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NOTE

Preparation of Spherical Rhodium Triiodide Based on Reaction Crystallization

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Reaction crystallization/precipitation in the industrial practice has a widely applications. To obtain easily solid-liquid separation process, it is necessary to control the morphology and the particle size of the product. The process of preparation rhodium(III) triiodide (RhI_3, the catalyst precursor for the Monsanto process) based on the different procedures 1, 2 and 3 have been optimized in order to minimize the cost of solid-liquid separation. The morphology and size of RhI_3 particles were investigated by scanning electron microscope. The results show that with the change of the physicochemical properties the critical parameters of control the morphology and size of the precipitation were different. The particle morphology based on the three routes was similar to spherical agglomeration and the particle diameter was *ca.* 20 μm. Furthermore, the filterability of the precipitation has also been greatly improved. Further research to find out why and how these factors working in industrial practice is underway.

Key Words: Rhodium(III) triiodide, Reaction crystallization, Solid-liquid separation.

Synthesis of acetic acid by methanol carbonylation is one of the most important catalytic reactions of industrialization. The Monsanto process, a major advance came in 1966 with the discovery of rhodium-iodide catalysts for the carbonylation of methanol by Monsanto company, was widely utilized by most commercial plants now. The catalyst precursor of the rhodium-iodide catalysts was rhodium(III) triiodide[1,2].

During the process of filter RhI_3, the filterability is very poor because of the smaller particle size and irregular shape of the compound. RhI_3 is insoluble compounds, which in aqueous solution crystallization is characterized by easy nucleation and the crystal is difficult to grow up. The reaction crystallization/precipitation is a complex process of mass-transfer and heat-transfer, which the critical factors of control the size of precipitation were different with the change of physical and chemical conditions[3,4]. The objective of this paper is to investigate the influences between the process parameters and the cost of solid-liquid separation processes of RhI_3.

Rhodium(III) chloride hydrate and rhodium(III) oxide hydrate were prepared in our laboratory. All reagents were of analytical purity and used without any further purification. Rhodium(III) triiodide was prepared according to the reported method[5,6] (Fig. 1). Briefly, rhodium(III) chloride hydrate and rhodium(III) oxide hydrate were dissolved/suspension in water and treated with KI or HI. The mixture was stirred for 4 h and the precipitate was filtrated off, washed with water and dried *in vacuo* at 70 ºC. Particle shape and size of rhodium(III) triiodide was studied by HITACHI S-3400 scanning electron microscope (SEM).

$$RhCl_3 + 3KI = RhI_3 + 3KCl \quad \text{(route 1)}$$

$$RhCl_3 + 3HI = RhI_3 + 3HCl \quad \text{(route 2)}$$

$$Rh(OH)_3 + 3HI = RhI_3 + 3H_2O \quad \text{(route 3)}$$

Fig. 1. Synthetic routes of rhodium(III) triiodide

Synthesis of RhI_3 based on the route 1: The process of preparation RhI_3 based on the route 1 is that the aqueous solutions of RhI_3 and KI are mixed together at 90 ºC. The mixture was stirred for 4 h and controls the pH = 3 during the preparation. According to the preparation process, the particle diameter of *ca.* 16 μm and the particle morphology was similar to spherical agglomeration (Fig. 2).

During the process of preparation RhI_3 based on the route 1, pH value and temperature has the obvious influence on the morphology and filterability of RhI_3. When pH is greater than 3 and the temperature of less than 80 ºC, the RhI_3 particle size significantly smaller. In contrast, the effects on precipitation are not obvious when the stirrer speed in a certain range changes. Although the filter resistance of RhI_3 are improved

