Synthesis of TiO$_2$ nanoparticles on mesoporous aluminosilicate Al-SBA-15 in supercritical CO$_2$ for photocatalytic decolorization of methylene blue

Fei Changa,*, Gang Wanga, Yunchao Xiea, Min Zhaanga, Jian Zhaanga, Hai-Jian Yangb,**, Xuefeng Huc,***

a School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, PR China

b Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, Key Laboratory of Analytical Chemistry of the State Ethnic Affairs Commission, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, PR China

c Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, PR China

Received 13 September 2012; received in revised form 18 October 2012; accepted 18 October 2012

Abstract

In the present study, titania nanoparticles were first constructed on mesoporous aluminosilicate Al-SBA-15 in supercritical carbon dioxide (Sc-CO$_2$) and the resultant samples were characterized by a combination of various techniques, such as X-ray diffraction (XRD), nitrogen physisorption, $^{27}$Al MAS NMR, UV–vis diffuse reflectance spectroscopy, and transmission electron microscopy (TEM). It was identified that the Al species incorporated samples retained structures similar to that of the parent SBA-15. In addition, the content of titania loading varied with reaction temperature and time in Sc-CO$_2$. As-synthesized TiO$_2$/Al-SBA-15 samples were evaluated in terms of photocatalytic decolorization of methylene blue in aqueous solutions. It was observed that all TiO$_2$/Al-SBA-15 samples showed satisfactory decolorization efficiency that was much higher than those of TiO$_2$/SBA-15 and commercial TiO$_2$ under identical conditions, which could be mainly attributed to the effective adsorption capability, resulting from the extension of specific surface area after substitution of Si species with Al species.

Keywords: D. TiO$_2$; Aluminosilicate; SBA-15; Supercritical carbon dioxide

1. Introduction

Heterogeneous photocatalysis through semiconductor nano-oxides is shown to be an attractive technology for the control of environmental pollution and has become one of the most active research fields in recent years [1,2]. Among various metal oxide semiconductors used, titania has been the most investigated one, due to the effective photocatalysis, long-term thermal and chemical stability, low cost, and non-toxicity [3–5]. However, the nanosized titania produced in general procedures is greatly limited for practical applications because of the low specific surface area without pore system in structure. Besides conglomeration, nanosized catalyst in aqueous is prone to create a milky suspension and thus difficult to recover after reaction [1].

To solve these problems, extensive efforts have been devoted to fabricate supports with favorable features, which may meet shortfalls, although sometimes supported titania possesses low elimination efficiency [6]. SBA-15, a new type of ordered hexagonal-array mesoporous silica with two-dimensional $p6mm$ hexagonal structure, one-dimensional channels, thick walls, and high hydrothermal

*Corresponding author. Tel.: +86 21 55271722.
**Corresponding author. Tel.: +86 27 67842752.
***Corresponding author. Tel.: +86 535 2109157.
E-mail addresses: feichang@usst.edu.cn (F. Chang), yanghaijian@vip.sina.com (H.-J. Yang), xfhu@yic.ac.cn (X. Hu).
the framework of SBA-15 in supercritical CO2–ethanol prepared Ti-SBA-15 materials with Ti incorporated into many researches for developing green processes to prepare nanosized metal oxides, which are able to facilitate the transfer of metal solvation properties, high thermal stability and create new acid cites, but also extend the specific surface area to a certain extent. These traits enable Al-SBA-15 as a suitable catalyst and support.

Sc-CO2 with unique properties such as low viscosity, high diffusivity, near zero surface tension, ease of complete separation from the reaction products by simply controlling the temperature or pressure, etc., has been the focus of many researches for developing green processes to prepare nanostructured materials. Good solvation properties of Sc-CO2 are able to facilitate the transfer of metal precursors into SBA-15 channels to generate nanoparticles without blockage of mesopores. In addition, the solvents and impurities are easily removed after reaction, ensuring formation of pure materials. Liu et al. have prepared Ti-SBA-15 materials with Ti incorporated into the framework of SBA-15 in supercritical CO2–ethanol solution through a post-synthesis. Han et al. have produced monolayer and double-layer of titanium dioxide grafted SBA-15 using a surface sol–gel process in Sc-CO2. The obtained materials with large surface specific surface area, ordered channels, and confined titania nanoparticles, are beneficial to facilitate the photocatalytic processes. However, the preparation of titania nanoparticles over mesoporous Al-SBA-15 using Sc-CO2 technique has not been reported yet, as far as we know.

