

A novel synthesis process of ETS-4 titanosilicate using commercial anatase in the absence of fluoride ions

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Abstract: A novel synthesis process for ETS-4 titanosilicate using commercial anatase as the titanium source in the absence of fluoride ions was studied. Fluoride ions and traced ETS-4 seeds have important roles in forming ETS-4 structures. However, the method using ETS-4 seeds instead of fluoride ions to improve product purity and productivity is environment-friendly. ETS-4, ETS-4(NS), and ETS-4(NaF) were respectively synthesized using traced ETS-4 seeds, without seeds, and with fluoride ions. The as-synthesized samples were identified by X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis. Adsorption isotherms and adsorption heats of nitrogen and methane on the prepared ETS-4 were also measured. The results showed that ETS-4 samples could be prepared using anatase in the absence of fluoride ions, with good purity, comparable physicochemical properties, and excellent adsorption properties.

Keywords: titanosilicate; anatase; gas adsorption; microporous materials

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1. Introduction

The structure of microporous titanosilicate ETS-4 is similar to that of Zorite mineral, with an ideal composition of $M_8Ti_5Si_{12}O_{38} \cdot nH_2O$ ($M = K, Na$) [1-2]. The effective pore size of ETS-4 is about 0.37 nm and can be easily tuned by progressive dehydration (molecular gate effect). ETS-4 can be selected as an adsorbent for the separation of methane/nitrogen, oxygen/argon, and oxygen/nitrogen [3] because of its special structure and characteristics. In particular, its Sr-exchanged variant, Sr-ETS-4, is a stable adsorbent for the separation of N_2 and CH_4 in pressure swing adsorption processes [4]. The adsorption separation of N_2 and CH_4 is challenging because of low adsorption loadings and selectivity on most molecule sieve adsorbents. ETS-4 may play an important role in obtaining highly concentrated methane from landfill gases and purifying methane from natural gases, especially in times of energy shortage. Therefore,

studies on ETS-4 synthesizing processes are becoming increasingly important.

Sodium silicate, fumed amorphous silica, and colloidal silica could all be used as silica sources in the synthesis of ETS-4 [5]. $TiCl_3$, $TiCl_4$, TiF_4 , $Ti(SO_4)_2$, and $TiOSO_4$ as titanium sources in the synthesis have also been published since the first discovery of ETS-4 in 1990. Nano Degussa P25 TiO_2 was an alternative titanium source, but fluoride ions were required in the initial reaction of the mineralization of zeolites [6]. In this paper, the use of commercial anatase as a cheap titanium source for the preparation of ETS-4 was studied. Furthermore, both fluoride ions and traced ETS-4 seeds in the initial reaction solution were tested. ETS-4 seeds replacing fluoride ions in the initial reaction solution would solve additional environmental problems such as fluoride wastewater treatment. We would like to present an economical and environment-friendly process for ETS-4.

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The results from the three ETS-4 preparation methods (adding fluoride ions, adding ETS-4 seeds, and not adding fluoride ions or ETS-4 seeds in the initial reaction solutions) were discussed. These products were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). Adsorption isotherms and isosteric heats of nitrogen and methane on the ETS-4 prepared with ETS-4 seeds were also investigated and compared with previous published data.

2. Experimental

2.1. Synthesis of ETS-4

In the preparation of ETS-4, 12.5 g of colloidal silica solution (30wt% SiO₂, Ludox), 2.5 g of NaOH, 2 g of NaCl, 1 g of anatase, and 0.2 g of seeds of ETS-4 were mixed with 12.5 g of water. Then the solution was vigorously stirred for 30 min. The formed slurry was transferred into a 300 mL stainless steel autoclave (Parr instrument) for further crystallization at 230°C for 24 h. Then the resulting precipitation was filtered and washed with deionized water three times. The ETS-4 product was placed in an oven at 70°C overnight for drying.

An ETS-4(NS) product using the same synthesis procedure (above) without the ETS-4 seeds in the initial solution was also prepared.

With the same procedure as ETS-4(NS), 0.25 g of sodium fluoride was added into the initial solution. The ETS-4(NaF) product was obtained for comparison.

