

Novel Adsorption Material for Thermal Energy Storage

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Abstract

Aluminophosphate APO-tric is a novel adsorption material for thermal energy storage. APO-tric is a microporous triclinic chabazite material with ordered microporous 3-dimensional channel structure. The framework is very flexible which increases the possibility of water adsorption into the structure. During adsorption of water molecules the chabazite structure is modified. This deformation is however completely reversible and can be eliminated by dehydration at 120 °C. The material shows a very good thermal stability up to 900 °C and a water adsorption capacity up to 0.32 g/g.

1. Introduction

Thermally stable hydrophilic microporous and mesoporous adsorbents have become of increasing interest as low temperature heat (e.g. solar energy) storage materials mostly in combination with water as working fluid. [1] Water is the most suitable working fluid, due to its high heats of condensation and adsorption on different surfaces. The water sorption behavior of a sorbent depends on many factors, such as the structure and the chemical composition (e.g. Si/Al ratio for aluminosilicates), the presence of charged species, type of framework structure, and hydration level. These porous materials exist in a hydrated form and the water in the pores governs their properties. Till now ordinary zeolites (e.g. zeolite A, zeolite Y, zeolite X) and silica gel were the most common products for thermo-chemical storage applications. [2] A significant improvement of targeted adsorption behavior was found recently for microporous aluminophosphate AIPO₄-18. [3] Aluminophosphates (AIPOs) are, due to the regular pore systems and networks similar to the zeolites, occasionally called zeotype material. Due to aluminophosphate neutral frameworks and the presence of low concentration of surface hydroxyl groups, it is expected that aluminophosphates have hydrophobic character. However, aluminophosphates often are described as hydrophilic materials, because they adsorb water even under low P/Po. Aluminophosphate materials exhibit isotherm type I or V due to lower hydrophilic strength compared to the electrostatic zeolite. It is known that most of the aluminophosphates are not hydrothermally stable, except some zeotypes, such as AIPO-5, -11 and -17 have moderate stability up to 600 °C. (Silico)aluminophosphates, e.g. SAPO-34 or AIPO-18, show superior sorption behaviour, which is depending on their composition and morphology. [4] One of the most promising adsorbent materials in terms of equilibrium data were found to be the microporous aluminophosphate AIPO-18 (AEI structure type code). Under relatively mild conditions, e.g. adsorption at 35 °C (1.23 kPa) and desorption at 90 °C (5.67 kPa), it shows useful loadings of up to 0.28 g/g depending on the synthesis procedure. [5]

We present here a new sorption material suitable for thermal energy storage. Aluminophosphate APO-tric is a microporous zeolite-like material with ordered microporous structure. In APO-tric, two fluoride ions bridge between two Al atoms in 4-ring connecting double-6-rings of the structure and thus distort the rhombohedral symmetry of chabazite [6]. After thermal treatment the template- and fluoride-free material adopts the rhombohedral symmetry of chabazite topology. The framework structure of this phase distorts back to triclinic symmetry of chabazite in the presence of water molecules. [7] The deformation is completely reversible.

2. Experimental

2.1. Synthesis and Characterization

APO-tric was hydrothermally synthesized from a fluoride medium using piperidine as a structure-directing agent. The as-synthesized sample was calcined in oxygen at 550 °C over night. The crystallinity of the APO-tric was examined by High Temperature X-ray powder diffraction (HT-XRD) using a Siemens diffractometer D5000 (Cu K α radiation) equipped with an HTK-16 high-temperature chamber. Data collection parameters were: range 5-35° 2 θ , step 0.026° 2 θ , time per step 4s. XRPD patterns were collected at constant temperatures in intervals of 100 °C between room temperature and 900 °C. Between the scans, the sample was heated at a rate of 10 °C / min in air. To confirm the phase purity, the powder patterns were compared with literature data. The morphology of the material was examined using a scanning electron microscope Zeiss Supra 35VP. Thermogravimetric investigation was performed with a SDT 2960 Thermal Analyzer. Prior to the TG measurement, the calcined sample was stored in a desiccator over saturated ammonium chloride solution for 2 days. For all measurements, samples were heated in a stream of nitrogen with a heating rate of 10 K /min. Specific surface area and porosity were evaluated by analysis of nitrogen adsorption isotherms measured on a Micromeritics ASAP 2020 instrument. The isotherm was recorded at 77 K. The sample was outgassed at 473 K for 2 h in the port of the adsorption analyzer. The BET specific surface area [8] was calculated from adsorption data in the relative pressure range from 0.05 to 0.3. The micropore volume was calculated from nitrogen adsorption data using HK [9] and α_s -plot method [10]. In addition, water adsorption and desorption measurements have been performed on a Setaram TG-DSC 111 coupled with the controlled humidity generator Wetsys.