In this investigation, fabrication of titania nanoparticles on mesoporous aluminosilicate Al-SBA-15 was first investigated by transfer and deposition of the titanium precursor with the assistance of Sc-CO2. The resultant TiO2/Al-SBA-15 samples were characterized with a collection of techniques. Similar Al-SBA-15 structure after loading titania was retained. These as-synthesized samples were used to decolorize methylene blue, a cationic thiazine dye, with higher photodegradable efficiency could be found for TiO2/Al-SBA-15 than that for TiO2/SBA-15 and commercial TiO2 under the same condition, as a result of the effective adsorption capability, resulting from the extension of specific surface area after substitution of Si species with Al species.

2. Materials and methods

2.1. Reagents

Ammonium chloride (NH4Cl) and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (pluronic P123, EO20PO70EO20, Mw ≈ 5800) were purchased from Sigma-Aldrich Chemicals. Commercial TiO2 was bought from Acros Organics. Other reagents such as aluminum tri-sec-butoxide (Al(O-sec-Bu)3), tetrabutyl orthotitanate (TBOT), tetraethyl orthosilicate (TEOS), hydrochloric acid (HCl), and methylene blue (MB) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used without purification and all aqueous solutions were prepared with deionized water.

2.2. Preparation of Aluminosilicate Al-SBA-15

The mesoporous aluminosilicate Al-SBA-15 was prepared according to the reference with a small modification: TEOS (9 mL) and Al(O-sec-Bu)3 (molar ratio of Si/Al=20, 0.5 g) in an HCl aqueous solution (pH=1.5, 10 mL) was stirred at 313 K over 3 h before adding to another HCl aqueous solution (pH=1.5, 150 mL) containing P123 (4 g). The resultant mixture was further stirred at 313 K for 24 h, and then transferred into a Teflon-lined stainless steel autoclave and aged at 373 K for 48 h. After cooling down to room temperature, the product was filtered, repeatedly washed with NH4Cl aqueous solution and distilled water, and dried overnight at 373 K in air. The target sample was finally obtained by calcination in air at heating rate of 2 K/min up to 823 K and maintaining at this temperature for 4 h to remove the copolymer template. As a reference, SBA-15 was also synthesized through the same procedure in the absence of aluminum source.

2.3. Preparation of TiO2/Al-SBA-15 in Sc-CO2

In the experimental, TBOT (0.2 mL) and Al-SBA-15 (0.4 g) were loaded on the bottom of the high-pressure stainless steel vessel (400 mL) and the small cage hanged underneath the lid, respectively. The small cage was covered with 100-mesh screen to ensure the transport and permeability of only molecular TBOT. The schematic diagram of experimental setup is shown in Fig. 1. After heating to a certain temperature, liquid CO2 was pressed into the vessel by a syringe pump up to 20 MPa. The vessel was maintained at these conditions for an assigned time. Subsequently, the resultant solid was centrifuged, filtered, washed three times with ethanol, and dried at 373 K for

Fig. 1. Schematic diagram of the apparatus.
The solid was calcined at 823 K for 5 h. By varying the reaction time and temperature, TiO$_2$/Al-SBA-15 ($n, m$) was produced, where $n$ represents the reaction time (h) and $m$ represents the reaction temperature (K).

The titania loading on mesoporous aluminosilicate Al-SBA-15 and silicate SBA-15 was measured using the ammonium sulfate–sulfuric acid digestion method [24].

2.4. Characterization

The crystalline phase of samples were analyzed by powder X-ray diffraction on a Bruker AXS D8 Advance X-ray diffractometer with a Cu K$_\alpha$ radiation source, at a speed of 2°/min within the range from 10° to 80° in 2θ. Nitrogen adsorption and desorption isotherms at 77 K were performed using an ASAP 2010 volumetric adsorption analyzer after samples had been degassed at 473 K for 2 h. The pore size distribution data were calculated by the BJH model from N$_2$ desorption isotherms. The solid-state NMR experiment was carried out at $B_0=9.4$ T on a Bruker AVANCE III 400 WB spectrometer. The corresponding resonance frequency of $^{27}$Al was 104.3 MHz. The sample morphology was examined by means of transmission electron microscopy (TEM, JEM-2100F) at an accelerating voltage of 200 kV. The UV–vis absorption spectra of the products were carried out on a Purkinje General T6 spectrophotometer (China). The UV–vis diffuse reflectance spectra were recorded on Hitachi U4100 UV–vis spectrophotometer using barium sulfate as standard.

2.5. Photocatalytic decolorization test

MB powder was dissolved in distilled water to make a stock solution of 20 mg/L. The pH value of MB solution was unregulated unless otherwise stated. Photocatalytic activity of samples was evaluated by batch experiments, using a LIMX-VII apparatus manufactured by Bylabo Precision Instrument Co. Ltd. (Xi’an, China). Under vigorously stirring, the mixture of 0.015 g catalyst and 30 mL MB solution was set in the dark for 30 min to guarantee the adsorption–desorption equilibrium between MB solution and photocatalyst before exposing to 500 W high-pressure mercury lamp with a wavelength of 365 nm, at an intensity of 156 mW/cm$^2$. The photocatalytic decolorization efficiency was checked through measurements of absorbance band of MB at 664 nm after a fixed irradiation time. The absorbance measurement of reaction solutions was performed after separating catalyst from reaction suspensions by centrifugation for 15 min (12,000 r min$^{-1}$).