2.2. Measurement and characterization

The crystalline properties of the ETS-4 samples prepared using the three synthesizing procedures were analyzed by X-ray diffraction (XRD, Philips PW1140/90 diffractometer with Cu K_α radiation) and scanning electron microscopy (FE-SEM, JEOL 6300F, 15 kV). Thermal stability was determined by combusting the ETS-4 samples at 30-500°C with a heating rate of 5°C/min under nitrogen (20 mL/min) using a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer (Switzerland). The measurements of Brunauer-Emmett-Teller (BET) and Langmuir surface areas were conducted with an ASAP 2010 analyzer (Micromeritics, USA) using N₂ and H₂ as probe gases at 77 K in the relative pressure range of 0.05-0.25. The isotherms of methane and nitrogen were also measured at 0°C and 30°C with ASAP 2010, respectively. The ETS-4 samples were degassed at 90°C for 8 h before the adsorption experiments.

3. Results and discussion

3.1. Sample crystallinity and morphology

The XRD patterns in Fig.1 shows that distinct peaks were observed in the samples of ETS-4, ETS-4(NaF), and ETS-4(NS), which represent the characteristic signatures of ETS-4 [7]. However, the patterns of the three samples all displayed a small amount of unreacted anatase impurities. In order to investigate the effect of an initial quantity of anatase and reaction time on the unreacted anatase, synthesizing experiments were done with less anatase and longer hydrothermal synthesis time. The results indicate that the peaks of anatase were always observed in the XRD patterns. Therefore, anatase impurity was contained in the ETS-4 product when commercial anatase was used as the titanium source. It is in a good agreement with Rocha's research [8] where they claimed pure ETS-10, another type of ETS titanosilicate, could not be obtained when using anatase as the titanium source. The XRD pattern of ETS-4(NS) (Fig. 1(b)) shows that the final product was ETS-4 with a large amount of AM-3 impurities [9]. Comparing with ETS-4(NS), the patterns of ETS-4 and ETS-4(NaF) (Figs. 1(a) and 1(c)) displayed clear crystal structures. The results revealed that the addition of either ETS-4 seeds or fluoride ions could improve the crystallinity and purity of the final ETS-4 product. However, using ETS-4 seeds instead of fluoride ions in this study would be friendlier to the environment.

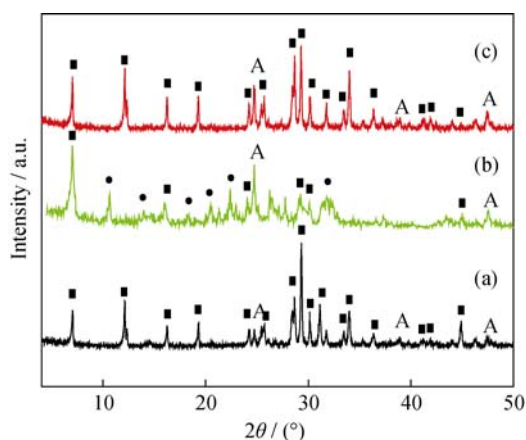


Fig. 1. XRD patterns of ETS-4(NaF) (a), ETS-4(NS) (b), and ETS-4 (c) (A - unreacted anatase; ■ - ETS-4; ● - AM-3 impurity).

The SEM morphologies of as-synthesized ETS-4 samples are shown in Fig. 2. Both ETS-4(NaF) and ETS-4 samples showed that the monolithic crystals segregated from one another with a rectangular morphology, which was in good

conformity with Ref. [10]. The particle sizes of both samples range from 5 to 10 μm . The morphology of ETS-4(NS) (Fig. 2(b)) is clearly different from those of ETS-4(NaF) and ETS-4, probably because the ETS-4(NS) sample contains a

large amount of impurities. Therefore, this morphology was in accordance with the previous XRD result (Fig. 1(b)), and it further confirmed that high-quality ETS-4 could only be obtained in the presence of fluoride ions or ETS-4 seeds.

