

Regular Article

Solvothermal-assisted evaporation-induced self-assembly of ordered mesoporous alumina with improved performance



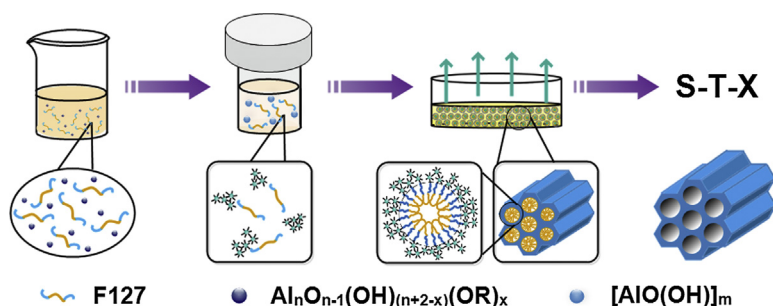
Dahai Pan^a, Wei Chen^a, Xiaodan Huang^b, Jun Zhang^b, Yannan Yang^b, Feng Yu^a, Shuwei Chen^a, Binbin Fan^a, Xiufeng Shi^a, Xingyu Cui^a, Ruifeng Li^{a,*}, Chengzhong Yu^{b,*}

^a College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, PR China

^b Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane 4072, Australia

GRAPHICAL ABSTRACT

Ordered mesoporous alumina materials with improved performance have been synthesized via a solvothermal-assisted evaporation-induced self-assembly route. The introduction of solvothermal treatment promotes the complete hydrolysis of organic aluminum precursors and the formation of cluster-like aluminum hydroxyl species with small sizes, advantageous for the self-assembly of ordered mesostructure in a broad range of evaporation conditions.



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ABSTRACT

A solvothermal-assisted evaporation-induced self-assembly (SA-EISA) approach has been developed for the synthesis of ordered mesoporous alumina (OMA) materials with high thermal stability and improved performance in catalysis. In conventional EISA process, the evaporation step is accompanied by the hydrolysis of organic aluminum precursors, thus the evaporation conditions have significant influences on the reaction and the final structure of OMA. In our approach, the solvothermal treatment step promotes the complete hydrolysis of aluminum precursors and produces partially condensed cluster-like aluminum hydroxyl species, which allows the formation of OMA in a broad range of evaporation conditions. Compared to mesoporous alumina obtained by conventional EISA process, OMA materials prepared by SA-EISA approach exhibit higher specific surface area, pore volume and thermal stability. When used as [supporting materials](#) for vanadium oxide catalyst, OMA materials obtained by the SA-EISA approach exhibit excellent activity, selectivity and stability for ethylbenzene dehydrogenation with carbon dioxide as a mild oxidant. Our contribution has provided new understanding in the synthesis of OMA materials with improved performance for catalytic applications.

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* Corresponding authors.

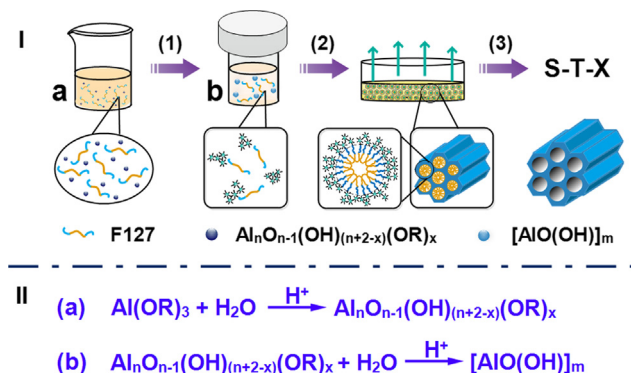
E-mail addresses: rfl@tyut.edu.cn (R. Li), c.yu@uq.edu.au (C. Yu).

1. Introduction

Mesoporous alumina materials have attracted great attention for their broad applications as catalysts or catalyst supports in many chemical processes, including the cracking, hydrocracking, and hydrodesulfurization of petroleum feedstocks [1–4]. Compared to conventional mesoporous alumina materials with relatively low surface area and pore volume, ordered mesoporous alumina (OMA) materials exhibit larger surface area and pore volume as well as uniform and tunable mesopore sizes, thus are better candidates in catalysis and adsorption [4–8]. OMA materials are commonly synthesized by two pathways: a nanocasting pathway using rigid pre-formed ordered mesoporous carbon or silica as the hard template [9–12] and a self-assembly pathway using surfactants and their supramolecular aggregates as the soft structure-directing template [5,8,12–14]. Compared to the nanocasting pathway, the soft-templating self-assembly pathway is more convenient. Unfortunately, unlike ordered mesoporous silica materials [15,16], aqueous solution synthesis of OMA is very difficult mainly due to the fast and complicated hydrolysis-condensation behavior of aluminum precursors [5,11,17].

