



Short communication

Unusual bulky solvent molecule encapsulation in the organic-amine-occupied 10-membered ring channels of aluminophosphate molecular sieve AlPO₄-11

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ABSTRACT

Highly crystalline aluminophosphate molecular sieve AlPO₄-11 was synthesized using both water and triethylene glycol (TEG) as solvent. The products were thoroughly characterized by powder X-ray diffraction analyses, thermogravimetric analyses (TGA), scanning electron microscope (SEM) analyses, and solid-state CP/MAS NMR analyses. The results showed that both AlPO₄-11s had high degree of crystallinity and good thermal stability. The AlPO₄-11 synthesized with triethylene glycol had a different morphology from that synthesized with water. Thermogravimetric analysis (TGA) and ¹³C CP/MAS NMR analyses showed that the bulky organic solvent molecules were encapsulated in the organic-amine-occupied channels of AlPO₄-11. This is the first observation that the bulky organic solvent molecules are included in the organic structure-directing agents occupied microporous aluminophosphate molecular sieves. The solvent molecules may act as a co-structure-directing agent in the formation of AlPO₄-11 under solvothermal conditions.

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Zeolites and related microporous crystalline materials with periodic 3D frameworks and well-defined pore structures have been widely used as ion-exchangers, catalysts, and adsorbents [1,2], which are usually produced under hydrothermal or solvothermal conditions. It is proposed that the framework of zeolites and related microporous crystals are formed by assembly of inorganic fragments around structure-directing agent. During the hydrothermal synthesis in which water is used as solvent, it is believed that water can be possibly encapsulated in the organic structure-directing agents occupied channels or cavities of such materials due to its small size.

In 1985, M. P. Dale performed the first solvothermal synthesis of zeolites in which ethylene glycol and propanol were used as solvent [3]. Since then, plenty of zeolites and microporous crystals have been synthesized using various alcohols and other organic solvents [4–9]. Structural analyses showed that the channel or cavity in most of the as-synthesized zeolites and related microporous crystals was almost fully occupied by the organic structure-directing agents. Thus, it is believed or pre-assumed that the bulky organic solvent molecules cannot be included in the solvothermally synthesized zeolites and microporous crystals. Hence, 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 as-synthesized ZSM-12 was suggested according to the blue shift of symmetric and asymmetric Si—O vibration modes in FTIR spectra [10].

Because it was proposed that the formation of zeolites and related microporous crystals was initiated by the assembly of inorganic fragments around organic structure-directing agent [1,11–25], the investigation on if the solvent molecules are included in the channel or cavity of zeolites and related microporous crystals may help us understand whether the solvent acts as a co-structure-directing agent in the formation of zeolites and microporous crystals under hydrothermal and solvothermal conditions.

Aluminophosphate molecular sieves were first reported in 1982 [26, 27], which possess neutral zeolitic open frameworks that are built up from strict alternation of AlO₄ and PO₄ tetrahedra through corner sharing. AlPO₄-11 (IZA code: AEL) was the first batch of AlPO₄ molecular sieve synthesized [26]. The framework of AlPO₄-11 exhibits a unidimensional channel system with 10-membered ring pores with a free diameter of approximately 6.5 × 4.0 Å [28–30]. It is well known that AlPO₄-11 can be synthesized under both hydrothermal and solvothermal conditions in the presence of more than 20 organic amines such as diethylamine, dipropylamine, diisopropylamine, n-butylethylamine,

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and 1,2-bis(4-pyridyl)ethane, the largest one [31,32]. Thus, it would be very interested to learn if the bulky solvent molecules can be encapsulated in the organic amine occupied 10-membered ring channels of aluminophosphate molecular sieve $\text{AlPO}_4\text{-11}$.

In this work, we synthesized the aluminophosphate molecular sieve $\text{AlPO}_4\text{-11}$ with water and triethylene glycol (TEG) as solvents and dipropylamine was used as organic structure-directing agent. The corresponding products were denoted as $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$, respectively. Combining the XRD, TGA, and NMR datas, for the first time, we found that the bulky solvent molecular of TEG can be encapsulated in organic-amine-occupied 10-membered ring channels of $\text{AlPO}_4\text{-11}$.

