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# Ordered crystalline mesoporous $\gamma$ -alumina fabricated by vacuum-promoted self-assembly and alkaline hydrothermal method

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## ABSTRACT

As a commonly adopted approach to mesoporous alumina (MA), evaporation induced self-assembly (EISA) method with precursors containing chloride (e.g.  $\text{AlCl}_3$ ) faces a challenge to yield an ordered MA with crystalline pore walls because the chloride ion ( $\text{Cl}^-$ ) could affect the assembly and crystallization, resulting from the strong coordination of  $\text{Cl}^-$  to aluminum. Herein, a vacuum-promoted self-assembly and alkaline hydrothermal approach was developed and realized the preparation of ordered crystalline MA from  $\text{AlCl}_3$ . The obtained MA possesses ordered mesoporous structure, crystallized pore walls, narrow pore size distribution, large surface ( $390 \text{ m}^2/\text{g}$ ) and shows a superior catalytic performances towards catalytic dehydration of ethanol to ethylene.

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## 1. Introduction

Mesoporous materials [1,2] with ordered mesostructure, uniform pore size, large specific area offers potential applications in catalysis, sorption, electrochemical energy storage and etc. Among them, mesoporous alumina (MA) has attracted great attention due to their extensive applications in catalysis or catalyst support [3,4]. However, the practical application is plagued by the poor thermal stability resulted from their amorphous or semi-crystalline pore walls. As a result, design and synthesis of MA with crystalline pore walls has long been a hot topic [5–8]. Recently, considerable efforts [9–12] have been devoted to reduce the synthesis cost of crystalline MA by using the inexpensive inorganic aluminum salts to replace aluminum alkoxides. Among the inorganic aluminum salts, anhydrous aluminum chloride ( $\text{AlCl}_3$ ) is one of the most adopted precursor towards MA [5,13,14] due to its unique hydrolysis reaction, favoring the sol-gel process without any precipitants. However, there is few report on the synthesis of crystalline MA from  $\text{AlCl}_3$  because the chloride ion ( $\text{Cl}^-$ ) could affect the assembly and crystallization, resulting from the strong coordination of  $\text{Cl}^-$  to aluminum [10,15,16].

Herein, a vacuum-promoted self-assembly and alkaline hydrothermal approach was developed to prepare ordered crystalline MA from aluminum chloride. In our method, vacuum serves as an

adjustor towards the acidity of the assembly system by fast evaporating the generated acid (HCl) so that an efficient assembly could occur. The following alkaline hydrothermal treatment was utilized to further eliminate the influence of  $\text{Cl}^-$  ion towards the crystallization. With the aid of vacuum and alkaline hydrothermal treatment, ordered crystalline MA from aluminum chloride was prepared. The final MA possesses ordered mesoporous structure, crystalline pore walls, narrow pore size distribution, large surface ( $390 \text{ m}^2/\text{g}$ ) and achieves a superior catalytic performances to industrial alumina towards catalytic dehydration of ethanol to ethylene.

## 2. Experimental section

**Synthesis:** Typically, 1.0 g Pluronic P123 ( $M_w=5800$ ,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , BASF) was dissolved in 30.0 ml anhydrous ethanol to obtain the template solution. Then, 1.33 g anhydrous  $\text{AlCl}_3$  was added into the template solution with magnetic stirring till a homogeneous solution was obtained. The mixed solution of template and precursor was dipped into a Petri dish, which was put into a vacuum desiccator at  $40^\circ\text{C}$  to undergo solvent evaporation with the vacuum degree first at 0.05 atm for an hour, then at 0.01 atm for another two hours. After evaporation, a light gel was obtained. The obtained gel together with 25.0 ml aqueous ammonia (25 wt%) were transferred into an autoclave to undergo a hydrothermal treatment at  $120^\circ\text{C}$  for 24 h. Finally, the product

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was washed with distilled water for several times and dried prior to calcination. The template was removed by calcination in air at 500–700 °C for 6 h (rate of 1 °C/min) and the obtained products were denoted as MA-T(T: calcination temperature/°C).

**Characterization:** X-Ray diffraction (XRD) patterns were recorded on a Philips X'Pert X-ray diffractometer with a Cu K $\alpha$  radiation (40 kV, 40 mA). Transmission electron micrograph (TEM) and Selected area electron diffraction (SAED) images were obtained with a JEOL 2100 microscope operated at 200 kV. N<sub>2</sub> sorption isotherms were measured using a Micromeritics ASAP2020 analyzer at –196 °C. Before measurements were taken, all samples were degassed at 300 °C for 6 h. The specific surface area is calculated by Brunauer–Emmett–Teller (BET) theory and the pore size distribution is determined by adsorption branch via Barrett–Joyner–Halenda (BJH) method.

**Catalytic test:** The catalytic dehydration of ethanol on MA-500 and industrial alumina (Sigma-Aldrich) were carried out in a fixed-bed system at the atmospheric pressure. 0.1 g of catalyst was placed onto a quartz wool plug located in a quartz U-tube. Through a micro liquid pump with rate of 0.01 ml/min, the anhydrous ethanol is pumped into a vaporizer kept at 200 °C and conveys into the microreactor. The reaction products were analyzed online by gas chromatography (GC), using a flame ionization detector.

