A facile route to aqueous phase synthesis of mesoporous alumina with controllable 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 based on a sol—gel process via hydrolysis of aluminium isopropoxide associated with a structure-directing agent (SDA) as template in an acidic aqueous system. The effect of template type, template addition amount and inorganic aluminium precursor doping on the structural properties of the resulting MAs were systematically investigated. Four templates, including two non-ionic triblock copolymers P123 and F127, an amine based cationic quaternary surfactant cetyltrimethylammonium bromide (CTAB) and an anionic surfactant sodium dodecyl sulfate (SDS) were examined at varying amount. Three inorganic aluminium precursors, viz aluminium sulfate, aluminium nitrate and aluminium chloride, were used as the substitution aluminium sources to aluminium isopropoxide. The MAs synthesized were characterized using thermogravimetry — differential thermal analysis (TG—DTA) for decomposition and mass loss characteristics upon calcination, X-ray diffraction (XRD) for bulk crystallinity, transmission electron microscopy (TEM) for nano-scale morphology and N_2 physisorption techniques for porous structural properties. For a given SDA, increasing the amount of surfactant addition markedly improved the porosity of the MA synthesized. In terms of the ability to influence the structural properties of the resulting MAs such as BET surface area, pore volume and pore size, the SDAs tested followed a descending order of F127 > P123 > CTAB > SDS. MAs with the greatest pore volumes and pore sizes with narrow PSDs were obtained when the doping ratios of $Al(NO_3)_3$, $AlCl_3$ and $Al_2(SO_4)_3$ were 15%, 30% and 2%, respectively. Depending on the type and addition amount of SDA and the aluminium precursor composition, the BET surface area, pore volume and pore size of MAs could be adjusted in the ranges of 178 m^2 g^{-1} ~ 358 m^2 g^{-1}, 0.4 cm^3 g^{-1} ~ 1.9 cm^3 g^{-1} and 5.5 nm—30.1 nm, respectively.

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1. Introduction

Synthesis of mesoporous alumina (MAs) with controlled structural properties including BET surface area, pore volume and pore size has been the subject of intensive academic and industrial research driven by their wide applications in various fields such as catalysis, adsorption and separation, and sensing [1—3]. This is ascribed to their crystalline framework, intrinsic acidic—basic characteristics and controllable structural properties. The synthesis of MA with adjustable mesoporous structure has been a long-standing goal and many synthesis routes have been developed. Among them, the sol—gel process is regarded as one of the most

promising approach [4—6]. It involves complicated organic—inorganic assemblies using surfactants as structure-directing agents (SDAs) to form a hybrid organic—inorganic mesophase by simultaneous condensation of Al ions and self-assembly of surfactant molecules [3,7]. Upon the hydrolysis of alumina precursor in the presence of a surfactant, the formation of an intermediate boehmite/surfactant nanocomposite is expected to occur. This process has attracted a great deal of attention due to its easily accessible and reproducible characteristics in fabricating MA. Moreover, it allows the control of pore size and surface area by adjusting the synthesis variables [5].

Up to now, most of the sol—gel process has been conducted using the non-ionic triblock copolymer P123 as the template in ethanol [6,8,9]. The structural properties of the resulting MAs strongly depend on the properties of the intermediate boehmite/surfactant composites assembled by Al-containing species and SDA

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molecules [10]. P123 is an amphiphilic molecule which belongs to the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) PEO–PPO–PEO family. In this synthesis system, P123 molecules can self-assemble to form micelles consisting of a PPO core and a corona with hydrated PEO segments and then adsorb onto the Al nanoparticle surface to form the densely packed layers [10]. Although there have been numerous reports on the synthesis of MAs via the sol–gel process, the SDA employed has been largely limited to the non-ionic triblock copolymer P123, the use of new non-ionic SDAs as well as cationic and anionic SDAs has been rarely reported.

Recently, a major improvement has been made by using water as the synthesis medium and, consequently, crystalline mesoporous γ-Al$_2$O$_3$ with high surface areas has been achieved [3,4,7]. The sol–gel process conducted in the aqueous medium has the advantage of producing colloidal sols with varying viscosity and high stability, which would be of interest and potential for large-scale production [7].

In the authors' previous work using the sol–gel route in an aqueous system [11], the structural properties of MA were modulated through the manipulation of P123 and HNO$_3$ additions, inorganic aluminium precursor Al(NO$_3$)$_3$ doping ratio and calcination temperature. As a result, MAs with controllable structural properties were obtained [11]. To the best of our knowledge, it is the first time that the substantial enhancement of MA mesoporosity induced by the addition of metallic salts together with the change in triblock copolymer has been demonstrated. Understanding the effect of synthesis conditions on MA synthesis would enable the control of the mesoporosity features.

In the present contribution, an extended investigation into the effect of template and inorganic aluminium precursor is reported in detail. Besides, the widely studied non-ionic triblock copolymer P123, another template F127, belonging to the same PEO–PPO–PEO family, an amine based cationic quaternary surfactant cetyltrimethylammonium bromide CTAB, and an anionic surfactant sodium dodecyl sulfate SDS were studied at varying amount. In addition, three inorganic aluminium precursors including aluminium sulfate, aluminium nitrate and aluminium chloride were trialled with varying substitution fractions relative to the total aluminium.

2. Experimental

2.1. Materials and MA synthesis

MAs were synthesized using the previously reported recipe [11]. In brief, 2 mol of hot water (85 °C) was added to 20 mmol of aluminium (in the form of aluminium isopropoxide with or without the inorganic aluminium precursors) under vigorous stirring in a 100 mL flask (Schott Pty Ltd) for 15 min. Then, 0.097 mL HNO$_3$ (68%, Fluka) was added and the mixture was stirred and maintained at 85 °C for 12 h, during which the flask was kept uncovered in the first 2 h to allow the evaporation of isopropanol formed during the hydrolysis. A template was added to the sol and the mixture was kept under gentle stirring for another 12 h period at room temperature. Finally, an MA product was obtained by drying the sol in air in an electric oven operating at 70 °C for 12 h, followed by calcination at 700 °C in air for 4 h.