Evaporation induced self-assembly (EISA) is another successful soft-templating approach [18–20] in the synthesis of mesoporous metal oxide materials with various compositions [20–27], including OMA materials [5,17,28]. To date, a series of OMA materials with different mesostructures have been obtained [14,28–34], and their pore sizes can be tailored by changing the hydrophobic chain length of surfactants [8,12] or adjusting the molar ratio of catalyst to aluminum precursor in the initial synthetic solution [35,36]. During the EISA process, the use of non-aqueous solvents (such as ethanol), and in some reports organic complexation agents [5,8,31], can effectively slow down the hydrolysis-condensation rate of organic aluminum precursors [such as aluminum isopropoxide, $\text{Al}(\text{OR})_3$] and induce the self-assembly of OMA materials. However, in non-aqueous volatile solvents, the surfactant molecules generally lose their hydrophilic/hydrophobic properties [13]. Moreover, the retarded hydrolysis and condensation leads to intermediate aluminum species with hydrophobic $-\text{OR}$ groups [37,38], which is difficult to interact with surfactant headgroups [5,12,31]. The self-assembly between surfactant templates and aluminum species is triggered only during the solvent evaporation process by progressively increasing the surfactant concentration and hydrolysis and condensation degree of aluminum species [13,20,39]. Therefore, many parameters that could influence the solvent evaporation conditions and the precursor hydrolysis-condensation reactions, such as temperature, relative humidity, catalysts, solvent evaporation rate, etc. [13,22,39–41], have impact on the final assembled structures. It is challenging to prepare OMA materials in a broad range of evaporation conditions utilizing the conventional EISA strategy.

Herein, we report a solvothermal-assisted evaporation-induced self-assembly (SA-EISA) route to synthesize OMA materials (Scheme 1, I). Compared to previous strategies to slow down the hydrolysis and condensation of organic aluminum precursors [5,17], our approach is to strategically increase the hydrolysis and condensation of aluminum precursors and to enhance the interaction between surfactants and aluminum species. The introduction of solvothermal treatment promotes the complete hydrolysis of organic aluminum precursors by replacing all $-\text{OR}$ with $-\text{OH}$ groups and the formation of cluster-like aluminum hydroxyl species with small sizes (Scheme 1, II), advantageous for the self-assembly of ordered mesophase during the evaporation step. After calcination to remove organic template, the OMA materials are obtained. Compared with the conventional EISA method, our approach can effectively reduce the impact of solvent evaporation



Scheme 1. (I) A flow chart of the SA-EISA approach for the synthesis of OMA materials. (1) Solvothermal treatment promoting the complete hydrolysis of aluminum precursor to form cluster-like aluminum hydroxyl species with small sizes, and leading to an enhanced interaction between surfactant and aluminum species. (2) EISA process forming the mesophase with a 2D hexagonal structure, and (3) Calcination at 400 °C forming OMA materials. (II) The hydrolysis-condensation reactions without (a) and with (b) solvothermal treatment.

conditions (such as relative humidity and solvent evaporation rate) on the structure of OMA materials. Our achievements have added new understanding for the preparation of OMA materials, and provided a reliable and reproducible method for the synthesis of OMA materials with improved performance for various applications.

2. Experimental

2.1. Chemicals

Triblock copolymer F127 ($M_w = 12600$, $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) was purchased from Sigma-Aldrich. Citric acid, anhydrous ethanol, aluminum isopropoxide, 37 wt% concentrated hydrochloric acid, and ethylbenzene (EB) were obtained from Tianjin Chemical Reagent Co. All the chemicals were of analytical grade and used as received without further purification.

2.2. Synthesis of OMA materials

A typical synthesis is described as follows. 3.2 g of triblock copolymer F127, 0.4 g of citric acid, and 1.6 g of 37 wt% hydrochloric acid were successively dissolved in 20 mL anhydrous ethanol, followed by the addition of 3.26 g of aluminum isopropoxide under stirring. After being vigorously stirred at 32 °C for 24 h at a sealed condition, the reaction solution was transferred into an autoclave for solvothermal (ST) treatment at a given temperature (adjusted from 60 to 100 °C) for 24 h. The resultant reaction sol was transferred to a petri dish and underwent solvent evaporation at 60 °C for 24 h. The final solid products were calcined at 400 °C for 5 h to remove the organic template and were named as S-T-X, where S is the abbreviation of a sample, T denotes the ST treatment temperature, and X stands for the solvent evaporation conditions.

For comparison, OMA material prepared by the traditional EISA method reported by Yuan et al. [5] (without the ST treatment process) was designated as S-X.

In order to investigate the effect of solvent evaporation conditions (X) on the structural and textural properties of resultant products S-T-X and S-X prepared with different methods, three solvent evaporation conditions were selected, including a low relative humidity of 35% (A), a high relative humidity of 70% (B), and a slow evaporation rate (C). In A and B, the thickness of solution before evaporation was constant at 1.5 mm. In C, the relative humidity was 35% while the solution thickness was 3.0 mm (obtained from

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