

Preparation of mesostructured barium sulfate and its application in methane activation

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Abstract

Barium sulfate with lamellar and tubular microstructure was developed through a surfactant templating route under different synthesis conditions. Lamellar barium sulfate was synthesized through direct combination of Ba^{2+} and SO_4^{2-} in an aqueous solution containing sodium dodecyl benzene sulfonate (SDBS). Agglomerate barium sulfate nanotubes were obtained by the reaction of Ba^{2+} and CaSO_4 in the SDBS aqueous solution. Preparation of regular single barium sulfate nanotubes was achieved by the controlled hydrolysis of dimethyl sulfate in an aqueous solution containing Ba^{2+} and SDBS. As revealed by transmission electron microscopy characterization, the tube wall thickness was 7–8 nm, and the inner diameter was about 6 nm. When such mesostructured barium sulfate was loaded with VOSO_4 and sulfuric acid (100%), it performed excellently in catalyzing oxidative conversion of methane to methanol using molecular oxygen. The conversion proceeded at a relatively lower temperature (under 250 °C) than over general solid catalysts, and the selectivity to methanol remained high when methane conversion increased to an acceptable level. When the reaction proceeded stably, the one-pass conversion of methane was about 30%, and the selectivity to methanol could reach 50%.

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Keywords: Barium sulfate; Surfactant templating; Lamellar; Nanotube; Methane oxidation; Methanol

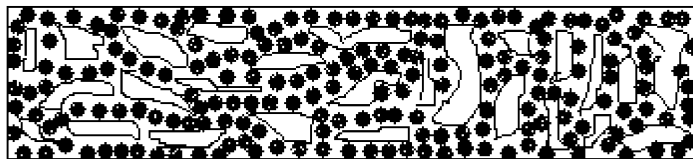
1. Introduction

The development of mesostructured inorganic materials has been widely considered one of the most promising areas in recent years. These materials have expected applications in many fields, including catalysis, coatings, membranes, and electronics. A vast body of knowledge of synthesis and physical and chemical properties has been accumulated and thoroughly reviewed [1–3]. Mesostructure build-up of a wide variety of inorganic materials, including metal sulfides, nitrides, oxides, phosphates, and polyoxometalates, has been attempted [4–10]. Generally, the self-assembly mechanism of structure-directing agents is used for the evolution of mesophases. The properties of structure-directing agents may have a significant effect on the alignment and patterning of the resultant mesophases. Surfactants are the most commonly used structure-directing agents.

Rapid progress in the synthesis of mesostructured materials has demonstrated the possibility of preparing mesostructured sulfates through the surfactant-templating route [11–13]. Such inorganics have two impressive properties that could stimulate extensive exploration of their mesostructure building and related application in catalysis [14]: they are thermally stable and chemically inert in many extreme conditions, and have attractive potential in the organization of mesostructures and the possibility of combining properties of different components in a unique composite material. To the best of our knowledge, there have been no detailed reports on the synthesis of mesostructured sulfates and related applications in catalysis.

In a recent communication [15], we reported the excellent performance of barium sulfate nanotube arrays in supporting sulfates for low-temperature methane activation. In the present work, we present detailed information on the preparation of three types of mesostructured barium sulfate (lamellar, agglomerate nanotube, and single nanotube) under various preparation conditions.

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Scheme 1. Schematic illustration of the catalyst particles diluted by fine inert glass beads (100 mesh).

2. Experimental

2.1. Synthesis of mesostructured barium sulfate

The surfactant-templating synthesis was used to develop such mesostructured materials. Anionic surfactant (SDBS) was the organic structure-directing agent. Barium sulfate was generated by three different methods: (1) direct combination of Ba^{2+} and SO_4^{2-} in aqueous solution, (2) reaction between CaSO_4 and Ba^{2+} in aqueous solution, and (3) controlled hydrolysis of dimethyl sulfate in the presence of Ba^{2+} in aqueous solution.