In order to investigate the effect of template type and addition amount on the structural properties of MA, four templates, including two non-ionic triblock copolymers P123 (EO$_{20}$PO$_{70}$EO$_{20}$, M$_{av}$ = 5800, Sigma–Aldrich) and F127 (EO$_{106}$PO$_{70}$EO$_{106}$, M$_{av}$ = 12,600, Sigma–Aldrich), a cationic cetyltrimethylammonium bromide (CTAB, Sigma–Aldrich) and an anionic sodium dodecyl sulfate (SDS, Sigma–Aldrich) were systematically trialled at varying

amount. Moreover, three inorganic aluminium precursors, including Al(NO$_3$)$_3$·9H$_2$O, Al$_2$(SO$_4$)$_3$·14H$_2$O and AlCl$_3$ were also imposed on the synthesis method to examine the effect of aluminium precursors and the different anions. For convenience in discussion in this manuscript, the MA samples synthesized in this work are nominally denoted in a general form of MAxAyAlB, where A (P, F, C, S) refers to the template types (P123, F127, CTAB, SDS) and B (N, S, Cl) refers to the doped inorganic aluminium precursors (Al(NO$_3$)$_3$, Al$_2$(SO$_4$)$_3$, AlCl$_3$), respectively. For P123, x refers to "x" g of P123 while for F127, CTAB and SDS, x denotes the equivalent moles of F127, CTAB and SDS per "x" g of P123. In addition, y signifies "y" mol% of inorganic aluminium precursor (if applicable) relative to the total 20 mmol of Al. For instance, MA0A indicates a MA sample synthesized without template. MA1P15AlN presents a MA sample prepared using 1 g of P123, 15% molar fraction (3 mmol) of Al(NO$_3$)$_3$ and then calcined at 700 °C. The detailed synthesis recipes and the resulting MA products are summarized in Table 1.

2.2. MA characterization

Structural parameters of MAs including the BET surface area, pore volume Vp, average pore size Da and pore size distribution (PSD) were determined from the nitrogen physisorption isotherms obtained using a Tristar 3020 volumetric analyser (Micromeritics Co. Ltd). The specific surface area was calculated from the adsorption branch using the BET method in the relative pressure (p/p_o) range of 0.05–0.3 [12]. Vp showed the total pore volume calculated from the adsorbed nitrogen amount at a relative pressure P/P$_0$ of 0.997 [13,14]. Da indicated the average pore diameter while Dp was

Table 1
MA labelling and corresponding synthesis conditions.

Samples	Template (g)	Aluminium source (mmol)
MA0A	0	Al(O-i-Pr)$_3$ 20
MA1P	P123 1.00	Al(O-i-Pr)$_3$ 20
MA2P	P123 2.00	Al(O-i-Pr)$_3$ 20
MA4P	P123 4.00	Al(O-i-Pr)$_3$ 20
MA1F	F127 2.17	Al(O-i-Pr)$_3$ 20
MA2F	F127 4.34	Al(O-i-Pr)$_3$ 20
MA4F	F127 8.68	Al(O-i-Pr)$_3$ 20
MA1C	CTAB 0.06	Al(O-i-Pr)$_3$ 20
MA2C	CTAB 0.12	Al(O-i-Pr)$_3$ 20
MA4C	CTAB 0.25	Al(O-i-Pr)$_3$ 20
MA10C	CTAB 0.62	Al(O-i-Pr)$_3$ 20
MA20C	CTAB 1.24	Al(O-i-Pr)$_3$ 20
MA1S	SDS 0.05	Al(O-i-Pr)$_3$ 20
MA2S	SDS 0.10	Al(O-i-Pr)$_3$ 20
MA4S	SDS 0.20	Al(O-i-Pr)$_3$ 20
MA10S	SDS 0.50	Al(O-i-Pr)$_3$ 20
MA20S	SDS 1.00	Al(O-i-Pr)$_3$ 20
MA1P10AlN	P123 1.00	Al(O-i-Pr)$_3$ 18 Al(NO$_3$)$_3$·9H$_2$O 2
MA1P15AlN	P123 1.00	Al(O-i-Pr)$_3$ 17 Al(NO$_3$)$_3$·9H$_2$O 3
MA1P20AlN	P123 1.00	Al(O-i-Pr)$_3$ 16 Al(NO$_3$)$_3$·9H$_2$O 4
MA1P1AlS	P123 1.00	Al(O-i-Pr)$_3$ 19.8 Al$_2$(SO$_4$)$_3$·14H$_2$O 0.1
MA1P2AlS	P123 1.00	Al(O-i-Pr)$_3$ 19.6 Al$_2$(SO$_4$)$_3$·14H$_2$O 0.2
MA1P3AlS	P123 1.00	Al(O-i-Pr)$_3$ 19.4 Al$_2$(SO$_4$)$_3$·14H$_2$O 0.3
MA1P10AlCl	P123 1.00	Al(O-i-Pr)$_3$ 18 AlCl$_3$ 2
MA1P20AlCl	P123 1.00	Al(O-i-Pr)$_3$ 16 AlCl$_3$ 4
MA1P30AlCl	P123 1.00	Al(O-i-Pr)$_3$ 14 AlCl$_3$ 6
MA1P35AlCl	P123 1.00	Al(O-i-Pr)$_3$ 13 AlCl$_3$ 7