3. Results and Discussion

According to X-ray analysis, the product obtained after hydrothermal synthesis was crystalline and exhibits the triclinic deformation of CHA-type XRD pattern. Nor other crystalline phase even amorphous material was detected. When calcined samples were exposed to the air humidity, the structure symmetry changed from the rhombohedral to the new triclinic one. The deformation is completely reversible. The material shows thermal stability up to 900 °C (Fig. 1).

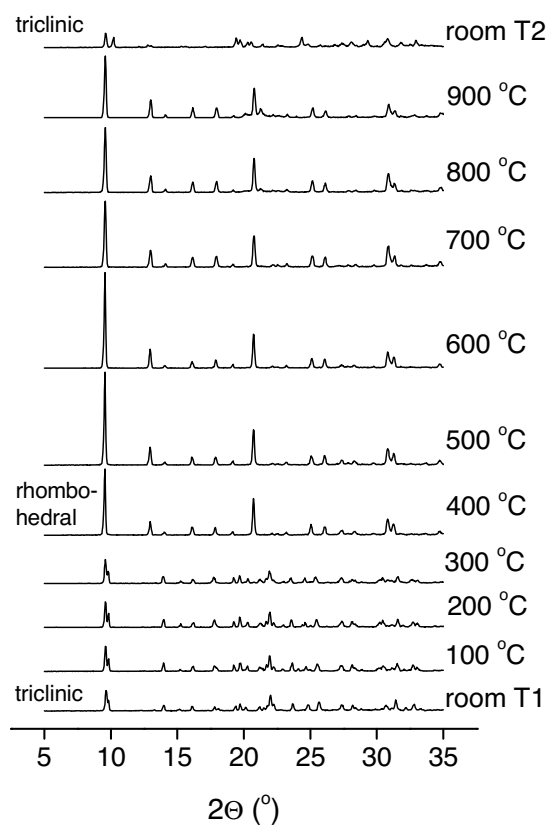


Fig. 1. High temperature XRD of APO-tric.

For an estimation of the APO-tric capacity towards water, the sample was stored in high humidity atmosphere and subsequently subjected to TG analysis. Figure 2 shows TG/DTG curves of APO-tric material. Water was desorbed up to 50 °C and 120 °C due to physically and chemically bonded water molecules on and inside the APO-tric structure, respectively, evidencing two different adsorption sites for water molecules. The water loss is 23 %.

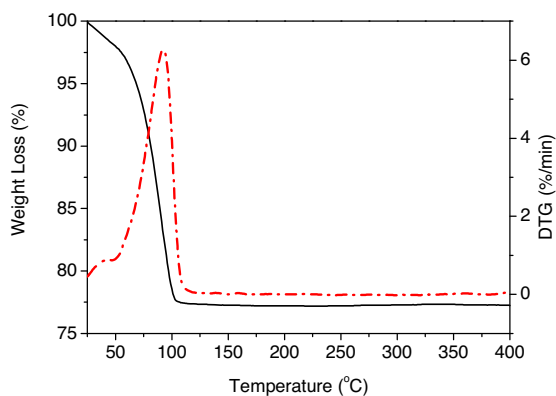


Fig. 2. TG/DTG curves of APO-tric.

The size and morphology of APO-tric powder was examined by SEM. 20 μm square-shaped crystals were observed predominantly in the sample (Fig. 3).

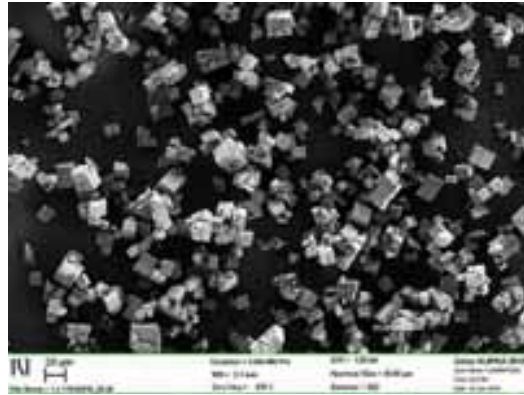


Fig. 3. SEM picture of APO-tric.

