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 m²/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. N₂ 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 NH₃-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 NOx conversion 100% when the reaction temperature is over 600 °C.

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...
catalyst exhibits satisfactory catalytic activity in the selective cat-
alytic reduction of NO with methane (CH₄).

2. Experimental and analytical methods

2.1. Chemicals and synthesis

Fatty alcohol polyoxyethylene ether AEO-7 (Mav = 575–605, RO(CH₂O)₇O-H, n = 7) was purchased from BASF. Aluminum iso-
propoxide, 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 iso-
propoxide were added into the above solution with vigorous stir-
ing. The mixture was covered with PE film, stirred at room tem-
perature 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⁻¹ 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⁻¹.

2.2. Catalyst preparation

Supported copper catalyst containing 5 wt% copper was pre-
pared by impregnation method of as-synthesized super-micropo-
rous alumina and for comparison, commercial γ-Al₂O₃ with
an ethanol solution of Cu(NO₃)₂ 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 re-
action was performed in a quartz tube reactor with a mixture of NO,
H₂, He (NO 2180 ppm, CH₄ 2050 ppm, He balance, GHSV
5750 h⁻¹) feeding 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. N₂ adsorption at 77 K was performed
on a Quantachrome analyzer to study the micro- and meso-
porosity 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 ob-
tained from the t-plot method in pressure range 0.2–0.5. The BET
surface areas were obtained from the N₂ adsorption isotherm in the
relative pressure range of 0.05–0.15. Total pore volumes were ob-
tained at pressure 0.95. ²⁷Al MAS NMR spectra were recorded on a
Varian Unity Inova spectrometer operating at 78.155 MHz (0.3 is as
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 micro-
scope 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
(NH₃-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 tem-
perature 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 Ma-
terials 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 inlet 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
denoted super-microporous alumina (denoted as SMA). SMA had a
large BET specific surface area of 665 m²/g and pore volume of
0.26 cm³/g treated at 400 °C. The large specific surface area and
narrow pore size distribution promised its potential application in
the field of catalysis.
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