



# Preparation and characterization of super-microporous alumina with crystalline structure



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## ABSTRACT

Super-microporous alumina (pore size between 1 and 2 nm) with polycrystalline walls and high surface area (more than 650 m<sup>2</sup>/g) was synthesized successfully via an evaporation induced self-assembly (EISA) pathway using readily available and inexpensive nonionic surfactant fatty alcohol polyoxyethylene ether (AEO-7) as the template. N<sub>2</sub> adsorption-desorption results showed that the obtained materials are super-microporous when removing the template at 400 °C, then if the calcination temperature increase from 600 °C to 1000 °C, a breakdown of the walls separating adjacent pores allows the transformation to mesopores (pore size > 2 nm). FTIR pyridine adsorption and NH<sub>3</sub>-TPD measurement suggested the presence of strong Lewis acid sites. Transmission electron microscopy (TEM) measurements indicated that the alumina possesses the disordered “wormhole-like” super-microporous structure with polycrystalline walls. Loaded with copper, the catalyst exhibited outstanding activity in the selective catalytic reduction of NO with methane and could achieve a NO<sub>x</sub> conversion 100% when the reaction temperature is over 600 °C.

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## 1. Introduction

Alumina is popular for a variety of applications, because of its unique catalytic, adsorption, optical, and electronic properties; thus, the control of physicochemical properties of this material is the key topic of ongoing research [1–3]. Among them, alumina was widely employed as catalyst supports or catalysts and extensively studied owing to its acidic–basic surface and favorable textural properties. However, most traditional alumina with mesoporous or macroporous possess only textural porosity featured by low surface area and broad pore size distribution, which limits their practical applications. Therefore, preparation of the alumina with large surface areas, large pore volumes, narrow pore size distribution and suitable surface acidic–base properties for enhancing the catalytic performance has attracted wide research attention [4–9].

Porous materials displaying tailor-made pore sizes and shapes are particularly interesting in a great variety of real and potential applications where molecular recognition is needed, such as shape-selective catalysis, molecular sieving, and selective adsorption. Recently, the materials possessing regular pores in the super-

microporous range (1.0–2.0 nm) have also been paid special attention [10–12]. Furthermore in addition to being able to handle molecules that are too large to be processed by zeolites, super-microporous materials are expected to exhibit interesting shape and size selectivity in the conversion of such molecules. Shape and size selectivity is a desirable property that is generally lacking in mesoporous materials due to their larger pores.

Many methods, such as sol–gel [13–15], hydrothermal [3], precipitation [16], cation–anion double hydrolysis [17] and the microemulsion templating method [18], have been used to synthesize porous alumina. But there are few reports on super-microporous alumina with high surface area and narrow pore size distribution. Herein, we describe the synthesis of super-microporous alumina by using readily available fatty alcohol polyoxyethylene ether as the template via an evaporation-induced self-assembly (EISA) method. The as synthesized alumina materials possess wormhole-like pore array with the pore sizes in the range of 1–2 nm and crystalline frameworks, having acidic property and high thermal stability. The new materials will offer great potential applying for the shape-selective sensing, adsorption, and catalysis to overcome the limitation of traditional mesoporous molecular sieves and microporous zeolites. Loaded with copper, the

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catalyst exhibits satisfactory catalytic activity in the selective catalytic reduction of NO with methane (CH<sub>4</sub>).

## 2. Experimental and analytical methods

### 2.1. Chemicals and synthesis

Fatty alcohol polyoxyethylene ether AEO-7 (M<sub>av</sub> = 575–605, RO(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>H, n = 7) was purchased from BASF. Aluminum isopropoxide, nitric acid, and citric acid were purchased from Beijing Chemical Reagents. Copper (II) nitrate trihydrate was purchased from Acros Corp. All other chemicals were used as received.

In a typical synthesis, 1.5 g of AEO-7 was dissolved in 30 mL of ethanol at room temperature. Then 2.4 mL of 67 wt % nitric acid plus 0.75 g citric acid and 3.06 g (15 mmol) of aluminum isopropoxide were added into the above solution with vigorous stirring. The mixture was covered with PE film, stirred at room temperature for above 10 h, and then put into a 60 °C drying oven to undergo the solvent evaporation process. After 40 h of aging, the solution became a light-white solid. Calcination was carried out by slowly increasing the temperature from room temperature to 400 °C with 1 °C min<sup>-1</sup> ramping rate and kept at 400 °C for 5 h in flowing air. High-temperature treatment was carried out in air for 1 h with a temperature ramp of 5 °C min<sup>-1</sup>.

### 2.2. Catalyst preparation

Supported copper catalyst containing 5 wt% copper was prepared by impregnation method of as-synthesized super-microporous alumina and for comparison, commercial γ-Al<sub>2</sub>O<sub>3</sub> with an ethanol solution of Cu(NO<sub>3</sub>)<sub>2</sub> at room temperature for 12 h. Impregnated samples were dried in air at 120 °C for 24 h and then calcined at 400 °C for 5 h under air atmosphere. The catalytic reaction was performed in a quartz tube reactor with a mixture of NO, CH<sub>4</sub>, He (NO 2180 ppm, CH<sub>4</sub> 2050 ppm, He balance, GHSV = 7500 h<sup>-1</sup>) fed over the catalyst. A gas-chromatograph with a TCD detector was used to analyze the exit gases.

