Preparation and Characterization of Titania-silica Composite Particles by Pechini Sol-gel Method

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Abstract.Two Pechini sol-gel processes were used to prepare titania-silica composite particles. The dynamic oxidation behavior of the TiO_2-SiO_2 powders has been characterized by thermogravimetry-differential scanning calorimetry (TG-DTG-DSC). The crystal phase and microstructure of the composite particles were investigated by X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM). The effects of Si:Ti molar ratio and sol-gel process on the TiO_2-SiO_2 powders were studied. The preparation of the polymeric precursors can influence the morphology of obtained TiO_2-SiO_2 composite particles. The spherical TiO_2-SiO_2 composite particles which are 20 nm~400 nm in diameter appear in gel-1 system. However, the TiO_2-SiO_2 powders obtained by gel-2 system are irregular in shape and 2~15 μm in diameter which show a loose porous structure consisted of very fine granules.

1. Introduction

Titania-silica composite particles exhibit enhanced ultraviolet photocatalytic activity when compared with titania particles. It is traditionally used for heterogeneous catalysis [1, 2], electrochemical sensors [3], high-k dielectricmaterials [4], paints and so on. Titania-silica composite particles with various morphologies have been developed, such as porous particles, spheres and fibers [5, 6]. The microstructures, sizes and shapes have great influence on the properties of titania-silica composites, such as catalytic activity, thermal properties, photoactivity and chemical durability [7, 8]. The Pechini process [9-11] has the advantage of molecular level mixing of the components and low calcination temperature. And this method is usually applied to synthesize the nano or sub-micro powders with a more uniform size distribution. However, the influence of Pechini processing on the morphology of composite particles is unclear.

In the present work, Pechini sol-gel method was applied to prepare SiO_2 particles, TiO_2 particles and titania-silica composite particles. And a comparative study was carried out on the two Pechini sol-gel processes for the synthesis of titania-silica particles. We believe that the morphology of titania-silica composite particles can change with the preparation of

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polymeric intermediates. This study has general implications in the morphology controlled preparation of composite particles via Pechini sol-gel method.

2. Experimental Procedure

2.1Synthesis

Tetraethyl orthosilicate (TEOS, 98%, A. R.) solution was prepared by dissolving 0.02mol TEOS and 0.022mol citric acid (99.8%, A.R.) in 7.5ml ammonia (25%, A.R.). 11ml ethanol (99.7%, A.R.) and 11ml distilled water were added to the TEOS solution, and then 1.1g polyethylene glycol-6000 (PEG-6000, 99%, A.R.) was dissolved into the solution to obtain sol-1. Sol-1 was heated up to 85℃ for 6h to form gel. After drying at 140℃ for 6h and calcining at 600℃ with a heating rate of 5℃/min, the SiO_2 powders were synthesized.

Tetrabutyl titanate (TBOT, 98%, A.R.) solution was prepared by dissolving 0.02mol TBOT and 0.028mol citric acid in 18ml ammonia. 22ml ethanol and 18ml distilled water were added to the TBOT solution, and 3.4g PEG-6000 was dissolved into the solution to obtain sol-2. The subsequent processes were as the same as sol-1, and then the TiO_2 powders were prepared.

Route I: Sol-1 was heated up to 85℃ for 3h to form intermediate-1. Sol-2 was then added into intermediate-1. The mixture was aged for 3h with stirring to finish the synthesis of gel-1. The gel was dried at 140℃ for 6h in an oven. Finally, the dried gel-1 was calcined in air at different temperatures ranging from 400℃ to 800℃ with a heating rate of 5℃/min. The Si:Ti molar ratios of products A1, A2 and A3 were 5:1, 10:1 and 14:1 respectively.

Route II: Sol-2 was heated up to 85℃ for 3h to form intermediate-2. Sol-1 was then added into intermediate-2. The mixture was aged for 3h with stirring to finish the synthesis of gel-2. TiO_2-SiO_2 powders were prepared as the same thermal process as route I. Differently the dried gel-2 was calcined in air at 600℃. The Ti:Si molar ratio of products (B1) was 10:1.

2.2Characterization

XRD patterns of the calcined powders were carried out on an X-ray diffractometer (D/max-2200PC, Japan) using CuKα radiation (λ =1.5406Å) in an effort to investigate the phase transformations. Thermal analysis was conducted with thermal analyzer (STA409PC, Germany) using a heating rate of 10℃/min. FE-SEM (JSM-6700F, Japan) was utilized to examine the morphology of the obtained particles.