Fig. 1 shows the simulated powder XRD patterns of $\text{AlPO}_4\text{-11}$ and the experimental ones of as-synthesized $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ and the corresponding calcined samples at different temperatures. The XRD power patterns shown in Fig. 1 indicate that all $\text{AlPO}_4\text{-11}$ s have high degree of crystallinity. Taking $\text{AlPO}_4\text{-11-H}_2\text{O}$ as a reference, the relative degree of crystallinity of $\text{AlPO}_4\text{-11-TEG}$ is 77.72% [33]. Thermal stability studies show that both $\text{AlPO}_4\text{-11-H}_2\text{O}$ (Fig. 1a) and $\text{AlPO}_4\text{-11-TEG}$ (Fig. 1b) can keep intact without collapse towards thermal treatment at 800°C. Compared to the as-synthesized products, the degree of crystallinity of calcined $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ are decreased to 67.39% and 64.03%, respectively. These results show that even though the thermal stability of $\text{AlPO}_4\text{-11}$ synthesized with triethylene glycol as solvent is very good, it is still slightly less stable than that with water as solvent.

The scanning electron microscopy (SEM) images of $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ (Fig. 2) with low and high magnification reveal that their morphologies are different from each other. Crystals of $\text{AlPO}_4\text{-11-H}_2\text{O}$ (Fig. 2a, c) exhibit a sphere-like morphology. A large number of needle like crystals with a size distribution of 2–3 μm measured along *c*-direction are clustered into a sphere about 8 μm . $\text{AlPO}_4\text{-11-TEG}$ (Fig. 2b, d) also appears as spherical shape, but unlike $\text{AlPO}_4\text{-11-H}_2\text{O}$, it has a bigger size of about 20 μm formed by the aggregation of plate-like crystals with a size distribution of 2–3 μm measured along the direction perpendicular to *c*-direction. This phenomenon is consistent with the previous report that alcohols used as co-solvent would affect the morphology of molecular sieves during the synthesis process [34–38].

The TG curves of $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ (Fig. 3) under air atmosphere as well as the detailed weight losses at different stages summarized in Table 1 clearly show that the physically adsorbed water in $\text{AlPO}_4\text{-11-H}_2\text{O}$ (4.33 wt%) and $\text{AlPO}_4\text{-11-TEG}$ (5.19 wt%) is lost at temperature of 150°C. The weight loss of organic part for $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ is 9.35 and 14.11 wt%, respectively, indicating that more organic molecules are included in the channels of $\text{AlPO}_4\text{-11}$ when TEG was used as solvent. This extra weight loss of

organic part might be the solvent of TEG encapsulated in the channels of as-synthesized $\text{AlPO}_4\text{-11-TEG}$.

Fig. 4a shows the ^{27}Al MAS NMR spectra of $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$. There is an intense signal at 36.5 ppm, corresponding to the typical four-coordinated Al of $\text{AlPO}_4\text{-11}$ framework. For the spectra of $\text{AlPO}_4\text{-11-TEG}$, an intense signal at 7.2 ppm is also observed, which is very weak in the spectrum of $\text{AlPO}_4\text{-11-H}_2\text{O}$. This signal is assigned to octahedral Al in unreacted starting material [39–41] or the coordination of water or possibly even the organic alcohol to a tetrahedral Al site in the framework. This issue will be discussed in the following paragraph. ^{31}P MAS NMR spectra of the $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ are shown in Fig. 4b, which give an intense signal at –30 ppm for both products and a shoulder signal at –10.1 ppm for $\text{AlPO}_4\text{-11-TEG}$. The signal at –30.0 ppm can be ascribed to the tetrahedral P in the crystalline framework of highly crystallized $\text{AlPO}_4\text{-11}$ s, whereas the shoulder signal correlates to the unreacted P species, which is consistent with the SEM images.

