

Short communication

Encapsulation of bulky solvent molecules into the channels of aluminophosphate molecular sieve and its negative influence on the thermal stability of open-framework

Junhui Guo^{a,1}, Chao Wang^{b,1}, Jun Xu^b, Feng Deng^b, Wenfu Yan^{a,*}, Raj Pal Sharma^c, Ruren Xu^a^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China^b Wuhan Center for Magnetic Resonance, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, The Chinese Academy of Sciences, Wuhan 430071, PR China^c Department of Chemistry and CAS, Panjab University, Chandigarh 160014, India

ARTICLE INFO

Article history:

Received 30 January 2018

Received in revised form 25 February 2018

Accepted 9 March 2018

Available online 16 March 2018

Keywords:

Hydrothermal synthesis

Solvothermal synthesis

Zeolite

Aluminophosphate

Molecular sieve

Thermal stability

ABSTRACT

Three aluminophosphate molecular sieve $\text{AlPO}_4\text{-5s}$ were synthesized using water, ethylene glycol, and triethylene glycol as solvent. The products were thoroughly characterized by powder X-ray diffraction analyses, thermogravimetric analyses, scanning electron microscope analyses, and solid-state cross polarization magic angle spinning nuclear magnetic resonance analyses. The results showed that solvothermally synthesized aluminophosphate molecular sieve $\text{AlPO}_4\text{-5}$ from triethylene glycol was much less stable than that hydrothermally synthesized from water. Thermogravimetric analysis and ^{13}C cross polarization magic angle spinning nuclear magnetic resonance analyses confirmed that the bulky solvent molecules of triethylene glycol were encapsulated within the channels of $\text{AlPO}_4\text{-5}$ and was responsible for the significant decrease of the thermal stability of open-framework.

© 2017 Elsevier B.V. All rights reserved.

Zeolites and related microporous crystalline materials have been widely used as ion-exchangers, catalysts, and adsorbents [1–4]. Before and in the utilization of such materials, calcination is usually needed either to eliminate water and/or organic structure-directing agents encapsulated within their porosity or cavity or to regenerate them by eliminating the coke deposits in air or moisture. Therefore, high thermal and hydrothermal stability for such materials are the basic requirements for their potential applications. For zeolites, both intrinsic and external factors can affect their stability [5]. The intrinsic factors include the framework Si/Al ratio, defects, crystallinity, the type and size of charge-compensating cations, the coordination of cations after dehydration, and the framework topology. The external factors include the calcination environment, crystal size, and heating rate, etc. For a given zeolitic structure, it is important to keep its stability by controlling external factors. Thus, it is very necessary to investigate the external factors affecting the thermal stability of zeolitic structures.

During the formation of microporous crystalline materials, the organic structure-directing agents will be usually encapsulated in the open-framework if the organic species was used as structure-directing agent, which will occupy most of the room of porosity or cavity [6–

11]. It is well accepted that the small solvent molecules of water can be possibly included in the hydrothermally synthesized structures together with the organic structure-directing agent. Since M. P. Dale performed the first solvothermal synthesis of zeolites using ethylene glycol and propanol as solvent [12], solvothermal synthesis has been considered as an important method for the synthesis of molecular sieves. Since then, plenty of zeolites and microporous crystals have been synthesized using various alcohols and other organic solvents [13–17]. However, the information and investigation on if the organic solvent molecules, especially bulky organic solvent molecules, can be included in the structure of microporous crystals in the solvothermal synthesis is very rare. In a recent work, the encapsulation of organic solvent molecules in the pore structure of ZSM-12 was speculated according to the blue shift of symmetric and asymmetric Si–O vibration modes in FTIR spectra [18]. In 2004, Morris and co-workers reported the “ionothermal synthesis” of microporous materials in which bulky ionic liquids were used as both structure-directing agents and solvents [19]. The bulky ionic liquids were usually included inside the microporous crystals. However, these included species was usually treated as structure-directing agent instead of solvent. Very recently, we found that triethylene glycol solvent molecules can be encapsulated into the channels of as-synthesized aluminophosphate molecular sieve $\text{AlPO}_4\text{-11}$ [20]. However, such encapsulation has no influence on the thermal stability of $\text{AlPO}_4\text{-11}$.

* Corresponding author.

E-mail address: yanw@jlu.edu.cn (W. Yan).¹ These authors contributed equally.