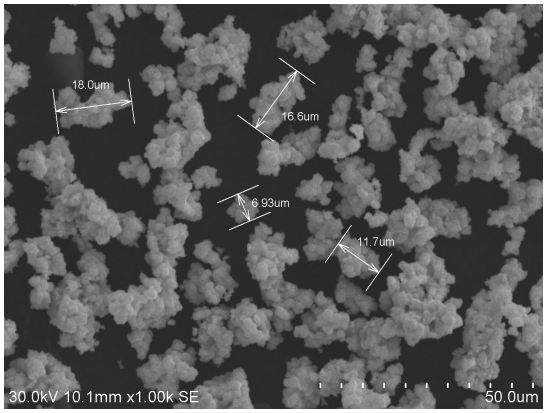

Fig. 2. SEM images of RhI_3 based on route 1

obviously under the conditions, but the particle morphology and the size control is not ideal, so further investigation is necessary to examine other factors, especially continuous precipitation and reactor[3,7,8].

Synthesis of RhI_3 based on the route 2: The process of preparation RhI_3 based on the route 2 is similar to route 1 and the concentration of HI is 45 %. Fig. 3 shows that the particle diameter is *ca.* 25 μm and particle with smooth surface.

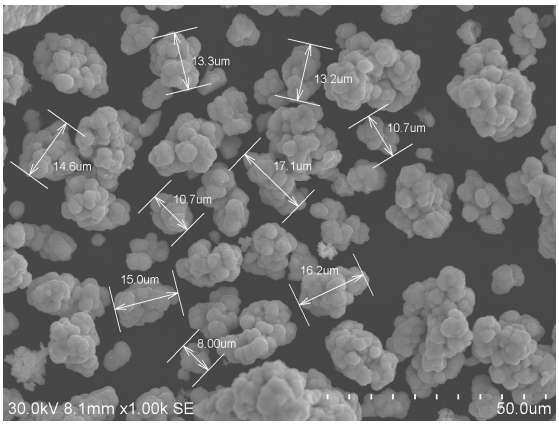

Fig. 3. SEM images of RhI_3 based on route 2

Interestingly, the concentration of rhodium(III) chloride hydrate was the critical factor of control the particle size and morphology of RhI_3. It is beneficial to the formation of spherical RhI_3 particles when the concentration of rhodium(III) chloride hydrate was between 0.2 and 0.5 mol/L. The experimental parameters indicated that ionic strength had a decisive effect on the morphology of the RhI_3 particle[9]. Although the uniformity of RhI_3 particle is not ideal, the filterability of the precipitation is the best among the three synthetic routes.

Synthesis of RhI_3 based on the route 3: According to the route 3 preparation RhI_3 is reported in the literature. It is found that the particle size is not uniform and the morphology is loose and porous (Fig. 4). Unfortunately, no matter how to optimize the process parameters, the morphology of precipitation has no significant improvement. The possible reason is that the rhodium(III) oxide hydrate is colloidal compounds and the morphology of it should be investigation primarily.

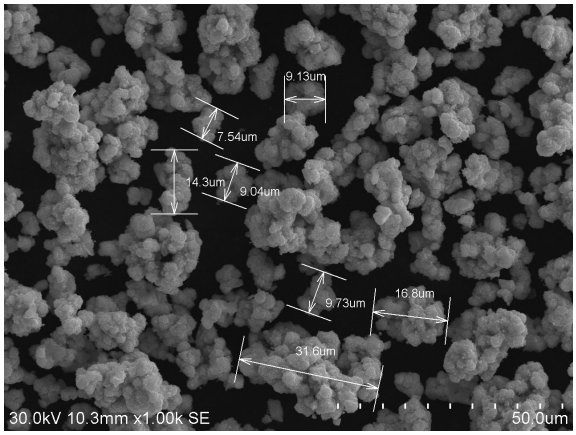

Fig. 4. SEM images of RhI_3 based on route 3

Conclusion

In summary, we have obtained the approximate spherical RhI_3 particle by optimize the precipitation processes and the filterability of the precipitation of RhI_3 has also been greatly improved. In industrial practice we are particularly concerned by the fact that it is even not always possible to scale up from laboratory findings to large scale. Therefor, our next goal is to find out why and how these factors working between small and large scale.

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