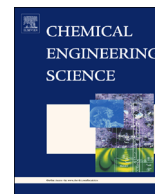




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# A tandem demetalization–desilication strategy to enhance the porosity of attapulgite for adsorption and catalysis



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## HIGHLIGHTS

- A tandem demetalization–desilication strategy was developed to enhance the porosity of attapulgite.
- The obtained material exhibited excellent performance for selective adsorption of CO<sub>2</sub> and catalysis.
- The inexpensive attapulgite may be a promising substitute of zeolite for adsorption and catalysis.

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## ABSTRACT

Due to its low cost and easy availability, the natural clay, attapulgite (ATP), is a promising substitute of relatively expensive zeolites for adsorption and catalysis. However, the narrow porous network of ATP hinders its practical applications severely. In the present study, a tandem demetalization–desilication strategy was developed to enhance porosity of ATP by adding NH<sub>4</sub>F followed the HCl treatment, for the first time. The HCl treatment leaches out the cations (including Mg, Ca, Al, and Fe) in octahedral sheets and generates silicon products, which block the pores of ATP. The subsequent addition of NH<sub>4</sub>F leads to the formation of a buffer solution, which is efficient in the removal of silicon products. As a result, abundant secondary porosity is created, which induces an obvious increase of surface area from 128 to 232 m<sup>2</sup> g<sup>−1</sup> and pore volume from 0.38 to 0.77 cm<sup>3</sup> g<sup>−1</sup>. The preliminary applications of the obtained material in adsorption and catalysis were also tested. The material exhibits obviously better performance in the selective adsorption of CO<sub>2</sub> from CH<sub>4</sub> and N<sub>2</sub> than pristine ATP, and the adsorption amount of CO<sub>2</sub> increases sharply from 23.5 to 57.5 mg g<sup>−1</sup>. In the Friedel–Crafts alkylation reaction of benzyl bromide with toluene, the obtained material can catalyze the conversion of 99.2% of benzyl bromide, which is 3.3 times as high as that catalyzed by pristine ATP. These properties make the obtained material highly promising in substituting zeolites for various applications.

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## 1. Introduction

Attapulgite (ATP, also called palygorskite) is a natural hydrated magnesium aluminum silicate mineral with nano-scaled, needle-shaped clusters (Granquist and Amero, 1948; Lu et al., 2015; Mu and Wang, 2015). There are large reserves of ATP in China, America, Spain, etc. The ideal structure of ATP is proposed with a formula of Mg<sub>5</sub>Si<sub>8</sub>O<sub>20</sub>(OH)<sub>2</sub>(OH<sub>2</sub>)<sub>4</sub>·4H<sub>2</sub>O. The actual composition in different regions varies due to partial replacement of Mg by Al and/or Fe. Its structure can be described as two bands of silica

tetrahedra linked by aluminum ions in octahedral coordination (Scheme S1). The tetrahedral sheet inverts its apical directions in adjacent ribbons, each ribbon alternating with channels (dimensions about 0.37 nm × 0.64 nm) along the fiber axis (Chen et al., 2011; Ma et al., 2009). ATP presents a highly ordered pore structure like zeolites (Lai et al., 2015), which makes it potential in adsorptive/catalytic applications because of the unique combination of properties such as hydrothermal stability, acidity, and the ability to stabilize metal species in the pores (Groen et al., 2007; Narsimhan et al., 2015). In industry, the price of ATP is about 200 USD per ton (Yin and Zhu, 2016), which is only one tenth of zeolite (Lv et al., 2014). Owing to its low cost, eco-friendliness, and special structure, great attention has been given to the utilization of ATP.

Current applications of ATP are mainly focused on some low value-added fields. One of the most important markets for

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industrial ATP is as a desiccant in various situations (e.g. litter for companion animals, usually cats) (Pappas et al., 2010). ATP also functions as a decoloring agent and a viscosity-increasing agent. In these cases, ATP is used primordially without any treatment or mixed simply with other additives. The development of high value-added applications of ATP (e.g. substituting zeolites as adsorbents and catalysts) is therefore extremely desirable. According to previous investigations and a deep analysis (Askari et al., 2012; Li et al., 2013; Zhang et al., 2013), it is found that the narrow porous network of molecular dimensions induces diffusion limitations of adsorbate/reactant molecules, which seriously hinders the availability of active sites, and the ATP volume cannot be utilized to its full extent.

Aiming to improve the performance of ATP, several methods have been adopted. Acid activation is a widely employed method. For example, hydrochloric acid (HCl) treated ATP was reported largely, and the composition, textural, and surface properties can be modified (Tang et al., 2014; Yang et al., 2010). However, the HCl aqueous solution preferentially extracted metal ions (e.g. Al or Mg) in octahedron (Boudriche et al., 2011). The improvement of porosity and catalytic performance was unapparent. In addition to acid activation, organic modification was implemented to enhance adsorption capacity and selectivity of ATP (Xu et al., 2013; Xue et al., 2011). Although the surface characteristics of ATP was modified by the organic groups, the pores and channels kept untouched. Some post-synthetic strategies (e.g. demetalization or desilication) have been developed for tailoring the pore architecture of zeolites (Wei et al., 2015). However, the development of an efficient method to enhance the porosity of ATP remains a great challenge.