Aluminophosphate molecular sieves were first reported in 1982 [21], and denoted as $\text{AlPO}_4\text{-}n$, where n represents a structure-type. These molecular sieves possess neutral zeolitic open frameworks that are built up from strict alternation of AlO_4 and PO_4 tetrahedra through corner sharing. $\text{AlPO}_4\text{-}5$ (AFI) was the first AlPO_4 molecular sieve synthesized [22]. The framework of $\text{AlPO}_4\text{-}5$ comprises a one-dimensional (1D) channel system of circular 12-membered rings with a free diameter of approximately $7.3 \times 7.3 \text{ \AA}$ [23]. It has been reported that the $\text{AlPO}_4\text{-}5$ is thermally stable to $1000 \text{ }^\circ\text{C}$, above which it transforms to the AlPO_4 analog of tridymite [24].

In this work, we report an unusual influence of solvents on the thermal stability of $\text{AlPO}_4\text{-}5$ synthesized with water, ethylene glycol (EG) and triethylene glycol (TEG) as solvents and triethylamine was used as organic structure-directing agent. The corresponding products were denoted as $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$, $\text{AlPO}_4\text{-}5\text{-EG}$ and $\text{AlPO}_4\text{-}5\text{-TEG}$, respectively. We confirm that bulky solvent molecules can be encapsulated in the channels of $\text{AlPO}_4\text{-}5$ together with the structure-directing agent of triethylamine and such encapsulation has a significant negative influence on the thermal stability of $\text{AlPO}_4\text{-}5$. The $\text{AlPO}_4\text{-}5$ synthesized with triethylene glycol as solvent collapsed at the temperature as low as $300 \text{ }^\circ\text{C}$, far from $1000 \text{ }^\circ\text{C}$.

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of $\text{AlPO}_4\text{-}5$ synthesized with solvents of water, EG and TEG and the corresponding calcined samples at different temperatures. The XRD power patterns shown in Fig. 1a indicate that all $\text{AlPO}_4\text{-}5$ s have high degree of crystallinity. Taking $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$ as a reference, the degree of crystallinity of $\text{AlPO}_4\text{-}5\text{-EG}$ and $\text{AlPO}_4\text{-}5\text{-TEG}$ is 38.2% and 40.7%, respectively. The degree of crystallinity is calculated by comparing the summation of the intensities of the six prominent peaks in the 2θ range of 7 to 25° (i.e. 7.42 , 12.88 , 14.88 , 19.72 , 20.96 , and 22.36°) [25]. Thermal stability studies show that $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$ is stable up to $800 \text{ }^\circ\text{C}$ (Fig. 1b), which is consistent with the previously reported results [24]. Similarly, $\text{AlPO}_4\text{-}5\text{-EG}$ is also stable up to $800 \text{ }^\circ\text{C}$ (Fig. 1c). However, compared to the as-synthesized $\text{AlPO}_4\text{-}5\text{-EG}$, its degree of crystallinity of the calcined $\text{AlPO}_4\text{-}5\text{-EG}$ at $800 \text{ }^\circ\text{C}$ decreased to 56.4%. During the calcination, $\text{AlPO}_4\text{-}5$ starts to form at $600 \text{ }^\circ\text{C}$. Surprisingly, $\text{AlPO}_4\text{-}5\text{-TEG}$ is much less stable

than $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$ and also less stable than $\text{AlPO}_4\text{-}5\text{-EG}$ (Fig. 1d). At $150 \text{ }^\circ\text{C}$, obvious $\text{AlPO}_4\text{-}5$ -tridymite starts to form. Compared to the as-synthesized $\text{AlPO}_4\text{-}5\text{-TEG}$, the degree of crystallinity of calcined $\text{AlPO}_4\text{-}5\text{-TEG}$ at $150 \text{ }^\circ\text{C}$ is decreased to 78.1%. At $300 \text{ }^\circ\text{C}$, the framework of $\text{AlPO}_4\text{-}5\text{-TEG}$ completely collapses, which is far from 800 or $1000 \text{ }^\circ\text{C}$. These results show that the solvent of TEG has significantly negative influence on the thermal stability of the framework of $\text{AlPO}_4\text{-}5$. Considering that $\text{AlPO}_4\text{-}5\text{-EG}$ and $\text{AlPO}_4\text{-}5\text{-TEG}$ have very similar degree of crystallinity but significant difference in thermal stability, we conclude that the low stability of $\text{AlPO}_4\text{-}5\text{-TEG}$ is not caused by the degree of crystallinity but by the solvent of TEG.

