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Synthesis of mesoporous TiO_2/γ-Al_2O_3 composite granules with different sol composition and calcination temperature

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Abstract

Mesoporous TiO_2/γ-Al_2O_3 composite granules were prepared by combining sol–gel method and oil-drop method. After calcination at 450 °C, the composite granules showed anatase and γ-Al_2O_3 phases with the specific surface area of 240–310 m^2/g. The phase composition and pore structure of the granules can be controlled by calcination temperature and the mixing ratio of boehmite sol and titania sol. The product granules can be used as a photocatalyst or adsorbent in moving or fluidized bed reactors.

Keywords: Alumina; Titania; Granulation; Sol–gel; Pore structure; Nanostructure

1. Introduction

The support materials, like ceramic oxide powder, with high surface area and thermal stability have been the interest for various applications in many chemical processes. There are some drawbacks to synthesize a single-phase oxide material with desirable properties. One of promising approaches has focused on the supports consisting of composite that integrate the favorable aspects of the constituents. For example, titanium dioxide (TiO_2, titania) has received significant attention because of its numerous applications in photocatalysis and catalyst support [1]. However a relatively low surface area and poor structural stability at high temperatures are major disadvantages. Alumina (Al_2O_3) has been usually applied to several fields as a support material due to its high surface area and abrasion resistance, even though Al_2O_3-supported catalyst has relatively low activity [2,3].

For these reasons, TiO_2–Al_2O_3 composite oxide has been prepared to overcome the shortcomings [4–6]. The composite was used in the dehydrosulfurization catalyst [7,8] and photocatalyst [9]. To obtain a well-controlled composite, it is very important to choose a suitable preparation route. Conventionally, TiO_2–Al_2O_3 composite powders are formed from a mixture of Al_2O_3 and TiO_2 powders ball-milled for the subsequent shaping and sintering [10]. This method has hardly produced mixed powders homogeneously.

Furthermore, industrial applications in many separation and reaction processes require the use of the composite in the granular form. However, the granules prepared by conventional methods, i.e. tumble growth, tabletting and extrusion, suffer from some drawbacks such as poor mechanical strength and low attrition resistance [11]. In our previous work [12], spherical alumina granules were prepared by the sol–gel granulation process with various calcinations temperature. It was found that the structural properties of the granules were affected by the calcinations temperature. However, to our best knowledge, no significant work has been reported on the synthesis of TiO_2–Al_2O_3 composite granules with high surface area, controlled porosity and tailor-designed pore size distribution. In this study, mesoporous TiO_2–Al_2O_3 composite granules were prepared by combining sol–gel method and oil-drop method. Effects of the TiO_2/Al_2O_3 ratios and calcinations temperature on the various physical properties of the composite granules are reported with sophisticated characterizations.

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2. Experimental

2.1. Preparation procedures

Spherical TiO_2/γ-Al_2O_3 composite granules of 1–2 mm in diameter were prepared by the sol–gel granulation process reported by elsewhere [12–14]. Boehmite and titania sols were prepared separately by the methods reported earlier. Initially, 2 M stable boehmite sols were synthesized from hydrolysis and condensation of aluminum isopropoxide, ALISOP (Aldrich, Mw=204.25, 98% purity), using the modified Yoldas process [13]. This method, which avoids the evaporation step, was used as a direct preparation of high-concentration boehmite sol. The precursor ALISOP is first hydrolyzed in 500 ml distilled water at 80–85 °C, and after stirring for 1 h, the resulting slurry (with AlOOH precipitates) was peptized with 1 M HNO_3, at an HNO_3 to AlOOH molar ratio of 0.07. The sol was refluxed overnight for more than 12 h at 95 °C. The remnant alcohol was evaporated by refluxing the sol exposed to air for 2 h at 95 °C.

0.5 M titania sols were synthesized by hydrolysis and condensation of titanium tetraisopropoxide, TTIP (Aldrich, Mw=284.26, 97% purity). TTIP was dissolved in isopropanol at room temperature and in a water-free atmosphere. Then, this solution was added slowly into the distilled water with stirring at high speed for 1.5 h, thus white precipitates formed. The precipitates obtained was separated and washed repeatedly with distilled water until the precipitates became free of alcohol. These precipitates were converted into a stable sol by dispersing in 1000 ml of water, followed by peptization with an addition of 1M HNO_3 solution. Then, the solution was refluxed at 80 °C for 12 h [15].

