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Morphology and crystal structure of A1-doped TiO_2 nanoparticles synthesized by vapor phase oxidation of titanium tetrachloride

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Abstract

Al-doped titanium dioxide nanoparticles with precisely controlled characteristics were synthesized in an aerosol reactor between 900 °C and 1500 °C by vapor-phase oxidation of titanium tetrachloride. The effect of process variables (reactor temperature, initial $TiCl_4$ concentration, residence time and feeding temperature of oxygen) on particle morphology and phase characteristics was investigated using TEM, XRD, EDS, ICP and XPS, etc. The average particle size increased with decreasing oxygen feeding temperature and increasing reaction temperature, residence time and $TiCl_4$ concentration. The presence of aluminum during gas phase reaction increased the rate of phase transformation from anatase to rutile and altered the particle morphology from polyhedral to irregular crystals. TiO_2 and Al_2O_3 co-precipitated during particle formation which lead to the aluminum solid solution in titania. α-Al_2O_3 and Al_2TiO_5 were observed at $AlCl_3/TiCl_4$ ratios higher than 1.1 and reactor temperatures in excess of 1400 °C. The rutile content, which increased with increasing Al/Ti ratio and residence time, was at a maximum at about 1200 °C and decreased at both lower and higher reactor temperatures.

Keywords: Vapor phase deposition; Nanoparticles; Titanates

1. Introduction

Having a high surface activity, high refractive index and unusual photocatalytic activity, nanosized TiO_2 powder is extensively used in pigment, inorganic membranes, and as a photocatalyst in gas and water purification process. Titania, especially in its rutile form, is one of the most widely investigated oxides regarding defect structure and physical and chemical properties. Titania powders have been synthesized by gas phase oxidation of titanium tetrachloride [1–5], and commercial titania is primarily manufactured by the 'chloride process' where titanium tetrachloride vapor is oxidized in a flame [6–10]. Dopants are routinely added to control the phase composition and size of titania powders prepared by oxidation of $TiCl_4$ vapor, but the fundamentals of dopant addition have not been understood. Mackenzie [11] investigated titania crystallite growth and kinetics of anatase to rutile transformation in the presence of copper, iron, and zinc oxides in solid phase. He concluded that oxygen vacancies promoted crystallite growth and the anatase to rutile transformation. Hung et al. [12] obtained a mixture of TiO_2, Al_2O_3 and aluminum titanate on a microscopic scale when they synthesized TiO_2–Al_2O_3 composite particles in a counter flow diffusion flame. Powell et al. [13] prepared titania particles from the oxidation of titanium tetrachloride in a hot-wall, tubular, aerosol reactor and directly coated by SiO_2 in the gas phase. The

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presence of silicon, phosphorus, and boron halides during $TiCl_4$ oxidation retarded the anatase to rutile conversion and the gas phase sintering of titania [14]. Silicon was the most effective in suppressing the anatase to rutile conversion and in transforming the polyhedral pure titania particles to highly aggregated ones with large specific surface area.

Aluminum titanate has a potential use in thermal shock applications because of its thermal expansion coefficient. Recently the production of Al_2O_3–TiO_2 composite and Al_2TiO_5 nanoparticles is of growing interest because of their good chemistry and physics properties. Individual Al_2O_3, TiO_2 and SiO_2, as well as binary Al_2O_3–TiO_2 powders were obtained by sol–gel method, polymeric route [15]. The preparation of Al_2TiO_5–$Al_6Si_2O_{13}$ pseudobinary system has been realized by solid-state reaction starting with the mentioned above. Segadaes et al. [16] described a straightforward combustion synthesis technique to prepare submicron Al_2TiO_5 powders, using the corresponding metal precursors–urea mixtures, at low temperature and short reaction times. Lee et al. [17] prepared TiO_2 and Al_2O_3 solutions by hydrolyzing $Ti(OC_2H_5)_4$ and $Al(OC_3H_7)_3$, respectively. The two solutions were mixed to obtain a homogeneously mixed gel, which was dried and calcined to an Al_2O_3–TiO_2 nanocomposite powder. A process of coating Al_2O_3 particles with TiO_2 by hydrolysis of $Ti(OC_4H_9)_4$ using chemical vapor deposition in a rotary reactor has been developed by Li et al. [18]. The process resulted in (1) a coating film of TiO_2 which was compact and uniform with the fraction of TiO_2 being 0.1–10.0% and (2) an amorphous TiO_2 coating at a low reaction temperature converted to anatase at a reaction temperature higher than 400 °C. Shi et al. [19] synthesized TiO_2 and Al_2O_3–TiO_2 composite nanoparticles by the gas-phase oxidation of titanium tetrachloride in a high temperature tubular aerosol flow reactor. They found that the particle size increased with increasing temperature, and a maximum rutile fraction was obtained at 1200 °C and an $AlCl_3$ to $TiCl_4$ feed ratio of 0.09.