The scanning electron microscopy (SEM) images of $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$, $\text{AlPO}_4\text{-}5\text{-EG}$, and $\text{AlPO}_4\text{-}5\text{-TEG}$ (Fig. S1) with low and high magnification reveal that their morphologies are significantly different from each other. $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$ crystals (Fig. S1a, d) exhibit a rod-like habit with a size distribution of $10\text{--}15 \text{ }\mu\text{m}$, which is a typical morphology for the hydrothermally synthesized $\text{AlPO}_4\text{-}5$. Compared to the crystals of $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$, the crystals of $\text{AlPO}_4\text{-}5\text{-EG}$ (Fig. S1b, e) have a much smaller aspect ratio. The typical crystal size for $\text{AlPO}_4\text{-}5\text{-EG}$ is about $2.5 \text{ }\mu\text{m}$. When the solvent is TEG, aggregated tablet-like crystals were obtained (Fig. S1c, f). Compared to the crystals of $\text{AlPO}_4\text{-}5\text{-EG}$, the aspect ratio of $\text{AlPO}_4\text{-}5\text{-TEG}$ crystals was further significantly decreased, consistent with previous report that poly ethylene glycol (pEG) can significantly decrease the aspect ratio of transition metal substituted $\text{AlPO}_4\text{-}5$ crystals [26].

Thermogravimetric (TG) curves of three $\text{AlPO}_4\text{-}5$ s (Fig. 2) under air atmosphere and the detailed weight losses at different stages summarized in Table S1 clearly show that the physically adsorbed water in $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$ (6.60 wt%), $\text{AlPO}_4\text{-}5\text{-EG}$ (7.18 wt%), and $\text{AlPO}_4\text{-}5\text{-TEG}$ (4.37 wt%) was lost at temperature of $150 \text{ }^\circ\text{C}$. Previous studies showed that the triethylamine in hydrothermally synthesized $\text{AlPO}_4\text{-}5$ is fully protonated and charge balance is achieved through the inclusion of hydroxide ions in the channels [27,28]. Upon heating, deprotonation of the structure-directing agent first occurred, forming triethylamine and eliminating hydroxide ions as water. Further heating results in the progressive loss of ethylene to form lower amines and finally ammonia via sequential Hofmann elimination reactions, which is consistent with the

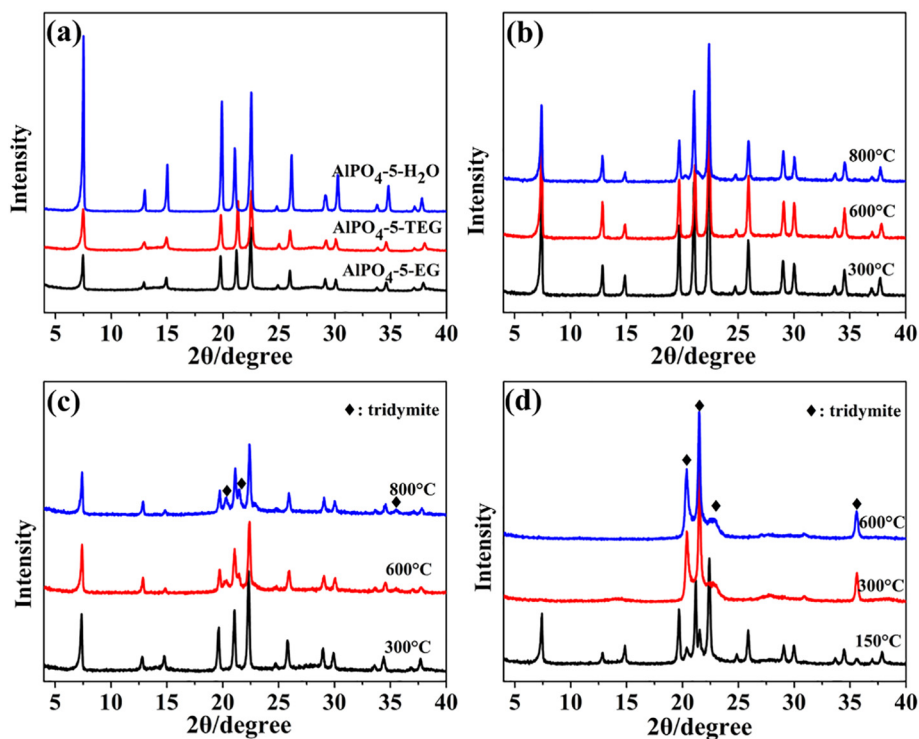


Fig. 1. XRD patterns of $\text{AlPO}_4\text{-}5$ synthesized with solvents of water, EG and TEG (a) and the calcined $\text{AlPO}_4\text{-}5\text{-H}_2\text{O}$ (b), $\text{AlPO}_4\text{-}5\text{-EG}$ (c) and $\text{AlPO}_4\text{-}5\text{-TEG}$ (d) at different temperatures. The marks indicate aluminophosphate version of tridymite.

Download English Version:

<https://daneshyari.com/en/article/7748535>

Download Persian Version:

<https://daneshyari.com/article/7748535>

[Daneshyari.com](https://daneshyari.com)