Investigation of Water Assisted Phase Transformation Process from AlPO₄-5 to AlPO₄-tridymite

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Abstract

Water assisted phase transformation process from crystalized $\text{AlPO}_4\text{-5}$ to $\text{AlPO}_4\text{-tridymite}$ was studied by the combination of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and *in situ* multinuclear MAS NMR. It is found that water first activates the residue amorphous aluminophosphate in crystalized $\text{AlPO}_4\text{-5}$ sample through hydrolysis and condensation reaction. Then the activated aluminophosphate species reassemble into $\text{AlPO}_4\text{-tridymite}$ crystalline. Meanwhile, $\text{AlPO}_4\text{-5}$ transforms into orthorhombic phase during heating process. With further crystallization of $\text{AlPO}_4\text{-tridymite}$, the amorphous phase is gradually consumed, and mass transportation between $\text{AlPO}_4\text{-5}$ and $\text{AlPO}_4\text{-tridymite}$ is established through gradually amorphization of $\text{AlPO}_4\text{-5}$. Finally, most of the $\text{AlPO}_4\text{-5}$ transforms into the thermodynamically stable dense phase $\text{AlPO}_4\text{-tridymite}$.

Keywords: $\text{AlPO}_4\text{-5}$, molecular sieves, *in situ*, multinuclear NMR, phase transformation

1. Introduction

Microporous aluminophosphate materials as zeolite analogues, are a class of important molecular sieves applied in the fields of catalysis, separation, gas storage.[1-4] Since Wilson and co-workers first reported the synthesis of microporous crystalline aluminophosphates, a series of $\text{AlPO}_4\text{-}n$ (n denotes a structure type) with rich structure diversities have been synthesized via hydrothermal, solvent-thermal, and ionothermal synthesis.[5-8] Although many structures have been reported, most of the syntheses are based on trial and error experiment due to the lack of clear understanding the crystallization mechanism involved in the synthesis process.[9] During molecular sieve crystallization process, phase competition governed by both the kinetic and thermal dynamic factors is a common phenomenon.[10-12] Thus, thermal dynamic metastable molecular sieves with large pore size or partially condensed anionic frameworks usually appear during molecular sieve synthesis process. For example, the appearance of VPI-5, $\text{AlPO}_4\text{-}5$, SIZ-2 during $\text{AlPO}_4\text{-}5$, $\text{AlPO}_4\text{-}18$, $\text{AlPO}_4\text{-}11$ synthesis, and even occurrence of phase transformation from $\text{AlPO}_4\text{-}11/\text{AlPO}_4\text{-}5$ to more stable dense phase $\text{AlPO}_4\text{-}tridymite$ have been reported.[13-17] Investigation of phase transformation is very important for us to understand the crystallization mechanism of molecular sieves, because the similarities exist for the inorganic species reassembling into new phases. Until now, most of the investigations are focused on the initial crystallization process to synthesis targeted zeolites where intermediate phase appears, and very few detailed studies on the phase transformation of

isolated crystallized samples by post-treatment except high temperature calcination have been reported.[18-20] Moreover, most of these investigations about phase transformation are performed under *ex situ* condition, lacking of real-time *in situ* information on how the phase transformation occurs at molecular level. Thanks to recent availability of *in situ* high temperature high pressure MAS NMR rotor developed by our group,[21-23] which enables us to conduct *in situ* experiments. Herein, the mechanism associated with a typical phase transformation process from isolated crystallized $\text{AlPO}_4\text{-5}$ to $\text{AlPO}_4\text{-tridymite}$ at the presence of small amount of water was reported and investigated utilizing *in situ* multinuclear MAS NMR combined with powder XRD and SEM.

2. Experimental

2.1. Sample preparation

Aluminum isopropoxide ($\text{Al}(\text{OiP})_3$, Sigma-Aldrich, >98%) and H_3PO_4 (Fisher Scientific, 85%) are the aluminum and phosphorus sources. Triethylamine (TEA, Sigma-Aldrich, >99.5%) was used as template reagent. $\text{AlPO}_4\text{-5}$ molecular sieves were synthesized with the gel composition $\text{Al}_2\text{O}_3\text{:P}_2\text{O}_5\text{:TEA:H}_2\text{O}$ is 1:1.32:1.2:46. Typically, 0.627 g H_3PO_4 was diluted by 2.0 g H_2O , and 0.837 g $\text{Al}(\text{OiP})_3$ was added under magnetic stirring. After stirring for 3 h, 0.239 g TEA was added dropwise, and the mixture was stirred for another 3 h to get a homogeneous gel. Then the gel was transferred into the Teflon-lined stainless steel autoclave, crystallized at 150 °C for 12 h. After crystallization, the solid samples were obtained by centrifugation, and dried under flowing N_2 gas at room temperature.