3. Results and discussion

3.1. $^{27}$Al MAS NMR

Fig. 2 depicts the $^{27}$Al MAS NMR spectrum of the Al-SBA-15 sample. It exhibits two obvious signals at ca. $\delta=0$ ppm from octahedral AlO$_6$ groups corresponding to extra-framework aluminum species and ca. $\delta=52.9$ ppm from tetrahedral aluminum species of AlO$_4$ units [25], respectively. The presence of last signal demonstrates that most aluminum ions have been effectively incorporated into the virgin SBA-15 framework, as we expected.

3.2. XRD patterns

Fig. 3 represents the wide angle X-ray powder diffraction patterns of synthesized TiO$_2$/Al-SBA-15 samples. Pure Al-SBA-15 exhibits a single broad peak, characteristic of amorphous silica [26]. Samples TiO$_2$–Al-SBA-15 (2, 313), TiO$_2$–Al-SBA-15 (4, 313), TiO$_2$–Al-SBA-15 (8, 313), and TiO$_2$–Al-SBA-15 (4, 323) shows evident peaks centered at 25.3° (101), 37.8° (004), assigning to characteristic diffraction of anatase TiO$_2$ phase [27], which are not observed in other samples. In addition, the intensity of anatase peak at 25.3° gradually decreases with increase of the reaction time and temperature, which tallies well with the variation of titania loading in Table 1, indicating that short reaction time and low temperature are beneficial to enhance the titania content over Al-SBA-15. The titania crystalline size is calculated to be nearly 10 nm, a little larger than the average pore size of about 6 nm in Table 1. As a result, we...
concluded that anatase phase with big crystallite size was formed on the external surface and small crystallite sized or amorphous anatase phase was distributed inside the channels, leading to the shrinkage of pore size as in Table 1.

### 3.3. Nitrogen adsorption

Fig. 4 displays the N$_2$ adsorption–desorption isotherms of Al-SBA-15 and various TiO$_2$/Al-SBA-15 catalysts synthesized at different times and temperatures by supercritical CO$_2$: (a) Al-SBA-15, (b) 2 h, 313 K, (c) 4 h, 313 K, (d) 8 h, 313 K, (e) 4 h, 323 K, (f) 4 h, 333 K, and (g) 4 h, 343 K.

Table 1 shows the textural properties of sample Al-SBA-15, TiO$_2$/SBA-15, and TiO$_2$/Al-SBA-15. $A_{BET}$ value of TiO$_2$/SBA-15 is smaller than those of TiO$_2$/Al-SBA-15 samples, as a result of the substitution of Si$^{4+}$ species with Al$^{3+}$ ions, which is in line with the Ref. [14]. The specific surface area of TiO$_2$/Al-SBA-15 gradually decreases compared to that of Al-SBA-15, indicating the planting small crystallite anatase or amorphous semiconductor within the ordered channels of the support [30]. A slight increase of the pore volume with the increase of the synthesized time and temperature, which is well consistent with the relatively low content of titania loading over the mesoporous samples. However, the variation of pore diameter from different samples is somewhat out of accord with the titania content, possibly attributing to the coexistence of big crystallite sized anatase outside the channels and small crystallite sized or amorphous anatase inside the channels, as stated above. From the Table 1, the content of titania loading on Al-SBA-15 decreased with the extension of reaction time, which might be owning to the fact that prolonging the reaction time was beneficial to export instead of import of titanium precursor by Sc-CO$_2$. Meanwhile, temperature was another effect on the content of TiO$_2$ loading. In our experimental, raising temperature upto 323 K could enhance the TiO$_2$ content, but further raising temperature could contrarily reduce the TiO$_2$ content, possibly owning to the comprehensive effect of low dissolving capability and high mass transfer of Sc-CO$_2$ under a high temperature.

### 3.4. UV–vis diffuse reflectance spectra

The UV–vis diffuse reflectance spectra of various different samples TiO$_2$/SBA-15 and TiO$_2$/Al-SBA-15 are shown in Fig. 6. Some samples containing small crystallite sized or amorphous anatase titania inside the channels like TiO$_2$/SBA-15(4, 323) and TiO$_2$/Al-SBA-15(2, 313) exhibit an absorption edge of less than 375 nm, indicating blue shifts from the absorption edge of bulk anatase titania by well known quantum size effect for semiconductors along with the decrease of particles size [31,32]. Other samples show an absorption edge of over 375 nm, attributing to the existence of big crystallite sized anatase outside the channels in these samples. These are in accordance with the results of XRD patterns and TEM measurements in the following section. The corresponding band gap
energies were calculated according to the relation $E_g = \frac{1240}{\lambda}$ onset and were listed in the Table 1.