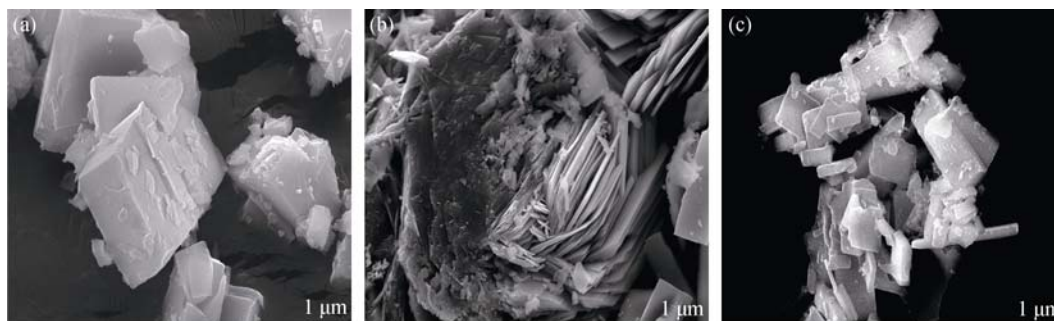


Fig. 2. FE-SEM images of ETS-4(NaF) sample (a), ETS-4(NS) sample (b), and ETS-4 sample (c).

3.2. Heat treatment and thermal stability

To investigate the effect of dehydration on the structure of as-synthesized ETS-4 samples, water-loss curves (Fig. 3) were determined by thermogravimetry (TG) and differential thermogravimetry (DTG). The profile of the water-loss curve was in good agreement with the literature [11]. It shows continuous water loss as a function of temperature in the range of 30 to 300°C. The initial weight loss below 100°C could be attributed to the loss of its loosely bound moisture. The peak centered at about 216 °C could be ascribed to the desorption of structural water. The profile becomes completely flat at around 300°C, indicating that ETS-4 had lost all of its moisture. It is worth mentioning that the structure-collapsing temperature of the sample is quite different from the value reported by Kuznicki *et al.* [11], wherein ETS-4 collapsed near 200°C. The difference is probably because the thermal stability of the ETS-4 structure depends a lot on the synthesis conditions.

3.3. Adsorption isotherms and isosteric heats of adsorption

The BET surface area of ETS-4 with nitrogen adsorption

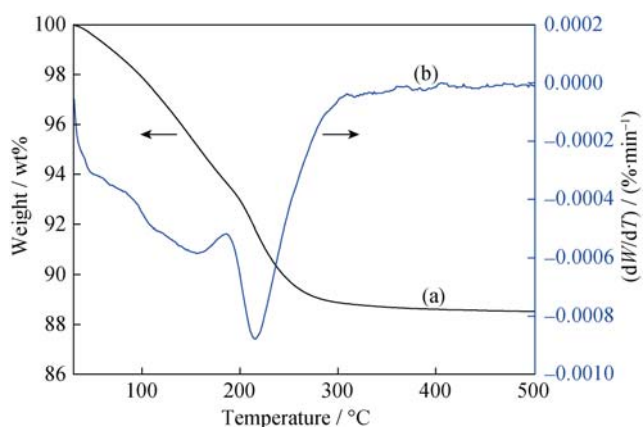


Fig. 3. TG (a) and DTG (b) curves of synthesized ETS-4.

at 77 K was quite low, as expected, at about 3.5 m^2/g . This phenomenon is likely attributed to the ETS-4 having very narrow pores which limit the access of N_2 molecules at this temperature. This data was fully consistent with Armaroli's experiment [12]. In order to investigate the details of the textural properties of ETS-4, an adsorption measurement of smaller diameter H_2 gas was carried out at 77 K, as shown in Fig. 4. The Langmuir surface area of ETS-4 with H_2 was 210 m^2/g , slightly less than the value (247 m^2/g) reported by Prasanth *et al.* [13], which could be attributed to the small amount of unreacted anatase impurity.

