Preparing Methods and Its Influencing Factors about Nanoparticles Based on Dendritic Polymer

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Abstract. Based on the properties, structure and application of dendritic polymer, this paper analysed the methods of the preparation of nanoparticles using dendritic polymer, detailed preparation process, technical parameters and application effect about a single metal nanoparticles, bimetallic nanoparticles, sulfide and halide nanoparticles. The influencing factors of the preparation about nanoparticles were discussed, including the molecular algebra, the molar ratio of the metal ions to the dendritic polymer, and so on.

Keywords. Nanoparticles, preparing methods, dendritic polymer, influencing factors

1 Introduction

Dendritic polymer is used as a template to prepare nanoparticle [1] application range is more and more wide in recent years [2]. At present, based on dendritic polymer, it has been successfully prepared a variety of metal nanoparticles, oxide nanoparticles and halide nanoparticles, such as Au, Ag, Pt, Cu, AgBr, Au-Ag and ZnO etc. The prepared nanoparticle has the advantages of good dispersion, high stability, large surface area and high activity, and it is widely used as catalysts for industrial production.

The dendritic polymer are highly branched, which is a large molecule of single disperse with dendritic three-dimensional structure. It is obtained by the method of convergent or divergent based on the branch element (dendron).

Polyamide (PAMAM) is the development of more mature dendritic polymers [3]. According to the different of reproduction, divided into different Algebra (Gn) PAMAM dendritic polymers. OCH_3 terminal is half generation PAMAM dendritic polymers, and NH_2 terminal is whole generation PAMAM dendritic polymers. Then the specific algebra can be determined by the number of times that the branching unit is repeated.

Dendritic polymers have the following structural characteristics:

(1) Precise molecular structure.

(2) The high geometry symmetry.

(3) A large number of functional groups, and the surface modification and modification can be carried out.

(4) The intermolecular in the cavity.

(5) Relative molecular weight control.

(6) The molecule itself is a nanometer size.

Based on the above characteristics, dendrimers have many advantages:

(1) The unique chemical composition and structure of the tree form, so that it can get a very good "reproduction", to ensure that the product of the single dispersion.

(2) There are a large number of cavities inside the dendritic polymer, which can fully wrap the nanoparticles to prevent the aggregation of the nanoparticles and improve their stability.

(3) The nanoparticles are mainly restricted by steric hindrance, the surface of which is not passive, and still keep high activity.

(4) In the catalytic reaction, the special structure of the dendritic polymer can be used as a nano grade filter to select the substrate.

2 Preparation of nanoparticles

The cavity of the dendritic polymer provides space for the formation of nanoparticles, so that the product is stable and controllable in size. Under different reaction conditions, such as the water phase, the organic solvent, the reducing agent and the electromagnetic wave radiation, the preparation of the nano particles by the dendritic polymer is more and more mature. In the process of preparing nano materials, based on the preparation of single metal nanoparticles, bimetallic nanoparticles, halide nanoparticles, sulfide and oxide nanoparticles were synthesized.

(1) Single metal nanoparticles

According to the position of metal nanoparticles and dendritic polymer, it can be divided into two types: the molecular template and the outer template. Molecular template is within the metal ions and dendritic polymer active functional group，so a single molecule formed nanoparticles in the cavity. The outer molecular template is the active functional group of the metal ions and the outer surface of dendritic polymer, which is reduced to form a group of nano particles. In the preparation of metal nanoparticles, this two methods are very practical. Synthesis of Cu nano clusters with PAMAM dendritic polymer as molecular template, the synthesis of nanoparticles is simple, easy to operate, and the controllability of product characteristics. Thereafter, Pt, Au, Ag, Pd, Ni, Rh and other metal nanoparticles were successfully prepared.

When using methanol as solvent, the PAMAM G5.5 dendritic polymer as template, the metal Pt nanoparticles can be obtained by $NaBH_4$ reduction. When the ratio of the amount of G5.5 and PAMAM Pt^{2+} is changed, the two different synthesis methods of the molecular template and the outer template can be realized. The particle size of nanoparticles prepared by the template method is smaller than that of the outer template method. Knecht et al. considered that the reduction reaction is a self catalytic process.

Dendritic polymer as a template to heat 70 min at 100℃, the metal Ag nanoparticles with high stability and small particle size can be synthesized in one step, and the particle size of the product increases with the increase of temperature.

In the aqueous phase, the metal Ag nanoparticles were prepared by UV irradiation with the dendritic polymer as the template. Moreover, the size of the nanoparticles was increased with the increase of the reaction time, until the Ag ion was completely reduced. So that the appropriate reaction time is very important.

Pd metal nanoparticles were Prepared of using G6.0PAMAM dendritic polymer as templates, and to G4.0 PAMAM dendritic polymer as template can get Rh and Pt nanoparticles [4].

As can be seen, the direct reduction method for the synthesis of metal nanoparticles has two main steps using dendritic polymer as template. The first step is the complexation reaction of metal ions and dendritic polymer. The second step is generates metal element with complex metal ions by chemical means, then to form nanoparticles.

(2) Bimetallic nanoparticles

Bimetallic nanoparticles are different from single metal nanoparticles. It is the synergistic effect of the two kinds of metal, so that it can greatly improve the catalytic range and catalytic efficiency. The advantage about the preparation of bimetallic nanoparticles by dendritic polymer is very prominent.

There are three methods for the preparation of bimetallic nanoparticles: synchronous complexing method, sequential complex method, partial substitution method. Among which the former two types are the main methods.