3.5. TEM

Fig. 7 shows the microstructures of sample TiO$_2$/Al-SBA-15 synthesized at the temperature of 323 K and the time of 4 h. It is apparently discerned the presence of small titania nanoparticles inside the stripe patterns of Al-SBA-15 structure as black spots and large titania nanoparticles on the external surface of Al-SBA-15 as bulk forms. The micrographs of sample TiO$_2$/Al-SBA-15 show well-ordered hexagonal arrays of mesopores, indicative of a 2D hexagonal mesostructure without destruction even after titania loading. The pore diameter estimated from the micrograph is around 6 nm, which is in a good accordance with the N$_2$ adsorption measurement.

3.6. Photocatalytic decolorization of MB

Fig. 8 shows the photocatalytic decolorization capability of synthesized samples over cationic dye MB. It is obvious that all samples display satisfactory removal efficiency. After 80 min, all samples could accomplish the complete decolorization of MB under the same experimental condition. The samples TiO$_2$/Al-SBA-15(4, 323) with 21.7% titania content and TiO$_2$/Al-SBA-15(8, 313) with 3.3% titania content show the highest and lowest removal efficiency upon MB, respectively. As a result, the photo-degradable capability of samples was partially associated with the TiO$_2$ content on Al-SBA-15, that is to say, with the variation of number of active cites.

Fig. 9 shows the comparative study of the photocatalytic decolorization capability of TiO$_2$/Al-SBA-15(4, 323), TiO$_2$/SBA-15(4, 323), and commercial TiO$_2$ on MB. It is apparent that both adsorption and degradable capability of TiO$_2$/Al-SBA-15(4, 323) are much higher than TiO$_2$/SBA-15(4, 323) and commercial TiO$_2$ as well. It can be explained by the following reasons. Much large specific surface area of TiO$_2$/Al-SBA-15 samples show strong adsorption capability not only on the dye molecules, but also on the significant amounts of water and hydroxyl groups around the active sites, thus enhance degradable efficiency [33]. We have tried a comparative study of MB adsorption on both Al-SBA-15 and SBA-15 and found that much higher adsorption capability on MB was observed using Al-SBA-15 as a sorbent. In this sense, even lower titania content on Al-SBA-15 still shows higher photocatalytic degradability comparing to sample TiO$_2$/SBA-15. Meanwhile, mesopores in the framework of TiO$_2$/Al-SBA-15 facilitates the import of dye molecules and export of degraded species and therefore facilitate the
photodecolorization process [22]. In addition, titania nanoparticles dispersed over the mesoporous materials own a high specific surface area and are thus beneficial to the photodecolorization as well [34]. As a result, presence of regular mesopores, confined titania nanoparticles, and large specific surface area together contributed to the enhanced photocatalytic degradability of TiO$_2$/Al-SBA-15 in comparison with TiO$_2$/SBA-15 and commercial TiO$_2$. Coupling with the simple preparation using a green technique and excellent photocatalytic degradability, TiO$_2$/Al-SBA-15 may have potential employments in the field of environmental protection and remediation in the future.

4. Conclusions

The preparation of titania nanoparticles on mesoporous aluminosilicate Al-SBA-15 in Sc-CO$_2$ was first reported in this present study and the resultant samples were characterized by a combination of various techniques. The aluminum species incorporated samples maintained a structure similar to that of the original SBA-15. The content of titania loading on Al-SBA-15 changed along with the reaction temperature and time in Sc-CO$_2$. From the analysis, large crystalline sized titania nanoparticles were formed on the external surface and small crystalline sized titania nanoparticles or amorphous titania were incorporated into the mesopores. The as-prepared samples were evaluated with regard to photocatalytic decolorization of MB in aqueous solutions. All TiO$_2$/Al-SBA-15 samples showed satisfactory decolorization efficiency, which was much better than TiO$_2$/SBA-15 and commercial TiO$_2$ under the same condition. The phenomenon may possibly own to the presence of regular mesopores, confined titania nanoparticles, and large specific surface area.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (Grant no’s 21207089, 51073175, 41076040, and 20807036), the Innovation Program of Shanghai Municipal Education Commission (Grant number 11YZ113), the Special Research Fund in Shanghai Colleges and Universities to Select and Train Outstanding Young Teachers (Grant number slg10014), and the project-sponsored by SRF for ROCS, SEM for financial support.

References