Phase transformation was conducted at *in situ* MAS NMR rotor. Typically, 0.1 g crystallized $\text{AlPO}_4\text{-5}$ powder and 20 mg H_2O was loaded in the 7.5 mm *in situ* MAS NMR rotor. Then the rotor was sealed for *in situ* MAS NMR investigation at 150 °C. The samples at different stages of phase transformation were obtained under the same *in situ* condition, which is monitored by *in situ* ^{27}Al MAS NMR, and was then extracted from the NMR rotor for XRD and SEM study.

2.2. Characterization

All the X-ray diffraction patterns were collected at a Philip PW3040/00 X'Pert powder X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$), in the 2θ range of 5-50° and scan rate of 1°/min.

SEM images were obtained using the FEI Quanta 200FEG scanning electron microscope, and energy dispersive spectroscopy (EDS) analysis was carried out using this microscope equipped with an X-ray energy analyzer.

In situ ^1H , ^{31}P , ^{27}Al , MAS NMR measurements were carried out on a Varian 300 MHz NMR spectrometer using a 7.5 mm HX MAS probe with a spinning rate of 3.2-3.5 kHz at resonance frequencies of 299.9, 121.4, 78.1 MHz respectively. The varying temperature experiments were conducted by the commercial available heating stack provided by Varian company, and the real temperature in the rotor was calibrated by ethylene glycol.[24]

^1H MAS NMR spectra were recorded using a pulse width 5 μs for a $\pi/4$ pulse, and 32 scans were accumulated for each spectrum with a 5 s recycle delay. Chemical shifts were

referenced to adamantane at 1.82 ppm. ^{31}P MAS NMR spectra were recorded using a pulse width 3 μs for a $\pi/4$ pulse with ^1H TPPM decoupling, and 128 scans were accumulated with 2 s recycle delay. The chemical shifts are externally referenced to 85% H_3PO_4 at 0 ppm. ^{27}Al MAS NMR experiments were acquired using a pulse width 2.25 μs for a $\pi/4$ pulse, 64 scans, and a 1 s recycle delay. The spectra were externally referenced (*i.e.*, the 0 ppm position) to 1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution.

3. Results and Discussion

3.1. XRD

XRD patterns of the crystallized $\text{AlPO}_4\text{-5}$ sample and after different stages of phase transformation are shown in Figure 1. The crystallized $\text{AlPO}_4\text{-5}$ (Figure 1a) shows characteristic hexagonal phase. After heating 420 min (Figure 1b), the peaks of $\text{AlPO}_4\text{-5}$ at 19.9° , 20.9° , 26.2° and 30.2° become broad as the appearance of new peaks near the same position, and significant enhancement of the peak intensity of 22.5° (211) is also observed. These new peaks are attributed to orthorhombic $\text{AlPO}_4\text{-5}$ formed during heating process.[25, 26] This kind of phase transformation from hexagonal to orthorhombic or reverse process was observed in as synthesized $\text{AlPO}_4\text{-5}$ during heating or after calcination process. [25, 26] At the same time, very weak peaks belonging to dense phase $\text{AlPO}_4\text{-tridymite}$ rise at 20.3° , 21.5° , 23.0° and 35.5° . With prolonged heating time after 720 min (Figure 1c), the peak intensities of $\text{AlPO}_4\text{-tridymite}$ are further enhanced, and the broad background of amorphous phase merging under the peaks near $25\text{-}40^\circ$ become inconspicuous. There is no

obvious intensity change of $\text{AlPO}_4\text{-5}$, and the peaks of orthorhombic $\text{AlPO}_4\text{-5}$ at 21.1° , 26.0° , 30.1° and 34.5° become obvious with significant decrease of corresponding peaks of hexagonal phase. These changes mean most amorphous aluminophosphate is crystallized into $\text{AlPO}_4\text{-tridymite}$, and hexagonal $\text{AlPO}_4\text{-5}$ is transformed into the orthorhombic $\text{AlPO}_4\text{-5}$. After heating 1260 min, the remaining peaks are dominated by $\text{AlPO}_4\text{-tridymite}$ with minor residue peaks of $\text{AlPO}_4\text{-5}$. It can be concluded that during heating process as prepared hexagonal $\text{AlPO}_4\text{-5}$ transforms into orthorhombic $\text{AlPO}_4\text{-5}$, and $\text{AlPO}_4\text{-tridymite}$ crystallizes from amorphous aluminophosphate. With prolonged heating process, orthorhombic $\text{AlPO}_4\text{-5}$ transforms into more stable $\text{AlPO}_4\text{-tridymite}$.