For granulation process, both boehmite and titania sols were mixed together at a predetermined concentration, followed by stirring for 1.5 h. Before sol mixing, both boehmite and titania sols were ultrasonically dispersed by a homogenizer. After adding a small amount of 1 M HNO_3, the sol mixture was aged at 70 °C for 1–2 h until the mixture reached the gelation point. This partially gelled sol was transferred into droppers for the generation of sol droplets of about 5 mm in size. The droplets fell through a liquid bath consisting of a paraffin oil layer (mineral oil, from Yakuri Pure Chemicals Co. Ltd.) and a 10 wt.% ammonia solution layer [13]. The paraffin oil layer facilitated the droplets into spherical wet-gel granules by surface tension. The structures of the wet-gel particles were strengthened after aging in the ammonia solution for 1 h. The granules were then collected with a sieve and washed several times with alcohol and distilled water. After these wet granules were dried at 40 °C for 48 h, the granules were treated at various temperatures from 450 to 750 °C for 3 h at a heating rate of 1 °C min^{-1}. The product granules were labeled as PA, TA0.25, TA0.50 and TA0.75, respectively, for $TiO_2/(TiO_2+Al_2O_3)$=0, 0.25, 0.50 and 0.75.

2.2. Characterization techniques

The shape and size of the TiO_2/Al_2O_3 composite granules were observed using an optical microscope (Microscope System STVMS 305R, Sometech). An X-ray diffractometer

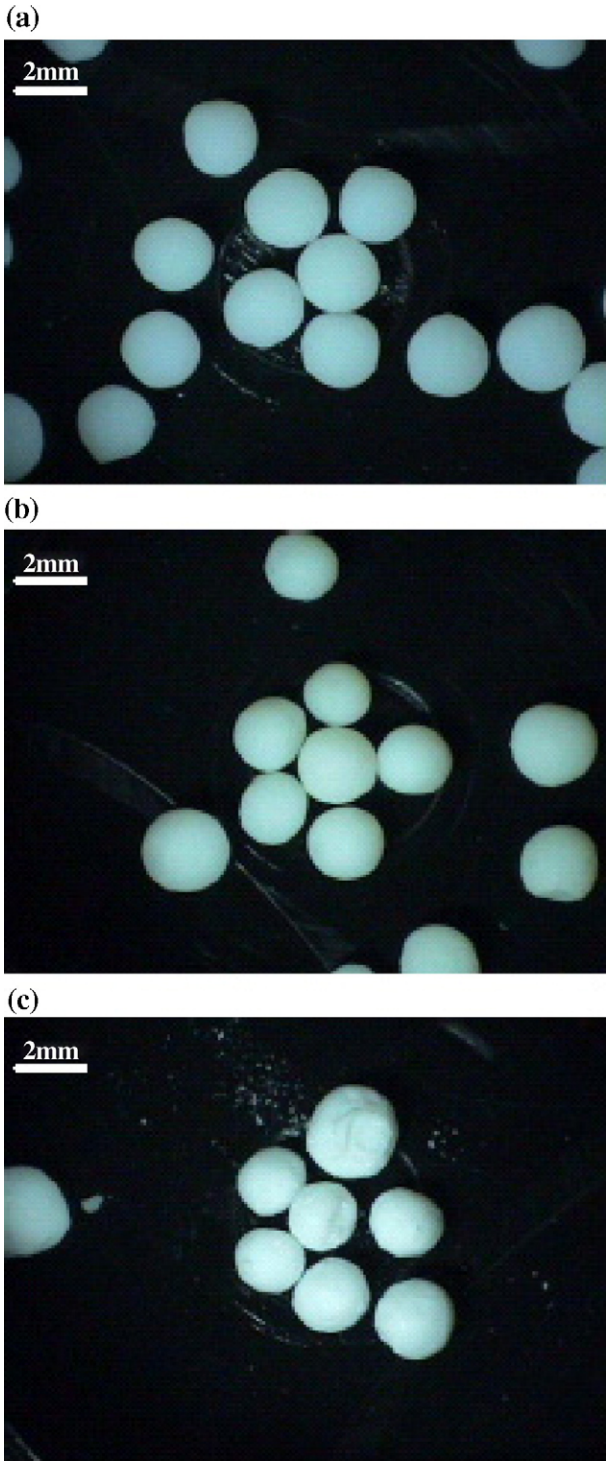

Fig. 1. Optical photographs of the TiO_2/γ-Al_2O_3 granules: (a) TA0.25, (b) TA0.50, and (c) TA0.75.

(M18XHF-SRA, Mac Science) was used for the identification of crystallinity with Ni filtered CuK_α (λ=1.54056 Å) radiation over the range of 2θ from 20 to 80°, with a scanning speed of 1° min^{-1}. The crystallite sizes (D_{hkl}) were calculated using the Scherrer relationship [16]:

$$D_{hkl} = K\lambda / B_{hkl}\cos\theta \quad (1)$$