### 2.3. Analytical methods

The XRD patterns were recorded using a Rigaku Dmax X-ray diffractometer, which employed Ni-filtered CuKα radiation and was operated at 40 kV and 80 mA. N<sub>2</sub> adsorption at 77 K was performed on a Quantachrome analyzer to study the micro- and mesoporosity in the samples. The micropore size distribution was calculated using the Density Functional (DFT) method pore size model applied to the adsorption branch of the isotherm. The microporous structure was obtained from the t-plot analysis of the adsorption branch of the isotherm. Micropore volumes were obtained from the t-plot method in pressure range 0.2–0.5. The BET surface areas were obtained from the N<sub>2</sub> adsorption isotherm in the relative pressure range of 0.05–0.15. Total pore volumes were obtained at pressure 0.95. <sup>27</sup>Al MAS NMR spectra was recorded on a Varian Unity Inova spectrometer operating at 78.155 MHz (0.3 is a pulse width), an acquisition time of 0.02 s and a pulse delay of 1 s. SEM was taken on JSM-6700F FESEM (field emission scanning electron microscopy) and operated at 10 kV. The elemental composition was determined by energy-dispersive spectroscopy (EDS) coupled with the SEM. Thermo-gravimetric measurements were carried out on a STA 409C Thermo-Gravimetric Analysis (TGA), and the sample was heated up from room temperature to 800 °C at the rate of 10 °C/min under air atmosphere. TEM was taken on the Hitachi H-9000 NAR transmission electron microscope under a working voltage of 300 kV. The acidities of the samples were determined by the pyridine adsorption technique.

Pyridine FTIR spectra was recorded with Shimadzu FTIR 8400 spectrometer. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was carried out on a TP-5076 apparatus equipped with a thermal conductivity detector (TCD). XPS analyses were performed with a V.G. Scientific Escalab 250 using focused (diameter of the irradiated area was approximately 500 μm) monochromated Al Kα (hν = 1486.6 eV, 150 W).

## 3. Results and discussion

### 3.1. Textural and structural characterization

TG profiles recorded in air were first used to determine the thermal treatment temperature of the as-prepared material. Fig. 1 shows two principal phenomena: the first one, the weight loss was observed up to 150 °C, which is attributed to the loss of physically adsorbed species such as water. Whereas the second, more prominent thermal event located in the 200–400 °C temperature range, is due partly to the remaining water included in the pores and mostly from the decomposition and oxidation of the organic matter. Above 400 °C, although the sample does not have pronounced more weight loss step, the TG curve continues descending, which may be caused by the combustion of possible residual template and the gradual loss of the hydroxyl groups in the porous structure. It appears that starting from 400 °C, the chosen calcination temperature, all the surfactant has been eliminated; thus releasing the expected porosity.

XRD patterns of as-synthesized precursor and sample calcined at 400 °C are presented in Fig. S1 and Fig. 2, respectively. All Materials show one strong and relatively broad diffraction peak by small-angle X-ray diffraction (SAXRD). Wide-angle X-ray powder diffraction (WAXRD inset) indicates that no distinct diffraction lines can be observed in the samples and the walls of samples seem to be amorphous or microcrystallinity.

The nitrogen adsorption-desorption isotherms (Fig. 3) of the material treated at 400 °C performed typical type I characteristic. As shown in the inset of Fig. 3, the material displayed narrow pore size distribution around 1.7 nm, which was located in the size range (1–2 nm) of the micropore defined by IUPAC. The samples were named super-microporous alumina (denoted as SMA). SMA had a large BET specific surface area of 665 m<sup>2</sup>/g and pore volume of 0.26 cm<sup>3</sup>/g treated at 400 °C. The large specific surface area and narrow pore size distribution promised its potential application in the field of catalysis.

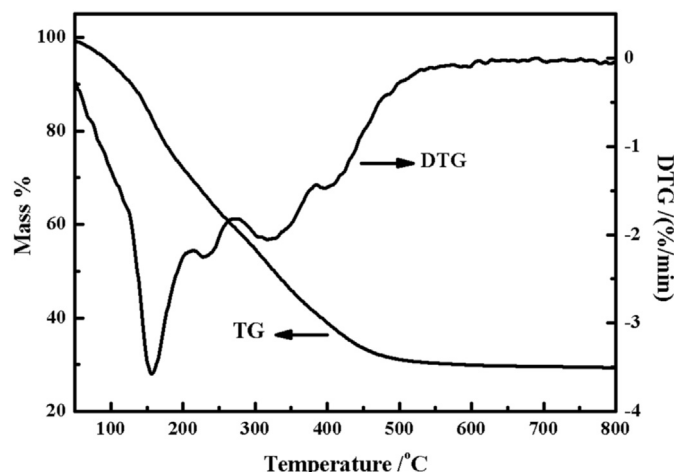


Fig. 1. TG-DTG curves for as synthesized precursor.

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