3.2. *In situ multinuclear MAS NMR*

In situ ^{27}Al , ^{31}P , and ^1H MAS NMR spectra following the phase transformation process are conducted to get molecular level insights. Figure 2 shows the stacked plot of *in situ* ^{27}Al MAS NMR spectra of the heating samples. Initially, the broad peak at 33 ppm in ^{27}Al MAS NMR spectra are attributed to $\text{AlPO}_4\text{-5}$, while the peak of amorphous phase generally observed near -13 ppm is not obvious due to the broad distribution of ^{27}Al chemical shift in amorphous phases.[27] There is no significant change until a sharp peak rises at 35.8 ppm at about 420 min. At the same time, the obvious spinning sidebands of this new peak rise correspondingly. The strong spinning sidebands indicate this phase has narrower chemical shift anisotropic (CSA) distribution and/or smaller quadrupolar interaction, i.e. the sites are highly ordered (symmetric). This peak can be attributed to four-coordinated aluminum ions

in AlPO_4 -tridymite. By carefully comparing the peak at 33 ppm, it's clearly shown there is no decrease of the signal at 33 ppm, but there is a net increase of the peak at 36 ppm, which explains the corresponding significant increase of total center peak signal intensities (intensities of sidebands were excluded) of ^{27}Al to maximum until 800 min in Figure 5. The increased signal intensities should result from the crystallization of the residue amorphous aluminophosphate, which has broad chemical shift distribution due to the amorphous properties. When the local environments of aluminum become more homogeneous with the formation AlPO_4 -tridymite, the chemical shift distributions decrease significantly. With prolonged heating process, the sharp peak further increases at the cost of the broad peak of AlPO_4 -5. After 800 min, as more AlPO_4 -5 transformed into AlPO_4 -tridymite, the corresponding spinning sidebands increase simultaneously, which result the decrease of center peak signal intensities, as is indicated in Figure 5. At about 1254 min, most of the broad peak near 33 ppm transforms into the narrow peak at 37 ppm. It's worth note there is about 1.5 ppm downfield shift of the peak when the temperature was decreased to room temperature (RT), which presents at 38.5 ppm (see supporting information Figure S1).

^{31}P MAS NMR spectra (Figure 3) show the main peak of AlPO_4 -5 at -29 ppm with broad shoulder at -24 ppm, the broad peak between -10 and -20 ppm is attributed to partially condensed P in amorphous phase, and minor dissolved phosphate complex at -0.2 ppm exchanges with phosphate partially connected with aluminum.[28, 29] After 130 min, the sharp peak at -0.2 ppm change into broad peaks near -7 ppm with enhanced peak

intensity, which is attributed to aluminophosphate complexes/terminal connected phosphate.[29, 30] The upfield shift of the peak means the condensation reaction between Al and P occurs or the exchange between solution phosphate and partial connected phosphate is enhanced. At the same time, the broad peak of amorphous aluminophosphate at -10 to -20 ppm decreases gradually. It means the amorphous phase is activated and their mass transportation between liquid solution is established which is evidenced by the broad -7.0 ppm peak. At same stage, the signal intensity of the $\text{AlPO}_4\text{-5}$ at -29 ppm suddenly jumps to about 2 times, which result in the significant enhancement of total signal intensities (Figure 5). The significant change of signal intensity may result from the pH change of the system altering the Q-factors of the probe during activation of the amorphous phase. After about 430 min, the peak near -7 ppm decrease gradually with the appearance of a new relatively narrow peak at -2.3 ppm, and the broad peak at -29 ppm becomes narrower and shifts to -31 ppm attributed to $\text{AlPO}_4\text{-tridymite}$ with enhanced intensity. The decrease of -7 ppm signal may result from the crystallization of amorphous phase, and thus the exchange of dissolved aluminophosphate phosphate and amorphous phase is decreased, which results in the gradual appearance of relative downfield sharp peak at -2.3 ppm. Thanks to the real time spectral acquisition the change trend can be observed from the initial stage. The corresponding total signal decrease gradually to 80% at 500 min, which may also due to the change of pH value at the opposite trend as the sudden increase of the signal intensities at 130 min. However, after about 800 min, the -2.3 ppm peak gradually

increases, and becomes broad finally stay at -1.7 ppm with the gradual disappearance of broad shoulder peak at -29 ppm, which is due to the gradual amorphization of $\text{AlPO}_4\text{-5}$, and the amorphous phase further transforms into in $\text{AlPO}_4\text{-tridymite}$ simultaneously.

