



Featured Letter

Alpha-amino acid assisted synthesis of ordered mesoporous alumina with tunable structural properties



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ABSTRACT

By using an alpha-amino acid as an interfacial protector and pH adjustor, we demonstrate the synthesis of the long-range ordered mesoporous alumina (OMA) via a modified solvent evaporation induced self-assembly (EISA) method. Characterization results of XRD, TEM, and N₂ adsorption-desorption indicate that the long-range highly ordered OMA was successfully obtained by using aluminum *iso*-propoxide as a precursor and Pluronic P123 as a template via the alpha-amino acid assisted EISA process. Moreover, by simply changing the alpha-amino acid, the textural property of the OMA was easily regulated, the extent of which depends on the molecular structure and coordination ability of the alpha-amino acid. The facile formation of the long-range highly ordered OMA was explained based on the function of the alpha-amino acids.

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1. Introduction

The ordered mesoporous alumina (OMA), which characterizes in a high surface area, a large pore volume and tunable pore size, a narrow pore size distribution, and nano-size effects in its mesoporous channels and on its pore walls, has important applications for catalyst and/or catalyst support [1,2]. Thus, much work on the synthesis of OMA with well controlled structure has been done [3]. Comparing with other methods such as the nanocasting route by using silica or carbon as a hard template [3], the sol-gel derived solvent evaporation induced self-assembly (EISA) process is proved a more effective method for synthesizing highly ordered OMA [4]. In the typical EISA process, the assembly of Pluronic P123 as a soft template and aluminum *iso*-propoxide as an aluminum precursor is simply conducted in an acidic ethanol solution, leading to the well-developed OMA [4]. Previous studies indicate that the acid used to adjust the pH of the solution such as HNO₃ or HCl has a strong influence on the formation of OMA, and the OMA is limited to be short-range ordered structure in the case of HCl [4]. Recent results reveal that the simultaneous addition of HCl and an organic acid such as citric acid or tartaric acid is effective to enhance the formation of the long-range ordered OMA [4–8].

Based on our understandings on the EISA process and the buffering property of alpha-amino acids, in this work, we demonstrate the

synthesis of the long-range ordered OMA via a modified EISA process by using the alpha-amino acid as an interfacial protector and pH adjustor. Results indicate that highly long-range ordered OMA was obtained in the presence of an alpha-amino acid, and its textural property was easily tuned in a relatively larger extent by simply changing the alpha-amino acid.

2. Experimental

The detailed procedure for the synthesis and characterization of OMA was provided in the Supporting Information. The material was named according to the alpha-amino acid used, i.e., Al₂O₃-Gly, Al₂O₃-Ala, Al₂O₃-Ser, Al₂O₃-Asp, Al₂O₃-Cys, Al₂O₃-Thr, Al₂O₃-Met, Al₂O₃-Phe, Al₂O₃-Trp for glycine, L-alanine, L-serine, D-aspartic acid, L-cysteine, L-threonine, L-methionine, L-phenylalanine, and L-tryptophan, respectively. For comparison, one sample was synthesized by following the same procedure and parameters but without the addition of an alpha-amino acid, and was named as Al₂O₃-Blank.

3. Results and discussion

The formation of ordered mesoporous structures can be directly evidenced from the (1 0 0) and (1 1 0) diffractions of small-angle XRD patterns as shown in Fig. 1. In the case of Al₂O₃-Blank, only one broad peak at 2θ of about 1.2° corresponding to the (1 0 0)

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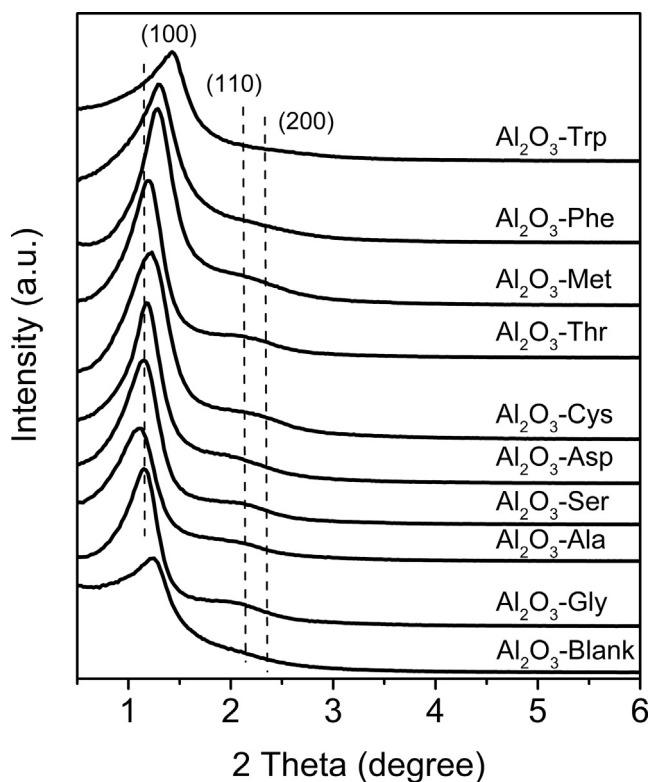


Fig. 1. Small-angle XRD patterns of the sample synthesized by using different alpha-amino acids.