Herein, we report for the first time a tandem demetalization–desilication strategy to enhance the porosity of ATP, in which ATP is treated by HCl aqueous solution followed by  $\text{NH}_4\text{F}$  (Scheme 1). During HCl treatment, the metal ions (i.e. Mg, Ca, Al, and Fe) in octahedral sheets are extracted, which leads to the generation of silicon products that block the pores partially. Afterwards the silicon products are removed by the buffer solution formed by the addition of  $\text{NH}_4\text{F}$ . This leads to the formation of abundant secondary porosity, so that the pore volume and surface area of the obtained material are enhanced almost 2 fold in comparison with pristine ATP. More importantly, the tandem treatment makes the active sites in the octahedral sheets highly accessible to guest molecules (i.e. adsorbates or reactants). As a result, the obtained material exhibits excellent performance for selective adsorption of

$\text{CO}_2$  from  $\text{CH}_4$  and  $\text{N}_2$ , which is evidently better than pristine ATP with regard to both adsorption capacity and selectivity. Moreover, the catalytic performance of the resultant materials in Friedel–Crafts alkylation reaction is greatly improved in both conversion and reaction rate.

## 2. Experimental section

### 2.1. Chemicals

ATP was kindly supplied by Xuyi Jiuchuan Clay Technology Co., Jiangsu, China. Benzyl bromide ( $\text{C}_7\text{H}_7\text{Br}$ , > 97.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Toluene ( $\text{C}_7\text{H}_8$ , > 99.5%), hydrochloric acid (HCl, > 36%), ammonium fluoride ( $\text{NH}_4\text{F}$ , > 96.0%), and hydrofluoric acid (HF, > 40.0%) were obtained from Shenbo Chemical Reagent Co., Ltd., Shanghai, China. All chemicals were used directly without further purification.

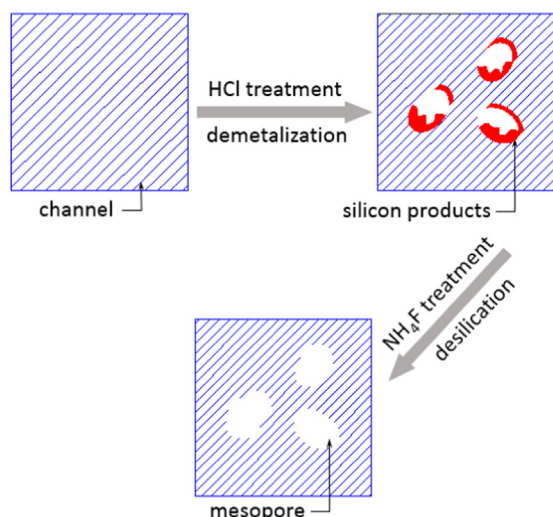
### 2.2. Materials preparation

Sample treatments were performed by reacting ATP with various solutions under different conditions reported in Table S1. The single treatments involving 30 mL solutions were executed under magnetic stirring in a round-bottomed flask equipped with a reflux condenser. In a typical experiment, ATP (1.0 g) was added to HCl or  $\text{NH}_4\text{F}$  solution with stirring for 120 min at designated temperature (80 or 25 °C). Afterwards the reaction was quenched and the resulting solid was filtered, washed by distilled water, and dried overnight at 110 °C. The samples treated by 1.0, 3.0, and 5.0 mol  $\text{L}^{-1}$  HCl solution were denoted as AH1, AH2, and AH3, respectively, while those treated by 0.5 and 1.0 mol  $\text{L}^{-1}$   $\text{NH}_4\text{F}$  solution (added 0.56 or 1.11 g  $\text{NH}_4\text{F}$  in 30 mL distilled water) were denoted as AF1 and AF2, respectively.

The tandem treatment was performed by reacting ATP with HCl solution followed by the addition of  $\text{NH}_4\text{F}$ . Detailed treatment conditions are shown in Table S1. In a typical process, 1.0 g of ATP was dispersed in 30 mL of 1.0 mol  $\text{L}^{-1}$  HCl solution and reacted at 80 °C for 120 min under stirring with reflux condenser. Then, the suspension solution was transferred to a plastic beaker containing 0.56 g  $\text{NH}_4\text{F}$  after cooling to ambient temperature. After stirring for 30 min at 25 °C, the mixture was filtered, washed with distilled water, and dried overnight at 110 °C. The product resulted from the tandem treatment was denoted as AH1F1-2. The yield of AH1, AF1, and AH1F1-2 was 79.8%, 95.3%, and 58.6%, respectively.

### 2.3. Characterization

X-ray diffraction (XRD) patterns of samples were recorded using a Bruker D8 Advance diffractometer with  $\text{Cu K}\alpha$  radiation at 40 kV and 40 mA. Data were recorded in the  $2\theta$  range of 5–60° with an angular step size of 0.02°. Nitrogen adsorption–desorption isotherms were measured using a Micromeritics ASAP 2020 automated gas adsorption analyzer at –196 °C. The samples were degassed at 150 °C for 5 h prior to analysis. The Brunauer–Emmett–Teller (BET) surface area was calculated with the relative pressure ranging from 0.04 to 0.25. The total pore volume was derived from the amount adsorbed at  $p/p_0=0.99$ . The pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method according to the adsorption branch of the isotherm. Scanning electronic microscopy (SEM) images were recorded on a Hitachi S4800 electron microscope operating at 20 kV. Transmission electron microscopy (TEM) was performed on a JEM-200CX UHR electron microscope operated at 200 kV. Fourier transform infrared (IR) spectra were recorded on a Nicolet Nexus 470



**Scheme 1.** Schematic diagrams for the tandem demetalization–desilication strategy to enhance the porosity of ATP.

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