High porosity of zeolitic materials causes their good adsorption properties. Large surface area of the pores is a preliminary condition for significant adsorption processes. Figure 4 shows nitrogen adsorption-desorption isotherm of APO-tric material, whereas structural parameters determined on the basis of this isotherm are listed in Table 1. The nitrogen adsorption-desorption isotherm for the sample studied is type I isotherm. Type I isotherms are characterized by a plateau which is nearly or quite horizontal and are given by the microporous molecular sieves (zeolites). [11]

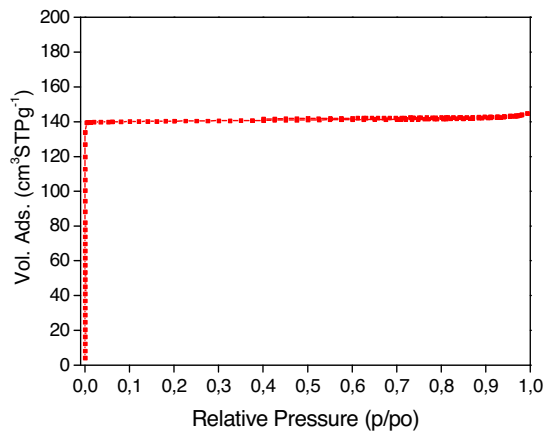


Fig. 4. Nitrogen physisorption isotherm of APO-tric.

Table 1: Textural properties of APO-tric.

S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mi} (cm^3/g)	S_{ex} (m^2/g)	S_{mi} (m^2/g)
422	0.221	0.214	5	417

Abbreviations: S_{BET} , the BET surface area; V_{tot} , total pore volume; V_{mi} , micropore volume; S_{ex} , external surface area; S_{mi} , micropore surface area;

The water uptake curves in Figure 5 show typical characteristics of microporous hydrophilic aluminophosphate molecular sieves. Similar to AlPO-18 [5] and AlPO-5 [12], APO-tric shows a steep adsorption step in a narrow relative pressure range. S shaped (type V) water sorption isotherms are results of adsorption mechanism proposed by Kornatowski. [12] The adsorption mechanism consists of covering of the adsorption surface with a layer of water molecules before the step, then capillary condensation (the step), i. e. a phase transition to liquid-like water at a definite relative pressure, and volume filling of micropores with liquid-like adsorbate. A maximum water load is 0.32 g/g. The S shape of the adsorption curve with a steep step is advantageous for low desorption temperature applications. A slight disadvantage is the hysteresis between the adsorption and desorption path as can be seen in figure 5, which is a known phenomenon of aluminophosphate molecular sieves. [13] The upright hysteresis loop at low relative pressure is an evidence for a direct interaction of water molecules with the framework. However, the S-shape behaviour allows a maximum water load within a heat transformation cycle.

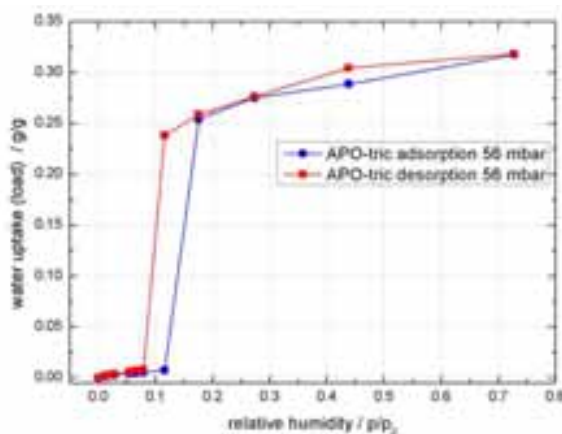


Fig. 5. Adsorption and desorption isotherm of APO-tric.

4. Conclusions

Aluminophosphate APO-tric is a novel thermally stable microporous hydrophilic adsorbent. Flexibility of the framework increases the possibility of water adsorption into the structure. During adsorption of water molecules the structure symmetry changed from the rhombohedral to the new triclinic one. The deformation can be removed by dehydration at 120 °C. APO-tric can adsorb larger amounts of water, which confirms the high water capacity of APO-tric hydrophilic material. The S shape of water sorption curves with steep step indicates that APO-tric adsorbent is convenient for solar thermal applications.

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