To clarify the ambiguities on the assignment of the signal at 7.2 ppm in the ^{27}Al MAS NMR spectra of $\text{AlPO}_4\text{-11-H}_2\text{O}$ and $\text{AlPO}_4\text{-11-TEG}$ and shoulder signal at –10.1 ppm in the ^{31}P MAS NMR spectra of $\text{AlPO}_4\text{-11-TEG}$, we carried out the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ heteronuclear correlation (HETCOR) experiments. In the HETCOR spectrum (Fig. 5), only one strong connectivity between the tetrahedral ^{31}P signal (–29.7 ppm for $\text{AlPO}_4\text{-11-H}_2\text{O}$ and –30.2 ppm for $\text{AlPO}_4\text{-11-TEG}$) and the tetrahedral ^{27}Al signal (36.8 ppm for $\text{AlPO}_4\text{-11-H}_2\text{O}$ and 36.2 ppm for $\text{AlPO}_4\text{-11-TEG}$) was observed, corresponding to the final product with $\text{AlPO}_4\text{-11}$ framework. It is noteworthy that the signal at 7.2 ppm in the ^{27}Al MAS NMR spectrum and the signal at –10.1 ppm in the ^{31}P MAS NMR are not observed in the HETCOR spectrum, indicating that the corresponding signal is from the unreacted Al species and unreacted P species, respectively. This result is also consistent with the SEM image with low magnification in Fig. 2.

The above observations in NMR analyses and thermogravimetric analyses prove that the frameworks of $\text{AlPO}_4\text{-11}$ s are well crystallized and the encapsulation of organic solvent molecules in the channels of as-synthesized $\text{AlPO}_4\text{-11-TEG}$ is highly possible, respectively. As stated above, the encapsulation of bulky solvent molecule in the organic amine occupied channels is usually very difficult. In order to obtain a clear confirmation on this issue, we carried out the ^{13}C CP/MAS NMR experiments. In the ^{13}C CP/MAS NMR spectrum of $\text{AlPO}_4\text{-11-TEG}$ (Fig. 6), the signals at 49.7 and 19.3 ppm can be attributed to two methylene groups and the signal at 11.0 ppm is assigned to methyl groups of the protonated dipropylamine, which is consistent with the previous report [42]. However, in addition to the three peaks of the organic template, we also observe that three extra signals at 72.7, 70.4, and 61.2 ppm, which can be attributed to the methylene groups of TEG molecules [43], indicating that the solvent molecules are included into the channel

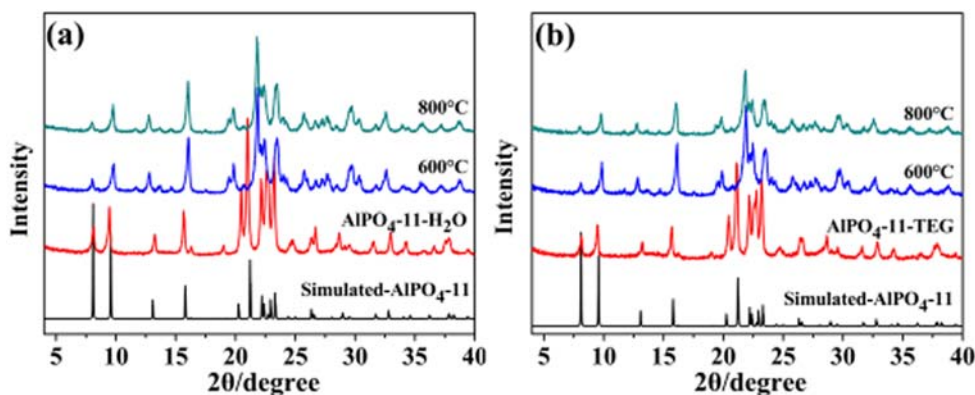


Fig. 1. Simulated powder XRD patterns of $\text{AlPO}_4\text{-11}$ s and the experimental ones of as-synthesized $\text{AlPO}_4\text{-11}$ s with solvents of water and TEG and the calcined $\text{AlPO}_4\text{-11-H}_2\text{O}$ (a) and $\text{AlPO}_4\text{-11-TEG}$ (b) at different temperatures.

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