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Ordered bimodal mesoporous boria–alumina composite: One-step synthesis, structural characterization, active catalysis for methanol dehydration

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ABSTRACT

Ordered bimodal mesoporous boria–alumina composite (OBMBAC) with high specific surface area and pore volume has been prepared through an evaporation-induced self-assembly (EISA) process using non-ionic block copolymer as a template without addition of any mineral acids such as HCl or H_2SO_4. Nitrogen adsorption test, low-angle X-ray diffraction (XRD) and high resolution TEM evidenced a novel bimodal mesoporous structure of the composite. The wide-angle XRD pattern showed that the composite was typical of poorly crystallized material. Solid MAS NMR and FT-IR analysis confirmed the chemical bonding of B—O—Al bonds in the composite. NH_3-TPD (Temperature programmed desorption) test showed that the composite possessed complex acid sites. And strong Lewis and Brønsted acid sites can be detected. In the reaction of methanol dehydration to dimethyl ether (DME), the composite demonstrated high catalytic activity in conversion of methanol (85%) and good selectivity (100%) of DME. These characteristics of the ordered bimodal mesoporous boria–alumina composite are desirable for future applications related to effective utilization of DME as "green energy source" or aerosol propellant.

1. Introduction

Ordered mesoporous silica materials have received enormous attention owing to their high surface areas, regular frameworks, and large pore sizes with narrow distribution [1], all of which lead to their multiple potential applications, including catalysis, chemical and biological separation, drug delivery, and electromagnetic wave shielding/absorption [2]. Various metal (Sn, Ti, Fe, Cu, Zr, Al, rare earth, etc.) [3–6] and non-metal (N, P, S, etc.) [7–10] elements could be introduced into the framework of mesoporous silica materials to adjust the surface acid-base performance. Metal ions incorporated mesoporous silica materials demonstrated adjustable acidity, which could be applied in various acid-catalyzed reactions [3,11]. In contrast, non-metal ion, such as nitrogen, incorporated mesoporous materials possessed medium–strong base performance, which have been applied as the base catalysts [7,12].

Unlike pure ordered mesoporous silica materials, non-siliceous oxide materials themselves have the acidity [13,14]. Thus they could be directly used as acidic catalysts. Especially, alumina-based mesoporous materials are especially important in catalysts or catalyst supports [15]. Among alumina-based materials, boria–alumina mixed oxides have been found playing vital roles in catalyzing various reactions, where the mixed oxides can be used not only as the direct active phase but also as the support for active phases (typically metals). When the boria–alumina mixed oxides are used as active phase, they can catalyze reactions such as the Beckmann rearrangement of cyclohexanone [16], the condensation of alcohols [17], and the partial oxidation of alkanes such as ethane [18]. Furthermore, boria–alumina supported Re species has been used for metathesis reactions [19], supported Pt species has been used for cyclohexene hydrogenation [20], and supported Ru species has been used for CO hydrogenation [21]. However, little research was conducted on the preparation of ordered mesoporous boria–alumina materials. Generating ordered mesopores in catalysts could be highly advantageous to the complement of catalysts [14].

Our group has been focusing on the synthesis of various ordered mesoporous materials [9,22], containing light elements such as B or N, as basic or acid catalysts and recently developed an environmentally friendly process for synthesizing metal ion-incorporated ordered mesoporous silica materials through an evaporation-induced self-assembly (EISA) route in the self-generated acidic conditions [6]. In our research, Sn or Al-doped SBA-15 mesoporous materials with good mesostructural ordering, high surface area and narrow pore-size distribution were successfully fabricated via the same self-assembly process in which no mineral acids were added and no hydrothermal treatment was needed. Other researches also prepared Zr or Sn incorporated mesoporous silica

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materials without adding any mineral acids, but an additional hydrothermal treatment for 24–48 h was necessary [5,11]. In continuation of our work on the development of new mesoporous inorganic materials, we herein reported the facile synthesis of ordered mesoporous non-siliceous oxide complex material, taking boria–alumina composite as an example, using a similar strategy under the self-generated acidic condition [6]. The chloride precursor ($AlCl_3$) used can partly hydrolyze to provide the proper acidity for the hydrolysis of aluminum isopropoxide and the self assembly between the alumina/boria species and triblock copolymer template. The as-synthesized boria–alumina composite demonstrated both high specific surface area and novel dual narrow mesopore size distributions (3.87 and 8.12 nm). The most important is that the as-prepared composite was found excellent high-temperature catalyst for the dehydration of methanol to form dimethyl ether (DME), with a conversion of 85%. That should draw much attention from researchers and industries as there is a growing demand to produce large amounts of DME to meet the globe requirements for clean diesel fuel and aerosol propellant.