### 3. Results and discussion

The structure of the obtained MA was characterized by X-ray diffractions (XRD). The small angle XRD pattern of MA-500 (Fig. 1a) shows an intensive diffraction peak around 1°, which can be indexed to the diffractions of 100 directions of ordered mesoporous structure. Upon high temperature calcination, the mesoporous structure could be maintained evidenced by the diffraction peak around 1° of the obtained MA-700, implying an excellent thermal stability of the mesoporous structure. Both of the wide angle XRD patterns (Fig. 1b) of MA-500 and MA-700 show three diffraction peaks that can be indexed to 331, 400 and 440 diffractions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, illustrating a crystalline mesostructure could be obtained by the presented method.

The morphology of the final product was characterized by transmission electron microscope (TEM) shown in Fig. 2. The TEM

images of MA-500 viewed along different directions reveal that the calcined product possesses an ordered mesostructures with pore size of ~4.0 nm. The SAED pattern of MA-500 shows three bright diffraction rings assigned to the (311), (400) and (440) reflections of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, further confirming the crystalline structure.

N<sub>2</sub> adsorption–desorption isotherms and corresponding pore size distribution (PSD) curves of MA-500 and MA-700 are shown in Fig. 3a. Both of N<sub>2</sub> sorption curves are type IV isotherms with a hysteresis loop at relative pressure of 0.4–0.6, which indicates the existence of mesopore. The specific surface areas (BET) are 390 m<sup>2</sup>/g for MA-500, 291 m<sup>2</sup>/g for MA-700 and the corresponding pore volumes are 0.47 and 0.42 cm<sup>3</sup>/g, respectively. The Barrett–Joyner–Halenda (BJH) pore size distribution curves calculated from the adsorption branches, depicted as the inset of Fig. 3 a-inset, show that the obtained mesoporous carbons have a narrowly distributed pore size centered at ~4.1 nm, consistent with the TEM measurements.

Further studies show that alkaline hydrothermal treatment plays a key role towards crystallization as evidenced by the small angle XRD pattern (Fig. 3b) of MA-500 fabricated without alkaline hydrothermal treatment, which displays an intensive diffraction peak around 1°, indicative of an ordered mesoporous structure, however, its' corresponding wide angle XRD pattern (Fig. 3b-inset) exhibits not any diffraction peak, suggesting an amorphous structure.

All the above characterizations confirm that ordered MA with crystalline pore walls could be obtained from AlCl<sub>3</sub> by the developed vacuum-promoted self-assembly and alkaline hydrothermal method. The key of the present approach to crystalline MA lies in the introduction of vacuum and alkaline hydrothermal treatment to eliminate the influence of chloric ion towards the assembly and crystallization. Mesoporous alumina with large surface area can find utility as catalyst support and solid acid catalyst such as catalyst for ethanol dehydration [17]. Here, the catalytic performances of the obtained MA-500 compared to an industrial alumina (186 m<sup>2</sup>/g) on ethanol dehydration to ethylene were investigated. Fig. 4 shows the effect of reaction temperature on the yields to ethylene over MA-500 and industrial alumina. Notably, the yields of ethylene on the two catalyst both increase as the temperature rise. While, the MA-500 achieves a higher yields of ethylene than industrial alumina at every reaction temperature from 260 to 340 °C. The maximum yields for MA-500 is high to

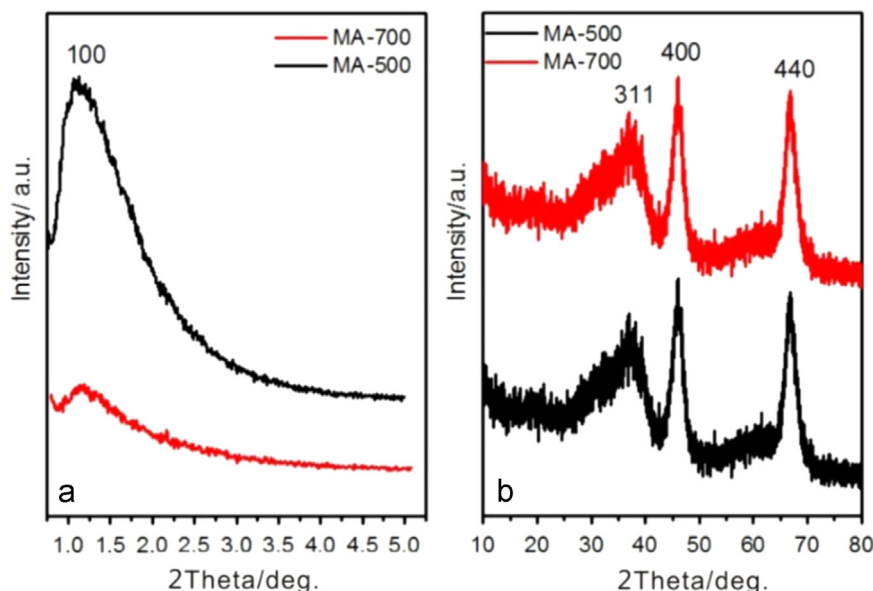


Fig. 1. Small angle XRD patterns, (a) and wide angle XRD patterns, (b) of MA-500 and MA-700.

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