In this study, a systematic experimental investigation is conducted into the vapor phase synthesis of Al-doped TiO_2 and Al_2O_3–TiO_2 composite particles by high temperature oxidation of titanium tetrachloride. The effect of process variables (reactor temperature, initial $TiCl_4$ concentration, residence time and feeding temperature of oxygen) on particle morphology and phase characteristics was carried out using TEM, XRD, EDS, ICP and XPS, etc, and the changes in particle morphology and phase composition are discussed by the creation of oxygen vacancies in the production particles.

2. Experimental

2.1. Particle synthesis

Fig. 1 shows the schematic of the employed experimental apparatus. After purified and preheated at temperatures between 600 °C and 900 °C, oxygen gas (Shanghai Wujing Chemical Factory, 98%) was then fed into the aerosol reactor at 0.08 $m^3\,h^{-1}$, and the flow of oxygen gas was usually in excess of the stoichiometric amount. Nitrogen gas (Shanghai Wujing Chemical Factory, 98%), purified by a N_2 purifier, was divided into four parts. The first part flowed through a rotor flowmeter at 0.036 $m^3\,h^{-1}$ outlet into

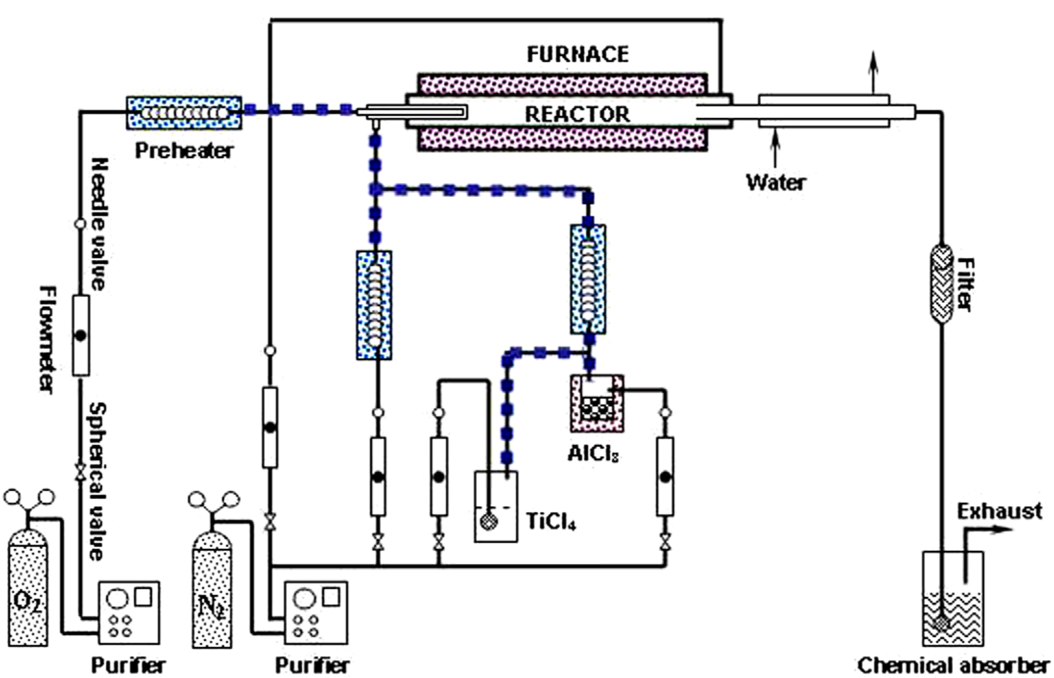

Fig. 1. Schematic of the apparatus used for synthesis of pure and Al-doped titania nanoparticles.