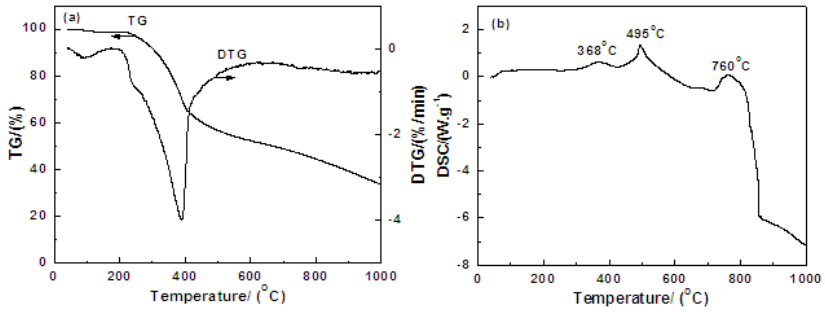

Fig. 1 (a) TG-DTG and (b) DSC graphs of gel-1.

3. Results and Discussion

TG-DTG-DSC curves of gel-1 are shown in Fig. 1. The first exothermal peak centered at 368℃ in DSC curve can be related to the formation of anatase TiO_2 phase and the deformation of polyethylene glycol. The exothermal peak at 495℃ can be attributed to the combustion of polyethylene glycol derivatives and citric acid. And the exothermic peak at 760℃ is due to the transformation from anatase TiO_2 to rutile TiO_2.

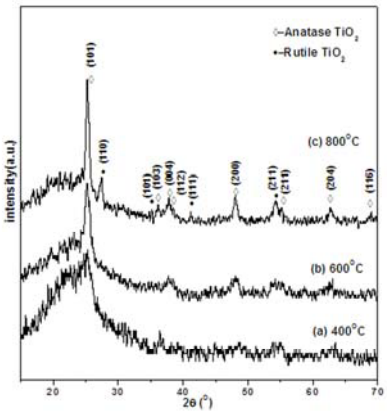

Fig. 2 XRD patterns of TiO_2-SiO_2 powders prepared by gel-1 calcined at different temperatures.

XRD patterns of TiO_2-SiO_2 particles prepared by gel-1 are shown in Fig. 2. All patterns contain a halo at about 23°. This halo indicates that the synthesized composites contain an amorphous structure which is due to amorphous silica. The observed peaks in XRD pattern for the powders calcined at 400℃ and 600℃ are due to anatase TiO_2 phase (JCPDS 21-1272). At 800℃, characteristic peaks of anatase TiO_2 and rutile TiO_2 (JCPDS 01-1292) appear. The anatase TiO_2 (101) peak is used to calculate crystallite size of the synthesized powders. It is found to be 15.1 and 11.4nm respectively for the powders calcined at 600℃and 800℃. The crystal size decreases with the increment of calcination temperature. This result may be due to the transformation from anatase TiO_2 to rutile TiO_2.

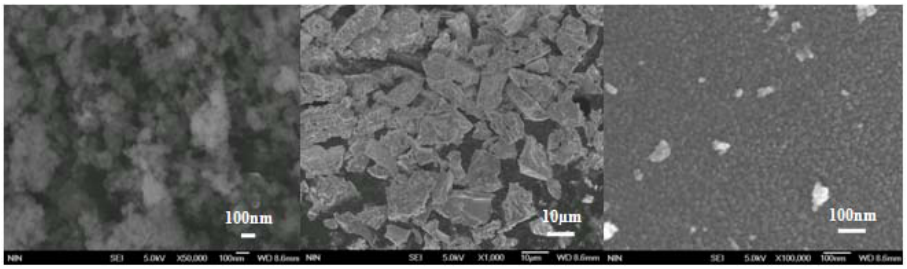

Fig. 3 FE-SEM images of (a) SiO_2 powders, (b) and (c) TiO_2 powders calcined at 600℃.

As shown in FE-SEM images of SiO_2 powders and TiO_2 particles calcined at 600℃ (Fig. 3), the SiO_2 powders are well dispersed and maintain spherical shape with average particle diameter of about 20nm. The TiO_2 particles have irregular in shape. The blocks are about 5~20 μm in diameter. And the big blocks consist of nano-meter spherical particles with about 20nm in diameter which is close to crystal size.

