



Synthesis of mesoporous alumina with tunable structural properties



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ABSTRACT

Mesoporous aluminas (MAs) with tunable structural properties including BET surface area, pore volume and pore size were successfully synthesized. The synthesis method was based on a sol–gel process via hydrolysis of aluminium isopropoxide associated with non-ionic block copolymer P123 as the structure-directing template in an acidic aqueous system. The MAs were characterized using thermogravimetry – differential thermal analysis (TG–DTA) for decomposition and mass loss characteristics during calcination, X-ray diffraction (XRD) for bulk crystallinity, transmission electron microscopy (TEM) for nano-scale morphology, selected area electron diffraction (SAED) for local crystallinity and N₂ adsorption – desorption techniques for porous structural properties. By tailoring the amount of P123 and HNO₃ addition, inorganic aluminium precursor Al(NO₃)₃ doping ratio and calcination temperature, MAs with controllable structural properties were obtained, leading to regular variations in the surface area (up to 409 m²g^{−1}), pore volume (0.4 cm³g^{−1} ~ 2.8 cm³g^{−1}) and pore size (5.0 nm ~ 33.1 nm). Bovine serum albumin (BSA) was employed to evaluate the adsorption capability of the synthesized MAs. It was found that the structural properties of MA had a crucial effect on the BSA adsorption capability, increasing dramatically with increasing surface area, pore volume and pore size. For the sample MA4P15AlN (surface area 287 m²g^{−1}, pore volume 2.8 cm³g^{−1} and pore size around 33.1 nm), the BSA adsorption amount reached 182.7 mgg^{−1} in 2 h, higher than other MA samples as well as a silicon based reference sorbent material, SBA-15 (133.3 mgg^{−1}).

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1. Introduction

Mesoporous alumina (MAs) have gained a great deal of interest from industry and academia for their potential in a wide range of applications, such as catalysis, adsorption and separation, and sensing [1,2]. This is attributed to their mesoporosity features such as tunable pore size, high surface area and large pore volume, which make MAs ideal for adsorption and catalysis applications [2]. MA is commonly synthesized using one of the following three methods: (1) a nanocasting method with carbon moulds as hard templates [3]; (2) solvent-deficient synthesis without structure-directing agents (SDA) [4]; and (3) sol–gel self-assembly process in the presence of a soft template such as a cationic, anionic, or nonionic surfactant as SDA [1,2,5,6]. Compared to the former two, the third pathway has attracted great attention due to its easily accessible and reproducible characteristics in fabricating MA through a solvent evaporation induced self-assembly (EISA)

process with a soft template under acidic conditions [7]. It is capable of bypassing the complex and time-consuming process of the first pathway and can also realize continuous modulation of pore size, better than the second, hard template method. In the third pathway, EISA can competently substitute the process of cooperative assembly of organic aluminium precursors, such as aluminium alkoxides, and surfactant templates, typically aluminium isopropoxide and Pluronic® P123, respectively, employed to afford mesoporous materials [7]. Up to now, most of the EISA process was conducted in ethanol with P123 as the template [7–9]. In this process, the hydrolysis behaviour of aluminium is very complicated and easily affected by the synthesis conditions such as acid, water and crystallization temperature, leading to the need of rather strict control of the conditions and consequently differed structural properties of the obtained MAs. Understanding the effect of synthesis conditions on MA synthesis would enable us to fine-tune their mesoporosity features.

Recently, a major improvement has been made by using water as the synthesis medium. As a result, crystalline mesoporous γ -Al₂O₃ with high surface areas was achieved [10–12]. Upon the hydrolysis of the aluminium precursor in the presence of a

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surfactant, the formation of an intermediate boehmite/surfactant nano-composite was identified to have occurred. However, to the best of the authors' knowledge, systematic work on the modulation of structural properties of MA is scarce, limiting the further penetration of MAs in heterogeneous catalysis and adsorption applications. Though Alphonse and co-workers [11] have tried to modify the structural properties of MAs by the choice of the boehmite precursor, surfactant, surfactant/AIOOH ratio and hydrocarbons addition, it is still a significant challenge to interpret the complex synthesis process and also to synthesize γ -Al₂O₃ with larger pores and higher surface areas.

In the present contribution, the effect of the amount of template P123 and HNO₃ addition, aluminium precursor Al(NO₃)₃ doping ratio, and calcination temperature on the structural properties of MA was systematically investigated. MAs with BET surface areas up to 409 m²g⁻¹, pore volumes in the range of 0.4 cm³g⁻¹ ~ 2.8 cm³g⁻¹ and pore sizes ranging from 5.0 nm to 33.5 nm with uniform and relatively narrow pore size distributions (PSD) were successfully synthesized. The adsorption capacity of bovine serum albumin (BSA) of the as-synthesized MAs was evaluated in the present work. Note that BSA (with a Stokes radius r_s of 3.48 nm) is an extensively used standard protein in laboratory studies of large molecule adsorption characteristics of mesoporous materials. Greatly enhanced BSA adsorption capability was demonstrated over the synthesized MAs with large contact interface and easily accessible porous channels.

