Preparation and characterization of sea-urchin like TiO_2 microspheres

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Abstract: High surface area "sea-urchin" TiO_2 microspheres were obtained via a facile hydrothermal method. In all cases, XRD, SEM and BET analysis show that the main formation of this material is anatase, the diameter of these microspheres is in the range of 200-300 nm, and 204 $m^2\ g^{-1}$ surface area. All data above may prove this unique shape TiO_2 can be a good supporter for Pt when it is used in field of catalysts.

Keywords: TiO_2, Microspheres, Catalysts.

1. Introduction

TiO_2 is one of the most frequently used material in research area of catalysis such as photocatalysts and carriers for supported metal/metal oxides. We have reported that nonporous TiO_2 (P25, JRC-TIO4) powder is one of the best carriers for colloidal deposition methods for preparation of supported metal catalysts. This includes three steps: (1) the preparation of Pt and Pt-based bimetallic particles stabilized by poly(*N*-vinyl-2-pyrrolidone) (PVP), (2) their deposition on supporting materials by simple mixing and filtering, and (3) heat treatment and H_2 reduction. Pt nanoparticles were highly-dispersed on TiO_2 supports after the post-treatment due to strong interaction between the support and Pt particles[1].

Recently, much attention has been focused on shape-controlled materials because catalytic properties can be improved by changing the morphology of materials. In this study, we investigated the efficacy of "sea-urchin" like TiO_2 powders as supporting materials. The TiO_2 powders have porous structures with higher surface area than TiO_2 P25. It is therefore expected that the powders can be used for preparation of highly-dispersed metal catalysts.[2-3]

2. Experimental

The "sea-urchin" TiO_2 microspheres were prepared by a simple hydrothermal method. First, 4.6 g urea was added to 2 M HCl aqueous solution. A few minutes stirring later, 0.575 ml TTIP (titanium isopropoxide) was dropped into the above solution under stirring. When the solution became transparent, transfer it to a 23 ml Teflon stainless steel, and kept it at 120 ^{0}C for 12 h. After the reaction finished and the steel naturally cooled to the room temperature, used deionized water to wash the white product several times, and then dried at 60 ^{0}C overnight.[4] Finally, calcined the white product at 0, 200, 300 and 400 ^{0}C with the heating rate of 1 ^{0}C/min. The samples were denoted as TiO_2-MS, TiO_2-MS-200, TiO_2-MS-300 and TiO_2-MS-400, respectively.

3. Results and discussion

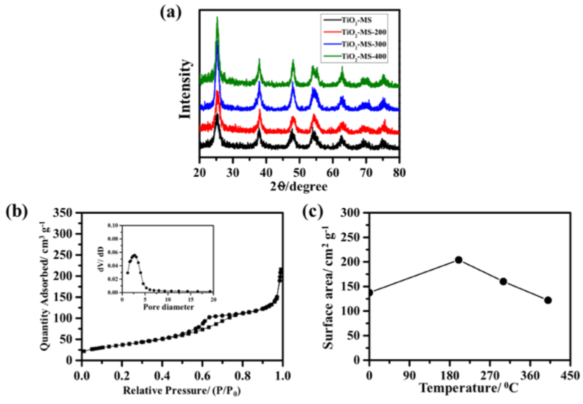

Figure 1. (a) XRD Patterns of TiO_2 at different temperatures. (b) N_2 adsorption–desorption isotherms of TiO_2-MS (Inset: pore size distributions from the adsorption branch through the BJH method). (c) the relationship between surface area and temperature.

XRD patterns of TiO_2 calcined at different temperatures are displayed in figure 1a. The crystal phase of the samples is identical. All of the diffraction patterns can be indexed to anatase TiO_2 (space group: I41/amd, JCPDS 01-0562) which are consistent with the precious report. The diffraction peak of the heated samples sat 25.34^0 is slightly stronger and narrower, which indicated that the crystalline size of the heated samples is larger than that of TiO_2-MS.

N_2 adsorption-desorption isotherms of TiO_2-MS (Figure 1b) shows a hysteresis loop, implying that the sample has mesoporous structures. BJH pore size distribution analysis confirmed the presence of mesopores with 2.71 nm in TiO_2-MS. Figure 1c shows the effect of calcination temperature on the BET surface area of TiO_2-MS. The surface area depended on the heating temperatures: the surface area is 137 m^2 g^{-1} before calcination and increased to 204 m^2 g^{-1} after heat treatment at 200 ^{0}C. This shows that calcination at a certain temperature helps to expand the surface area. Treatment TiO_2-MS samples at higher temperature (>200 ^{0}C) decreased their surface area. However, the surface areas were much larger than that of TiO_2 P25 (54 m^2 g^{-1}). On the basis of findings described above, it can be expected that the TiO_2-MS is a good supporting materials for deposition of metal nanoparticle.[5]

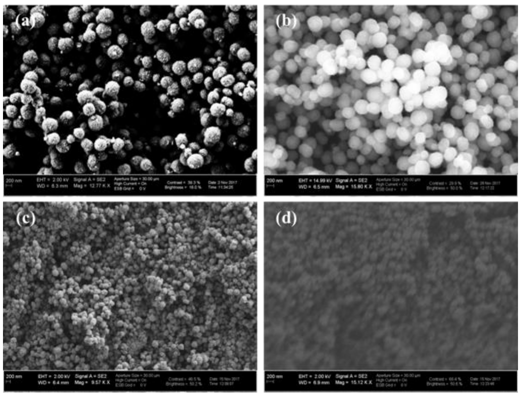

Figure 2. SEM images of samples (a) TiO_2-MS, (b) TiO_2-MS-200, (c) TiO_2-MS-300 and (d) TiO_2-MS-400.

SEM images of TiO_2-MS samples, depicted in figure 2, show that all the samples are consisted of uniform microspheres with the diameter was ~200-300 nm. In addition, even calcined the samples at different temperatures, their morphology did not change significantly. These findings, along with the results obtained from XRD and N_2 adsorption studies imply that the materials have good thermal stability. This also offers the possibility of using this material at high temperatures in catalytic system.

4. Conclusions

In conclusion, a simple hydrothermal method was designed for preparing this TiO_2 microspheres. Meanwhile, these microspheres were about 200 nm in diameter and have high surface area which can even reach 204.13 m^2 g^{-1}. We consider that such high surface area may make it possible for this “sea-urchin” like TiO_2 to be a strong supporter for Pt and widely used in the field of catalysts in the future.[6-7]

References

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