Lamellar barium sulfate was synthesized through direct combination of Ba^{2+} and SO_4^{2-} in aqueous solution containing SDBS. The SDBS (0.025 mol) was dissolved in 150 mL of deionized water in a 500-mL, three-necked, round-bottomed flask containing a magnetic stirring bar and fitted with an additional funnel and condenser. BaCl_2 (0.036 mol) dissolved in 50 mL of water was added to the solution dropwise under vigorous stirring. The solution became hazy. After 30 min of stirring, the solution was heated to reflux, then 50 mL of 0.7 M Na_2SO_4 aqueous solution was added dropwise over 90 min under vigorous stirring. After every several drops, the addition was momentarily stopped, to allow the block precipitate to homogenize. After all of the Na_2SO_4 was added, the reaction mixture was kept at reflux for 24 h, cooled to room temperature, and stored for several days. The solution was filtered to collect the solid material. The surfactant molecules in the resulting material were twice extracted by a 50-mL mixture of ethanol and diethyl ether (V/V = 2:1) and a 50-mL mixture of concentrated HCl and ethanol (V/V = 1/5). Finally, hot acetone was used to extract the fresh sample for 3 h or longer, to remove the remaining surfactant molecules.

Agglomerate barium sulfate nanotubes were synthesized by the reaction between Ba^{2+} and CaSO_4 in aqueous solution. Then 0.03 mol anhydrous CaSO_4 , 125 mL of aqueous solution containing SDBS (0.025 mol), and BaCl_2 (0.04 mol) were sealed in a 250-mL stainless steel autoclave and heated to 135 °C. The reaction continued for 8 h. The resulting mixture was cooled to room temperature and stored for several days. The solid materials were collected by filtration, and the surfactant molecules were removed as in the preceding method.

Single barium sulfate nanotubes were synthesized by controlled hydrolysis of dimethyl sulfate in aqueous solution containing Ba^{2+} and SDBS. The 0.025 mol SDBS was dissolved in 100 mL of deionized water and placed into a 500-mL three-necked, round-bottomed flask. Then 50 mL of 0.7 M Ba^{2+} aqueous solution was added dropwise. When the solution became hazy, 7 mL of pure dimethyl sulfate was added; the reaction mixture was kept at 80–85 °C under vigorous stirring for

36 h, then cooled to room temperature and stored for several days. The solid material was collected and purified as in the foregoing methods.

2.2. Preparation of the catalyst for methane oxidation and catalytic activity measurement

Well-developed BaSO_4 nanotubes were used to support VOSO_4 and concentrated sulfuric acid for oxidation of methane to methanol. VOSO_4 was introduced by impregnating the fresh nanotubes in VOSO_4 aqueous solution, followed by drying in vacuum at room temperature. Before the catalyst test, the fresh sample was doped with concentrated sulfuric acid (100–103%), which was prepared by bubbling SO_3 into 98% H_2SO_4 . In this case, the solubility of sulfate in concentrated sulfuric acid could be neglected because the amount of sulfuric acid used was just sufficient to dope the solid catalyst. Methane oxidation was conducted in a conventional fixed-bed reactor. The acidified sample was mixed with glass beads (100 mesh) of the same volume and packed in a conventional fixed bed reactor (Ti alloy, Φ 0.8 cm \times 30 cm). The catalyst particles were diluted by fine inert glass beads, as shown schematically in Scheme 1. The dead volume was filled with glass wool. Argon was used as a carrier gas. Argon, oxygen, and methane flows were controlled by mass flow control. The reactor column was heated in an electronic tube furnace with three independent heating units (1 cm \times 10 cm) controlled by temperature-program controllers (sensitivity ± 0.5 °C). The product analysis was performed on a DB5 column (30 m \times 0.25 mm) using a VG Trio200 with a thermal conductivity detector (TCD) or mass spectrometry (MS) detector. He was used as the carrier gas. The column temperature increased from 60 to 300 °C at a rate of 10 °C/min and maintained at 60 °C for 2 min. The working temperature of the TCD was 180 °C, and the ion source temperature of the MS detector was 200 °C. Conversion and selectivity are defined as

$$\% \text{conversion} \equiv \frac{[\text{CH}_4]_{\text{inlet}} - [\text{CH}_4]_{\text{outlet}}}{[\text{CH}_4]_{\text{inlet}}} \times 100$$

and

$$\% \text{selectivity to methanol} \equiv \frac{[\text{CH}_3\text{OH}]}{[\text{CH}_4]_{\text{inlet}} - [\text{CH}_4]_{\text{outlet}}} \times 100.$$

2.3. Characterization of the as-synthesized materials

X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic ratio of V(IV) to Ba^{2+} . The XPS measurement was carried on an ESCALab200I-XL (VG Science) spectrometer using Al-K_{α} X-radiation at 15 kV \times 20 mA, equipped with a hemispherical electron analyzer. All XPS peak

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