2. Experimental

2.1. Materials and MA synthesis

MA was synthesized in this work as follows. 2 mol of hot water (85 °C) was added to 20 mmol of aluminium (in the form of aluminium isopropoxide with or without Al(NO₃)₃·9H₂O, purchased from Sigma–Aldrich) under vigorous stirring in a flask. After 15 min, 0.097 mL nitric acid (HNO₃, 68%, Fluka) was added and the mixture was maintained at 85 °C for 12 h, during which the reaction flask was kept uncovered in the first 2 h to allow the evaporation of isopropanol formed during the hydrolysis. Template Pluronic® P123 (PEO–PPO–PEO triblock copolymer, M_w = 5800, Sigma–Aldrich) was added to the sol and the mixture was kept under gentle stirring for another 12 h period at room temperature. Then, a final MA sample was obtained by drying the sol in air in an electric oven operating at 70 °C for 12 h, followed by calcination at different temperatures in air for 4 h. In order to investigate the effect of P123 addition, HNO₃ addition, Al(NO₃)₃ doping ratio and calcination temperature on the structural properties of MA, different amounts of P123, HNO₃ and Al(NO₃)₃ were added and different calcination temperatures were systematically trialled. The synthesized MAs were nominally denoted in a general form of MA_xPyNzAlN-T, where x refers to “x” g of P123, y signifies “y” times of 0.097 mL HNO₃ added in synthesis, z denotes “z” mol% of Al(NO₃)₃ (if applicable) relative to the total 20 mmol of Al and T indicates the calcination temperature. Unless otherwise specified, the HNO₃ addition and temperature were 1N (0.097 mL HNO₃ per 20 mmol of Al) and 700 °C, respectively. For instance, MA1P15AlN means a MA sample synthesized with 1 g of P123, 15% molar fraction of Al(NO₃)₃ and then calcined at 700 °C. MA6P-500 presents a MA prepared using 6 g of P123 calcined at 500 °C without the doping of Al(NO₃)₃. The variations include: x = (0, 1, 2, 4, 6), y = (0, 1, 3, 5, 10), z = (0, 10, 15, 20) and T = (500 °C, 700 °C, 900 °C, 1100 °C). The synthesis recipes are summarized in Table 1. Note that the comprehensive modulating among the four factors over broad ranges is the key to the tuning of the structural properties of the synthesized MA.

Table 1
MA synthesis conditions.

Samples	P123 (g)	HNO ₃ (mL)	Aluminium source (mmol)	Calcination temperature (°C)
MA1P0N	1	0	Al(O-i-Pr) ₃ 20	700
MA1P	1	0.097	Al(O-i-Pr) ₃ 20	700
MA1P3N	1	0.291	Al(O-i-Pr) ₃ 20	700
MA1P5N	1	0.485	Al(O-i-Pr) ₃ 20	700
MA1P10N	1	0.970	Al(O-i-Pr) ₃ 20	700
MA0P	0	0.097	Al(O-i-Pr) ₃ 20	700
MA2P	2	0.097	Al(O-i-Pr) ₃ 20	700
MA4P	4	0.097	Al(O-i-Pr) ₃ 20	700
MA6P	6	0.097	Al(O-i-Pr) ₃ 20	700
MA1P10AlN	1	0.097	Al(O-i-Pr) ₃ 18 Al(NO ₃) ₃ ·9H ₂ O 2	700
MA1P15AlN	1	0.097	Al(O-i-Pr) ₃ 17 Al(NO ₃) ₃ ·9H ₂ O 3	700
MA1P20AlN	1	0.097	Al(O-i-Pr) ₃ 16 Al(NO ₃) ₃ ·9H ₂ O 4	700
MA6P-500	6	0.097	Al(O-i-Pr) ₃ 20	500
MA6P	6	0.097	Al(O-i-Pr) ₃ 20	700
MA6P-900	6	0.097	Al(O-i-Pr) ₃ 20	900
MA6P-1100	6	0.097	Al(O-i-Pr) ₃ 20	1100
MA4P15AlN	4	0.097	Al(O-i-Pr) ₃ 17 Al(NO ₃) ₃ ·9H ₂ O 3	700
MA6P15AlN	6	0.097	Al(O-i-Pr) ₃ 17 Al(NO ₃) ₃ ·9H ₂ O 3	700

For comparison, an SBA-15 sample was also prepared using a reported procedure [13], where P123 was also the surfactant template. In brief, P123 was dissolved in an HCl solution and stirred at 25 °C until the solution became clear, and addition of Tetraethylorthosilicate (TEOS, 98%, Aldrich) followed under moderate stirring. The molar composition of the gel was kept as P123: HCl: H₂O: TEOS = 1: 261: 11278: 60. The obtained gel was stirred at 25 °C for 24 h and then transferred into an autoclave at 100 °C for a further 48 h period. The white solid was collected by filtration, washed with distilled water, air-dried and then calcined at 550 °C for 4 h to remove the template.

2.2. MA characterization

Thermogravimetry – differential thermal analysis (TG-DTA) was performed on the synthesized MAs to obtain the decomposition mass loss characteristics during calcination using a thermogravimetric analyser (SDT Q600, TA Instrument), operating in air (50 mLmin⁻¹) with a heating rate of 5 °Cmin⁻¹ from 70 °C to 700 °C. Structural parameters including the BET surface area, pore volume V_p, average pore size D_a and pore size distribution (PSD) of the MAs were determined from the nitrogen sorption isotherms obtained using a Tristar 3020 volumetric analyser (Micromeritics Co. Ltd). The specific surface area was calculated from the adsorption data using the BET method in the relative pressure (p/p_0) range of 0.05–0.3. V_p shows the BJH desorption cumulative volume of pores between 17.0 Å and 3000.0 Å width. The pore size D_a denotes the average pore diameter determined from the BET while D_p is the pore diameter at the peak position of the PSD curve derived from the desorption branch of the isotherm using the BJH method. Wide angle x-ray diffraction (WAXD) from 10° to 80° was performed to obtain the crystalline structure of MA using an XRD (Empyrean, PANalytical, Cu-K α radiation at 40 kV, 40 mA). TEM imaging was acquired using a JEM-2100 JEOL electron microscope equipped with LaB6 filament and operating at 120 kV.

2.3. BSA adsorption

In a typical adsorption experiment, BSA was dissolved in sodium phosphate buffer (20 mM) at pH 4.9 (isoelectric point of BSA) to

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