Fig. 4 shows FE-SEM images of TiO_2-SiO_2 powders prepared by gel-1 calcined at 600℃. When the Si:Ti molar ratio is 5:1, the obtained powders contain spherical particles and irregular particles. With the increment of Si:Ti molar ratio, the size of particles does not change, but TiO_2-SiO_2 particles become nearly perfect spheres. The large particles of obtained TiO_2-SiO_2 powders are about 200~400 nm in diameter. Some particles which are smaller in diameter (approximately 20~50 nm) are around the large particles. Both the particle sizes of large and small particles estimated from FE-SEM are larger than that calculated from the XRD data. The reason for the above result is that the particles of gel-1 system are agglomerated powders which contain amorphous SiO_2 and anatase TiO_2.

Fig. 5 shows FE-SEM images of TiO_2-SiO_2 powders (B1) prepared by gel-2 calcined at 600℃. Compared B1 with A2 (see Fig. 4(b)), magnitude difference is found both in shape and particle size. Spheres can not be obtained by gel-2, and the TiO_2-SiO_2 powders prepared by gel-2 are irregular in shape and 2~15 μm in diameter. As shown in Fig. 5(b), the smooth surface of B1 is solid plate, but the inside part shows a loose porous structure consisted of very fine granules (about 20 nm).

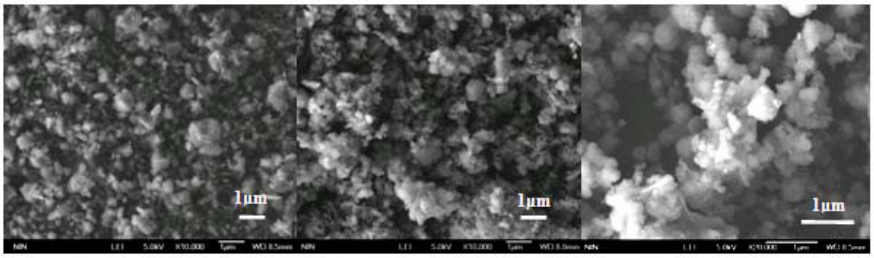

Fig. 4 FE-SEM images of TiO_2-SiO_2 powders prepared by gel-1 calcined at 600℃: (a) A1; (b) A2 and (c) A3.

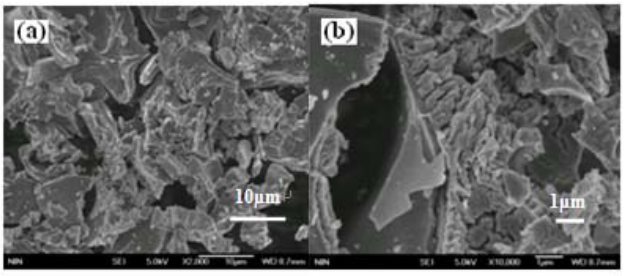

Fig. 5 FE-SEM images of TiO_2-SiO_2 powders prepared by gel-2 calcined at 600℃. Magnification: (a) 2000× and (b) 10000×

Compared Fig. 4 and Fig. 5 with Fig. 3, the morphology of TiO_2-SiO_2 powders is similar with that of the TiO_2 or SiO_2 particles，the sol of which is heated up first. However, owing to the addition of sol-2, the TiO_2-SiO_2 powders prepared by gel-1 have smoother surface and bigger particle size. Although the low-magnification FE-SEM images indicate that the TiO_2-SiO_2 powders prepared by gel-2 have similar morphology with that of TiO_2 powders, the high-magnification FE-SEM images of TiO_2-SiO_2 powders present a loose porous structure which is caused by the addition of sol-1. In the Pechini sol-gel process, polymer resin forms via the chelations and polyesterifications. The viscosity of sol increases. So the sol which is heated up first acts as template and plays a decisive role in the morphology of TiO_2-SiO_2 powders. In gel-1 system, because the SiO_2 template prevents the aggregation of TiO_2 particles, the micrometer-sized blocks can not be obtained. In gel-2

system, because TiO_2 particles exist as template and SiO_2 particles are well dispersed nano-spheres, the TiO_2-SiO_2 powders have similar surface morphology with TiO_2 particles, but have loose porous structure in inside part.