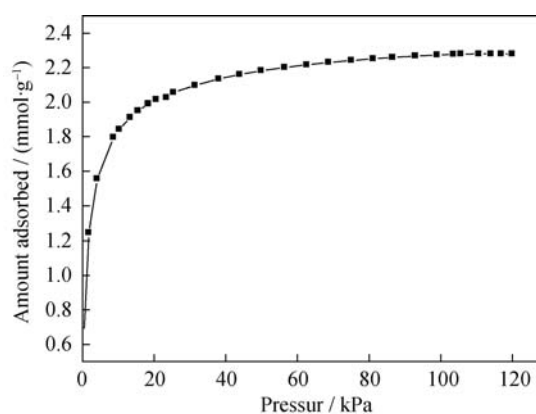


Fig. 4. Hydrogen adsorption isotherm of the synthesized ETS-4 at 77 K.

The equilibrium isotherms of N_2 and CH_4 were also measured at 0 and 30°C in the ETS-4 samples (Figs. 5 and 6). All the isotherms were completely reversible, suggesting no chemical adsorption happening. Also, the amounts of CH_4 absorbed were larger compared with those of N_2 , which could be attributed to the induced octopole moment that CH_4 exhibits and its large polarizability [14]. The adsorption amounts of N_2 and CH_4 agree well with Pillai's experiments [3].

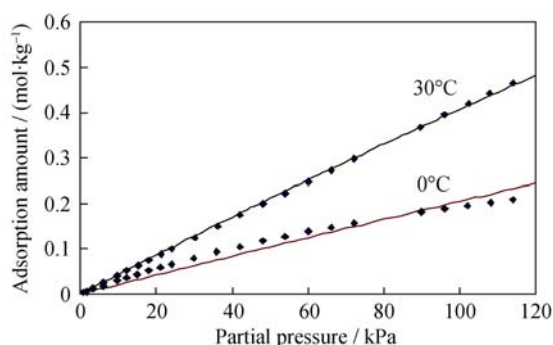


Fig. 5. N₂ adsorption isotherms on ETS-4 at at 0 °C and 30°C.

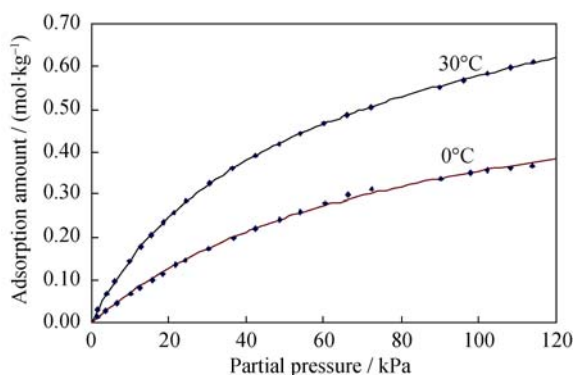


Fig. 6. CH₄ adsorption isotherms on ETS-4 at at 0°C and 30°C.

The nitrogen and methane isosteric heats of adsorption on ETS-4 (Table 1) were 17 and 23 kJ/mol, respectively, according to van't Hoff's equation

$$\Delta H_{ad} = RT^2 \frac{\partial(\ln P)}{\partial T},$$

where ΔH_{ad} represents the heat adsorption (J/mol), R represents the ideal gas constant (8.314 J/(mol·K)), P and T represent the pressure (kPa) and temperature (K). The CH₄ in ETS-4 showed a higher initial heat of adsorption because of its larger polarizability.

Table 1. Equilibrium adsorption capacity of N₂ and CH₄ at 102 kPa and 0°C and heats of adsorption of these gases in ETS-4.

Sorbate	Adsorption capacity / (mL·g ⁻¹)	-ΔH / (kJ·mol ⁻¹)
Nitrogen	9.4	17
Methane	13.0	23

4. Conclusion

ETS-4 was successfully prepared using commercial anatase as the titanium source in the absence of fluoride ions. The synthesis using ETS-4 seeds simplifies the process and is also environment-friendly. ETS-4 obtained in the presence of ETS-4 seeds exhibits high surface areas and pore volumes, in spite of containing a very small amount of im-

purities. Gas adsorption measurements confirmed that prepared ETS-4 had narrow micropores and the isotherms of N₂ and CH₄ were similar to that of the ETS-4 prepared using commercial sources. This study provided a low-cost synthesis process for ETS-4.

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