^1H MAS NMR spectra (Figure 4) indicate a broad peak at 7.2 ppm belonging to strong hydrogen bonded proton between protonated amine and aluminophosphate exchanging with water, and the peak shift to downfield continuously to 9.0 ppm at 150 min.[31-33] At the same time, the broad peak near 5.2 ppm becomes distinguishable, which is also attributed to protonated amine as this peak shift to downfield at 6.2 ppm when the temperature is lowered to 25 °C (see supporting information Figure S2). However, the 7.2 ppm peak is more sensitive to temperature, and it disappears when the temperature decreased to room temperature. The peak of water at 3.9 ppm increases initially due to the condensation reaction as the signal intensity of exchanged hydroxyl groups near 4 to 5 ppm decrease simultaneously. The peaks at 3.3, 1.5 ppm, and 2.3, 0.8 ppm are attributed to the proton of methylene and methyl groups respectively in protonated and free trimethylamine. The peak at 0.5 ppm is attributed to AlOH . The decrease of the signal intensity of AlOH initially confirms the condensation reaction between Al and P. The only significant change happens for the peak of water at 3.9 ppm during the whole transformation process, and it disperses into multiple peaks at 420 min. This phenomenon is the same as we observed during $\text{AlPO}_4\text{-5}$ crystallization, as during this process water catalyzed the reassembly of amorphous phase through hydrolysis and condensation reaction, which is confirmed by the

significant changes of the peaks range at 3.5 to 4.1 ppm during 425 to 565 min. Comparing ^{31}P NMR spectra, the ^{31}P peak at -7 ppm and the signal of amorphous phase at -10 to -20 ppm begin to disappear with the peak at -29 ppm shifting upfield, which means the reassembly of amorphous gel to form AlPO_4 -tridymite happens. Indeed, water play a critical role in the formation of AlPO_4 -tridymite, and when the parent sample was heated at 150 °C without adding water, no AlPO_4 -tridymite phase is formed (see supporting information Figure S3). After about 560 min, the signal of bulk water appears again, as excess water is released from the amorphous gel to form crystalline phase. The appearance of bulk water is accompanied with the appearance of the sharp peak at -2.3 ppm in ^{31}P MAS NMR spectra, which is attributed to dissolved aluminophosphate complexes. Finally, though most of AlPO_4 -5 and amorphous phase are transformed into AlPO_4 -tridymite according to the XRD patterns (Figure 1d), the signals belonging to protonated triethylamine remain at 1.5 and 3.3 ppm without significant change of signal intensities, which is reasonable, as the amount of phosphate is excess, and the released TEA in AlPO_4 -5 channel react with the excess phosphate acid. It's worth note most of ^1H MAS NMR peaks don't show significant change. These peaks result from the residue impurities and the crystal defect due to very high sensitivity of ^1H MAS NMR.

3.3 SEM and EDS

The morphology and composition changes during the phase transformation process were followed by SEM and EDS analysis. Figure 6a shows the SEM images of crystallized

parent $\text{AlPO}_4\text{-5}$ sample. The sample shows irregular aggregates, which are mainly composed by small typical rod morphology of $\text{AlPO}_4\text{-5}$ (I) and smooth surface (II). However, the compositions of the typical areas (I, II) are indicated P/Al (atom ratio) =1.1-1.2, which means some amorphous phase with excess phosphate covered the surface, which may exhibit smooth surface. When the sample was heated for 420 min (Figure 6b), the rod $\text{AlPO}_4\text{-5}$ (III) was exposed as amorphous phase is dissolved, the smooth surface disappears and becomes irregular aggregates (IV) with P/Al = 1, these kinds of aggregates are the newly formed $\text{AlPO}_4\text{-tridymite}$. For the sample heated for 720 min, though there is no significant change of XRD patterns of $\text{AlPO}_4\text{-5}$, the rod crystals (V) become smaller, and irregular aggregates of $\text{AlPO}_4\text{-tridymite}$ (VI) dominate with P/Al = 1. Finally, most of rod $\text{AlPO}_4\text{-5}$ diminish and remaining bulk aggregates of $\text{AlPO}_4\text{-tridymite}$ (VII) with P/Al=1 showing smooth surface.