4. Conclusions

In this paper, the SiO_2 particles, TiO_2 particles and TiO_2-SiO_2 composite particles could be synthesized by Pechini sol-gel processes. The obtained SiO_2 particles are spherical particles with average particle diameter of about 20nm. The obtained TiO_2 particles are big blocks consist of nano-meter spherical particles. The preparation of the gel can influence the morphology of the obtained TiO_2-SiO_2 composite particles. In the gel-1 system, the gel starts to crystallize at 400℃ with the anatase TiO_2 phase. The rutile TiO_2 phase appears in the composite powders calcined at 800℃. The TiO_2-SiO_2 particles synthesized at 600℃ in gel-1 system are spherical particles which contain the larger spherical particles (about 200~400 nm) and smaller particles (approximately 20~50 nm). However, the spheres do not appear in the gel-2 system, and the prepared TiO_2-SiO_2 powders are irregular in shape and 2~15 μm in diameter. Although the morphology of TiO_2-SiO_2 powders is similar with that of the TiO_2 or SiO_2 particles, the surface or inner structures are different owing to the addition of another sol.

5. Acknowledgement

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References

1. I. Lázár, J. Kalmár, A. Peter, A. Szilágyi, E. Győri, T. Ditrói, I. Fábián, Photocatalytic performance of highly amorphous titania–silica aerogels with mesopores: The adverse effect of the in situ adsorption of some organic substrates during photodegradation, Appl. Surf. Sci., 356 (2015) 521-531.
2. U. Sirimahachai, N. Ndiege, R. Chandrasekharan, S. Wongnawa, M.A. Shannon, Nanosized TiO_2 particles decorated on SiO_2 spheres (TiO_2/SiO_2): synthesis and photocatalytic activities, J. Sol-Gel Sci. Technol. 56 (2010) 53-60.
3. E.I. Morosanova, Silica and silica-titania sol-gel materials: synthesis and analytical application, Talanta 102 (2012) 114-122.
4. M.H. Weng, R. Mahapatra, P. Tappin, B. Miao, S. Chattopadhyay, A.B. Horsfall, N.G. Wright, High temperature characterization of high-κ dielectrics on SiC, Mat. Sci. Semicon. Proc. 9 (2006) 1133-1136.
5. R. Morozov, I. Krivtsov, V. Avdin, Z. Amghouz, S. A. Khainakov, J. R. García, Peroxo method for preparation of composite silica–titaniaspheres, J. Non-Cryst. Solids, 435 (2016) 8-16.
6. K. Kusakabe, M. Ezaki, A. Sakoguchi, K. Oda, N. Ikeda, Photocatalytic behaviors of silica-loaded mesoporous titania, Chem. Eng. J. 180 (2012) 245-249.
7. L.H. Wu, Y.F. Zhou, W.Y. Nie, L.Y. Song, P.P. Chen, Synthesis of highly monodispersed teardrop-shaped core–shell SiO_2/TiO_2 nanoparticles and their photocatalytic activities, Appl. Surf. Sci. 351 (2015) 320-326
8. Y.H. Zhang, L. Yu, S.M. Ke, B. Shen, X.H. Meng, H.T. Huang, F.Z. Lv, J.H. Xin, H.L.W. Chan, TiO_2/SiO_2 hybrid nanomaterials: synthesis and variable UV-blocking

properties, J. Sol-Gel Sci. Technol. 58 (2011) 326-329.
9. A. Mirzaei, K. Janghorban, B. Hashemi, M. Bonyani, S.G. Leonardi, G. Neri, Highly stable and selective ethanol sensor based on α-Fe_2O_3 nanoparticles prepared by Pechini sol–gel method, Ceram. Int. 42 (2016) 6136-6144.
10. Q.K. Wang, Q.B. Chang, Y.Q. Wang, X. Wang, J.E. Zhou, Ultrafine $CoAl_2O_4$ ceramic pigment prepared by Pechini-sacrificial agent method, Mater. Lett. 173 (2016) 64-67.
11. I.V. Krivtsov, M.V. Ilkaeva, V.D. Samokhina, V.V. Avdin, S.A. Khainakov, D.A Uchaev, J.R. Garcia, Synthesis of silica–titania composite oxide via "green" aqueous peroxo-route, J. Sol-Gel Sci. Technol. 67(2013) 665-669.