poly(EGDMA-co-VPy)@Pt and poly(EGDMA-co-VPy)@Rh, respectively. In the b, c and d curves, a new peak appeared with higher BE at 400.65, 400.0 and 399.97 eV, which demonstrated that parts of the N atoms occurred chemical shift to the high BE region, owing to the reduction of the electron cloud density of the N atom. Besides of polymer supporters Au, Pt and Rh nanoparticles were other parts in the composite system, so they are certain electron acceptor for the N atoms. In detail, the unshared pair electrons of the N atoms filled in the unoccupied outer orbital of metal atoms, inducing the result of the lower cloud density of the N atoms and the chemical shift of N1s. The greater the chemical shift, the bigger the degree of the electron donation of N atoms, which reflected the interaction of the N atoms and metallic nanoparticles. Thus the interaction between N atoms and metallic nanoparticles decreased from Au, to Pt and to Rh. This result accorded with that drawn from electronegativity of the three metals, proving that the metallicity of Au to Pt and Rh coordinated to the electron acceptability. As a result, the Au atom showed the preference to combine with other surrounding Au atoms among these three metals and then become the biggest nanoparticles. Therefore, in the case of the same polymer as the supporters, the particles sizes changed according to the electronegativity of metals.

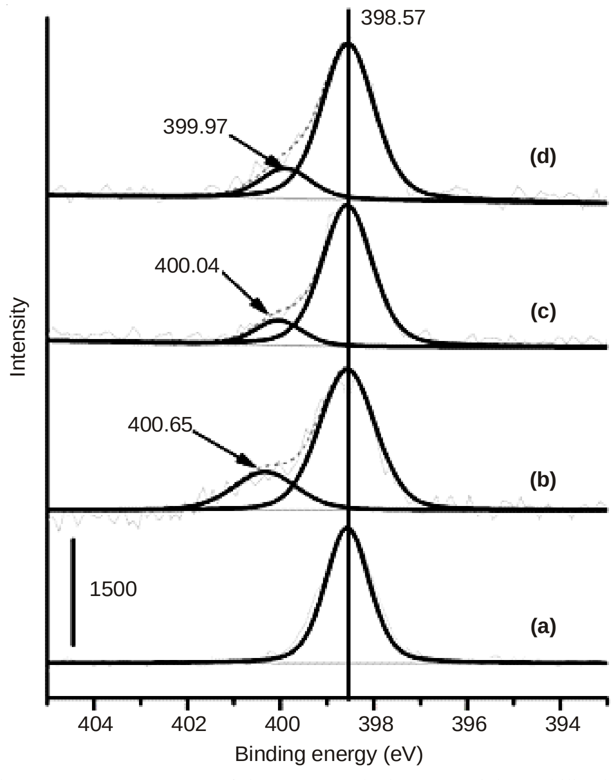

Fig. 2. N1s XPS spectra of the Au, Pt and Rh nanoparticles stabilized on various microsphereswith functional group: (a) poly(EGDMA-co-VPy) (blank sample); (b) poly(EGDMA-co-VPy)@Au; (c) poly(EGDMA-co-VPy)@Pt; (d) poly(EGDMA-co-VPy)@Rh

Conclusion

The microsphere-supported Pt and Rh nanoparticles with different sizes in the range of 4.39 and 0.98 nm were *in situ* prepared by reduction of the metallic precursor in the presence of functional polymer microspheres as supporters. All the Pt and Rh nanoparticles prepared in our experiment werein the well-distributed sizes and dispersed uniformly on the polymer-supporters. By introduction of the results of polymer-supported Au nanoparticles, it is revealed that the sizes of the metallic nanoparticles investigated in this work were in the relationship with the interaction between the metal and functional groups and the electronegativity of metals. With respect to the same metal, smaller diameter of the nanoparticles can be understood by the stronger interaction. On the other hand, larger electronegativity of the noble metalsimplies the bigger sizes of the nanoparticles for the same polymer supporter.

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