Based on the above analysis, it can be concluded that the phase transformation process is a recrystallization process. The phase transformation is strongly dependent on the environment of the system. As $\text{AlPO}_4\text{-5}$ was crystalized at the same temperature, and no $\text{AlPO}_4\text{-tridymite}$ is formed even with prolonged crystallization time. The isolated crystallized $\text{AlPO}_4\text{-5}$ sample contains mainly hexagonal $\text{AlPO}_4\text{-5}$ and minor amorphous aluminophosphate. With additional water added, hexagonal $\text{AlPO}_4\text{-5}$ transforms into orthorhombic $\text{AlPO}_4\text{-5}$, while the amorphous aluminophosphate transforms into $\text{AlPO}_4\text{-tridymite}$ during heating process. Water plays different roles for the two different

phase transformations. $\text{AlPO}_4\text{-5}$ phase transformation from hexagonal to orthorhombic may result from insufficient water as hexagonal $\text{AlPO}_4\text{-5}$ will change into orthorhombic $\text{AlPO}_4\text{-5}$ when heated without water. However, additional water catalyzes the reassembly of amorphous aluminophosphate to form $\text{AlPO}_4\text{-tridymite}$ as is indicated by the fluctuation changes of -0.2 to -7.0 ppm ^{31}P signal and the peak of water in ^1H spectra. Once most of the amorphous aluminophosphate transforms into $\text{AlPO}_4\text{-tridymite}$, water catalyzes the gradually amorphization of crystalline $\text{AlPO}_4\text{-5}$ and further crystallize into $\text{AlPO}_4\text{-tridymite}$. The gradually recrystallization can be confirmed by no significant change in *in situ* ^1H and ^{31}P MAS NMR spectra after 560 min as it reaches a steady crystallization period.

4. Conclusions

XRD, SEM and *in situ* NMR demonstrate a water assisted phase transformation process from $\text{AlPO}_4\text{-5}$ to $\text{AlPO}_4\text{-tridymite}$ via post-treatment. Initially, water activates the amorphous aluminophosphate in isolated $\text{AlPO}_4\text{-5}$ sample through hydrolysis and condensation reaction. The activated aluminophosphate species reassemble into crystalline $\text{AlPO}_4\text{-tridymite}$. At the same stage, $\text{AlPO}_4\text{-5}$ transform into orthorhombic phase. $\text{AlPO}_4\text{-tridymite}$ further crystalizes with prolonged heating time, when the amorphous phase is consumed, mass transportation between $\text{AlPO}_4\text{-5}$ and $\text{AlPO}_4\text{-tridymite}$ is established through gradually amorphization of $\text{AlPO}_4\text{-5}$. Finally, most of the $\text{AlPO}_4\text{-5}$ transforms into much more stable dense phase $\text{AlPO}_4\text{-tridymite}$.

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Figure Captions

Figure 1. XRD patterns of crystallized $\text{AlPO}_4\text{-5}$ (a) heating at 150 °C with different time in the rotor: b) 420 min, c) 720 min, and d) 1260 min.

Figure 2. Stacked plot of *in situ* ^{27}Al MAS NMR spectra of crystallized $\text{AlPO}_4\text{-5}$ heated at 150 °C. The spinning side bands were labeled with red asterisk.

Figure 3. Stacked plot of *in situ* ^{31}P MAS NMR spectra of crystallized $\text{AlPO}_4\text{-5}$ heated at 150 °C. The spinning side bands were labeled with red asterisk.

Figure 4. Stacked plot of *in situ* ^1H MAS NMR spectra of crystallized $\text{AlPO}_4\text{-5}$ heated at 150 °C. The spinning side bands were labeled with red asterisk.

Figure 5. The corresponding normalized relative total signal intensities of *in situ* NMR spectra.

Figure 6. SEM images of crystallized $\text{AlPO}_4\text{-5}$ (a) heating at 150 °C with different time in the rotor: b) 420 min, c) 720 min, d) 1260 min.

^1H MAS NMR

Graphic abstract