2. Experimental

2.1. Sample preparation

Ordered bimodal mesoporous boria–alumina composite (OBMBAC) was prepared by a combination of surfactant templating, sol–gel method, and evaporation-induced self-assembly (EISA), in which non-ionic block copolymer $EO_{20}PO_{70}EO_{20}$ (P123, M_n = 5800, Aldrich) was used as a structure-directing agent (where EO is poly(ethylene oxide) and PO is poly(propylene oxide)); aluminum isopropoxide (AIP), anhydrous aluminum chloride and boric acid acted as inorganic precursors. Under present conditions, no additional mineral acid was added to the synthesis mixture, in which aluminum chloride was not only used as aluminum source but also hydrolyzed to provide acidity. As following, 0.612 g of AIP was added to a clear solution containing 20 g of ethanol and 1 g of P123 under vigorous stirring. When the solution became milky, 0.267 g of anhydrous aluminum chloride was added under stirring for 4 h, followed by the addition of boric acid (0.31 g) into the above solution. The final stoichiometric composition in mol ratio of the synthesis solution was 0.086 P123:1.5 AIP:1 $AlCl_3$:2.5 H_3BO_3:217 EtOH. After constant stirring for 1 day in a closed system at room temperature, the resulting uniform solution was poured into a Petri dish (the diameter: 20 cm) to undergo an EISA process at 40 °C for 72 h and then 80 °C for 48 h. The dried gel was calcined at 400 °C for 6 h to obtain the final product.

2.2. Characterization

Nitrogen adsorption–desorption isotherms were collected on a Micromeritics ASAP2010 surface area and pore size analyzer at liquid nitrogen temperature (−196 °C). Prior to the measurements, the samples were dehydrated at 100 °C and then outgassed at 200 °C in vacuum for 4 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). The pore volume (V_{BJH}) and mean pore size (D_{BJH}) were derived from the adsorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method.

^{11}B and ^{27}Al solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectra was collected at room temperature (25 °C) using a Bruker AVANCE 500 (11.7 T) spectrometer operating at 130.35 MHz for ^{27}Al and 160 MHz for ^{11}B. The chemical shifts (δ) are reported in ppm. ^{27}Al spectrum was recorded at a rotation frequency of 15 K Hz and the reference was taken for $Al(H_2O)_6^{3+}$. ^{11}B spectrum was recorded with a rotation frequency of 14.5 K Hz and the reference was taken for $BF_3{\cdot}OEt_2$.

Fourier-transform infrared (FTIR) spectroscopic investigation was carried out on a Bruker Vector 22 spectrometer using the KBr pellet.

High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL 2010CX TEM operated at 200 kV. Samples for analysis were prepared by spreading them on a holey carbon film supported on a copper grid.

X-ray powder diffraction (XRD) pattern collected on a Rigaku D/MAX-c β instrument using CuKα_1 (λ = 0.15406 nm) radiation at 40 kV and 60 mA.

The content of boron was determined by the titration as the mannitol–boric acid complex using standard NaOH solution as a titrant.

Acidic properties of OBMBAC were determined by temperature programmed desorption of ammonia (NH_3-TPD). NH_3-TPD was performed on 200 mg of the catalyst with nitrogen (40 mL/min) as the carrier gas and a thermoconductor as the detector. The fresh sample was treated at 120 °C in nitrogen stream for 1 h. NH_3 was adsorbed at 120 °C from a gaseous mixture of NH_3 and N_2 up to the saturation of the surface. After purging with pure nitrogen at 120 °C for 2 h, NH_3-TPD curve was obtained in the range 120–700 °C with a heating rate of 10 °C/min.

Vapor phase dehydration of methanol on all the samples was carried out at a steady state in a vertical fixed-bed reactor. Prior to each experiment, the samples were crushed and then sieved. For each experiment, 0.5 g of the catalyst (size 40–60 mesh) was loaded to the reactor. The catalysts were first activated in situ in nitrogen at 300 °C for 1 h. Nitrogen saturated by pure methanol (the flow rate of liquid methanol is 0.04 mL min^{-1}, whereas the nitrogen is 40 mL min^{-1}) was used as feed, and the weight hourly space velocity (WHSV, defined as the weight of feed per hour per unit weight of catalyst loaded in the reactor) was monitored to 4 h^{-1}. Analysis of the reaction products was carried out by on-line gas chromatography using a Varian gas chromatograph (CP-3800).

3. Results and discussion

Powder X-ray diffraction (XRD) was used to assess the structural ordering and crystallinity of OBMBAC synthesized via an EISA process with no addition of any mineral acids. As shown in Fig. 1a, two strong major peaks at 1.3° and 0.84°, corresponding to 10.26 and 6.79 nm of *d*-spacing respectively, are observed in the small angle RXD pattern, giving a hint that the as-synthesized OBMBAC has a 2D hexagonal structure with a space group *P6mm*, though the periodicity is not very high. However, the reciprocal ration of two spacings couldn't follow the relationship $1:3^{1/2}$. Based on the further analysis, they can be both indexed to (100) reflections belonging to two independent hexagonal mesoporous systems which are named **HM-1** (d_{100} = 10.26 nm) and **HM-2** (d_{100} = 6.79 nm), respectively. The lack of other well-resolved peaks could be ascribed to the extremely fast formation rate of mesostructure that caused non-uniform micelles [23]. Wide-angle XRD pattern in Fig. 1b demonstrates that the as-prepared OBMBAC is quite poorly crystallized material. Thus it is very difficult to interpret the pattern in detail. However, the broad peak centered at ~27° should be ascribed to the mixture of boria-containing oxides. The peaks at the range of 42°–48° were possibly derived from γ-alumina, which have shifted to the higher angles compared with the pure γ-alumina [24]. It implies that the boria–alumina mixed phase exists in the as-prepared OBMBAC, expressed in the appearance of the very broad peaks in Fig. 1b.

The N_2 adsorption–desorption isotherms confirm the presence of bimodal mesopores in OBMBAC. The isotherms (Fig. 2a) are a