Synchronous complexing method is a method that two metal ions mixed with the dendritic polymer at the same time to prepare bimetallic nanoparticles. Au-Ag bimetallic nanoparticles can be obtained in the aqueous phase, and the test proves

that the bimetallic nanoparticles are not a simple mixture of single metal particle or core shell structure, but mixed together in the form of alloy. When near room temperature, the prepared Pt-Au bimetallic nanoparticles have higher activity for the catalytic oxidation of CO. Based on the PAMAM dendritic polymer templates, when $N_2H_4 \cdot H_2O$ as a reducing agent, it can get small size and uniform spherical Ag-Cu bimetallic nanoparticles; but with $NaBH_4$ as a reducing agent, get a long rod shaped Ag-Cu bimetallic nanoparticles [5].

It is found that the Bimetallic nanoparticles prepared by the sequential complex method are mostly the product of core-shell structure, but the Bimetallic nanoparticles synthesized by the synchronous complexing method are mostly in the form of alloy.

(3) Preparation of halide and sulfide nanoparticles

The nature of the halide and sulphide nanoparticles was influenced not only by the particle size, but also influenced by the particle size distribution, particle shape and stable performance. Therefore, it is important to prepare the shape and particle size uniformity, stable performance of halide and sulfide nanoparticles. With the further development of dendritic polymer in the preparation of nano materials, the halide and sulfide nanoparticles with special applications in the optical field can also be prepared.

When the AgBr nanoparticles were prepared, the ratio of the amount of Ag and PAMAM dendritic polymer was changed, and the nanoparticles with different particle sizes were obtained. Their catalytic ability gradually increased with decreases of the size about the nanoparticles. The AgI nanoparticles under the same preparation conditions, to G4.5-$COOCH_3$ template of the average particle size is 6nm, and PAMAM G5.0-NH_2 as template from particle diameter is 9nm. This is mainly due to the metal ion dendritic macromolecular template complexation reactions in different parts, the aggregation degree of different [6].

The stable CdS nanoparticles can be obtained by the template of dendritic polymer, and the particle size of CdS nanoparticles increases with the increase of molecular algebra [7].

The reaction process about synthesis halide or sulfide nanoparticles with dendritic polymer: first is the complexation of dendritic polymer with dendritic polymer template, then halide ions or sulfur ions with metal ions combine to form halide or sulfide nano clusters, so it is wrapped in the dendritic polymer to obtain nanoparticles.

(4) Preparation of oxide nanoparticles

PAMAM dendritic polymer were used as templates to prepare ZnO nanoparticles with high photocatalytic activity. Compared with other methods, the method has the advantages of low cost, simple operation, controllable particle size and so on.

3 Influence factors about the size of nanoparticle

The synthesis of nanoparticles with dendritic polymer is used in industrial production. The catalytic efficiency is closely related to the specific surface area of the catalyst. In general, the greater the specific surface area, the higher the catalytic efficiency. And the size of the specific surface area is related to the size of the nanoparticles, the smaller the size, the larger the specific surface area. So its size is very important to prepare nano particles. Influence factors about the size of nanoparticles include molecular algebra, metal ions and the molar ratio of dendrimers, the concentration of the inner and outer templates, the means of reducing etc.

(1) Molecular algebra

According to the different of molecular algebra, the absorbance of Au nano clusters shows that with the increase of molecular algebra, the absorbance increases, and the larger of the absorbance, the smaller of the nanoparticles.

(2) Molar ratio of metal ions to dendritic polymer

Dendritic polymer have a certain amount of capacity to react with metal ions. When the metal ion is too long, the metal atoms will be reduced to a large number of atoms together, the size will become larger. In addition, too much metal ions may also be combined with the external functional groups of dendrimers, so that the branches of large molecules act as an outer template. And when the metal ion is less, only a small amount of metal ions are reduced to form a small size of the nanoparticles.

When the other conditions were the same, the size of the nanoparticles increased with the increase of the molar ratio of the metal ions to the dendritic polymer.

4 Conclusion

The preparation of nanoparticles based on dendritic polymer is simple, easy to operate, and the product is controllable, which ensures the excellent performance in catalysis. From single metal nanoparticles to bimetallic nanoparticles, and then to metal compound nanoparticles, it is also possible to prepare more superior multi metal nanoparticles on this basis.

But due to the active characteristics of nanoparticles, it will have a variety of interference factors in the preparation process, so nanoparticles morphology control still need further study, the control standard of various reaction conditions need further exploration.

References

1. Percec V., Ahn C. H. and Ungar G. Controlling polymer shape through the self-assembly of dendritic side-groups: Nature Vol. 391 (1998), p. 161-164
2. Bhadra D., Bhadra S., and Jain S. A pegylated dendritic nanoparticulate carrier of fluorouracil: Int. J. Pharm. Vol. 257 (2003), p. 111-124
3. Rosen B. M., Lligadas G., and Hahn C. Synthesis of dendrimers through divergent iterative thio-bromo“Click” chemistry: J. Poly. Sci. PartA: Poly. Chem. Vol. 47 (2009), p. 3931-3939
4. Carino E. V., Knecht M. R., and Crooks R. M. Quantitative analysis of the stability of Pd dendrimer- encapsulated nanoparticles: Langmuir Vol. 25 (2009), p. 10279-10284
5. Li G. P. and Luo Y. J. Preparation and characterization of dendrimer-templated Ag-Cu bimetallic nanoclusters: Inorg. Chem. Vol. 47 (2008), p. 360-364
6. Weir M. G., Knecht M. R. and Frenkel A. I. Structural analysis of Pd Au dendrimer-encapsulated bimetallic nanoparticles: Langmuir Vol. 26 (2010), p. 1137-1146
7. Gu Y. L., Xie H., and Gao J. X. AFM characterization of dendrimer-stabilized platinum nanoparticles: Langmuir Vol. 21 (2005), p. 3122-3131