diffraction of the hexagonal mesostructure was observed. On the contrary, both the (1 0 0) diffraction and a clear (1 1 0) diffraction (2θ of around 2.1°) of the $p6mm$ space group appeared for the alumina synthesized with alpha-amino acids. Moreover, the d-spacing of the (1 0 0) diffraction and calculated thickness of the pore wall were strongly dependent on the amino acid used (Table 1). Thus, OMA was successfully synthesized, and its structure became more ordered in the presence of amino acids. As given in Fig. 2, the highly ordered hexagonal arrangement of cylindrical mesopores along [1 1 0] and [0 0 1] directions were clearly observed from TEM images. Irrespective of the amino acid, the pore wall of

OMA was exclusively γ - Al_2O_3 as revealed from the wide-angle XRD patterns (Fig. S1). Thus, by simply changing the amino acid, highly ordered OMA with crystalline γ - Al_2O_3 framework was obtained with a tunable thickness of pore walls from 2.56 to 3.60 nm.

From the nitrogen adsorption-desorption isotherms given in Fig. 3, a typical type IV isotherm with a steep H1 hysteresis loop was observed, indicating the presence of uniform cylindrical channels [9]. This was clearly seen from the pore size distribution determined by the BJH method by using the adsorption branch of the isotherm (Fig. S2). In comparison with Al_2O_3 -Blank, the more ordered OMA synthesized in the presence of amino acids can be apparently seen from the much narrower pore size distribution, which is well agreeable with the XRD and TEM results. From the calculated data given in Table 1, the textural property of the OMA can be easily regulated in a large extent by simply changing the amino acid, i.e., the average pore size of 4.1–6.3 nm, the total pore volume of 0.39–0.63 cm^3/g with much less micropores ($<0.02 \text{ cm}^3/\text{g}$), and the BET surface area of 292–362 m^2/g .

During the EISA process, the cooperative assembly of the template and the hydrolysis and condensation of the aluminum precursor is critical for the formation of highly ordered OMA [4]. Thus, the uniform assembly of the copolymer and the aluminum species into the organic-inorganic mesostructure is important for the formation of the OMA with different structural and textural properties, which are mainly influenced by the acidity of the solution, the hydrophobic/hydrophilic property of the amino acid, and the coordination ability of the carbonyl and the size of different amino acids. Due to the buffering property of the amino acid, the pH of the solution can be kept relatively stable during the evaporation process, leading to the highly ordered structure such as Al_2O_3 -Gly and Al_2O_3 -Ser. This is further supported from the varied textural properties of OMA synthesized in the presence of different amino acids, which can be correlated with the pK_a of the amino acid. To confirm this, experiments with the same procedure and parameters but L-lysine, L-arginine, and L-histidine were added, respectively. As indicated in Fig. S3, long-range ordered OMA was not formed as a result of their higher pK_a . Alternatively, it has been reported that the strong coordination of Cl^- with aluminum precursor can collapse the assembled mesostructure during the evaporation process, leading to the disordered structure [4]. Moreover, the addition of carboxyl acids ($-\text{COOH}$) is reported favorable for the formation of ordered OMA due to the moderate coordination

Table 1
Textural properties of the samples obtained by means of N_2 adsorption-desorption isotherms.

Alumina	R group ^a	Φ_A^b (nm)	S_{BET}^c ($\text{m}^2 \text{g}^{-1}$)	V_p^d ($\text{cm}^3 \text{g}^{-1}$)	V_{micro}^e ($\text{cm}^3 \text{g}^{-1}$)	D_p^f (nm)	d_{100}^g (nm)	T_w^h (nm)
Al_2O_3 -Blank	–	–	286.6	0.59	0.014	7.4	–	–
Al_2O_3 -Gly	–H	0.750	332.5	0.63	0.009	6.3	7.67	2.56
Al_2O_3 -Ala	– CH_3	0.861	298.9	0.58	0.010	6.3	7.94	2.86
Al_2O_3 -Ser	– CH_2 -OH	0.892	310.3	0.58	0.009	6.2	7.67	2.66
Al_2O_3 -Asp	– CH_2 -COOH	1.004	316.5	0.55	0.008	5.6	7.18	2.69
Al_2O_3 -Cys	– CH_2 -SH	0.922	354.1	0.57	0.012	5.4	7.54	3.31
Al_2O_3 -Thr	– $\text{CH}(\text{CH}_3)$ -OH	0.941	314.3	0.52	0.007	5.4	7.41	3.16
Al_2O_3 -Met	– (CH_2) -S- CH_3	1.120	361.9	0.52	0.008	4.8	6.85	3.11
Al_2O_3 -Phe	– CH_2 - C_6H_5	1.177	292.3	0.39	0.004	4.3	6.84	3.60
Al_2O_3 -Trp	– C_8NH_6	1.343	297.1	0.39	0.007	4.1	6.18	3.04

Notes:

^a R group in the alpha-amino acid of $\text{H}_2\text{N}-\text{CHR}-\text{COOH}$.

^b The size of alpha-amino acid calculated using Gaussian 09 software, and the details are given in Supporting information (Fig. S5 and Table 1S).

^c BET surface area.

^d Pore volume determined at $P/P_0 = 0.99$.

^e Microporous volume calculated by t-plot method.

^f BJH average pore diameter calculated from the adsorption branch.

^g d-spacing calculated from the first peak.

^h Pore wall thickness was calculated as follows $T_w = 2d_{100}/3^{1/2} - D_p$.

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