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# Synthesis, characterization and template removal of an iron-containing aluminophosphate molecular sieve with LAU topology

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ABSTRACT

Iron(II)-substituted LAU-zeotype aluminophosphate molecular sieve (denoted as FeAPO-LAU) was synthesized successfully by using imidazole as template in the solvothermal system. The detemplation process was studied to elucidate the stability and microporous characteristics of FeAPO-LAU. *In situ* temperature-dependent X-ray diffraction analyses indicated that the framework of FeAPO-LAU possessed higher thermal stability and maintained the framework integrity until 923 K. The organic templates could be removed by stage-temperature-programmed calcination using lower heating rate in $O_2$ atmosphere, which gave rise to the sample with surface areas of ca. 105 $m^2/g$. $NH_3$-temperature programmed desorption ($NH_3$-TPD) analysis showed that detemplated FeAPO-LAU had a weak acidity. Magnetic measurement revealed that both as-synthesized and detemplated FeAPO-LAU showed antiferromagnetic behaviour.

## 1. Introduction

Zeolites as an important class of inorganic crystalline materials are widely used in the fields of catalysis, adsorption, and gas separation [1]. With the emerging demands of applications, the development of novel zeolitic materials is of great interest [2,3]. Aluminophosphate molecular sieves (AlPOs) with rich structural diversity have become an important family of zeolitic materials since discovered by Wilson et al. in 1982 [4–7]. The structure of AlPOs is constructed by strict alternation of $AlO_4$ and $PO_4$ tetrahedra with an Al/P ratio of 1. The neutral framework and the lack of acidity of AlPOs limit their applications in catalysis. Hence, various heteroatoms are introduced into the framework of AlPOs to partially replace the lattice Al and P atoms, forming heteroatom-containing aluminophosphate molecular sieves (MAPOs, M = heteroatom) with acidic properties and catalytic activities [8–18]. For example, the replacement of $Al^{3+}$ with divalent metal ions (e.g., M = $Mg^{2+}$, $Zn^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Co^{2+}$) will generate negative charge in the framework and enhance the Brønsted acidity, making the MAPOs useful in the oxidative dehydrogenation of hydrocarbons [19–20,21], shape-selective oxyfunctionalization of n-alkanes [22] and isomerizations [23].

The MAPO molecular sieves are typically synthesized under hydrothermal or solvothermal conditions by using organic amines as templates. As a result, the organic templates are occluded in the final structure of as-synthesized product to stabilize the whole structure and balance the negative charge of the framework. Usually, the removal of the organic species is achieved by the calcination via a Hoffman elimination process [24–25,26], giving rise to the MAPOs with free spaces for use in catalysis, adsorption, and so forth. Many factors affect the release of organic templates, such as the M/Al ratio [27–28,29], the crystal size [30], the atmosphere and heating rate of the calcination [31], the nature of heteroatom [32], etc. However, the heteroatom-rich MAPOs (e.g., M/Al > 0.5) [29, 33] are difficult to detemplate by calcination while maintaining the microporosity of the product due to the following reasons: (1) the strong framework-template interaction, i.e., electrostatic, van der Waals and hydrogen-bonding interactions; (2) heteroatoms tend to escape from the framework during the detemplation resulting in the collapse of the inorganic framework. This greatly limits the applications of MAPO molecular sieves. Therefore much effort has been made to study the detemplation process of MAPOs, and develop suitable method to remove the template. For examples, cautious detemplation in vacuum opened the access to the pores of SBE-zeotype transitional-metal substituted aluminophosphates (M = Co, Mn, Mg; Al/M = 1) [27]. The Zn–STA–1 (Al/Zn = 4.5) with SAO zeotype maintained the framework integrity after calcination in ozone-enriched oxygen stream and showed a remarkable performance in the m–xylene isomerization [34].

In 1967, the aluminosilicate $|Ca_4(H_2O)_{16}|[Al_8Si_{16}O_{48}]$ with one-dimensional (1D) 10-ring channels, which has a zeotype LAU topology, was first synthesized by using alkali ions as templates [35]. Since then, the transition metal substituted gallophosphates MeGaPO (Me = Mn, Fe, Co and Zn) with LAU topology were synthesized by using pyridine, imidazole or 1-methylimidazole as templates,

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which had a Ga/M ratio of 2 [36,37] or 3 [38]. Recently, the transitional-metal substituted aluminophosphates MAPO-LAU (M = Co, Mn, Zn) with LAU topology and an Al/M ratio of 2 had been reported [39]. However, all these metal substituted gallophosphates and aluminophosphates could not maintain the structural integrity upon calcination and their frameworks collapse after the complete removal of templates.

In this work, an iron-containing aluminophosphate with LAU topology $|(C_3N_2H_5)_8|[Fe_8Al_{16}P_{24}O_{96}]$ (denoted as FeAPO-LAU) has been solvothermally synthesized by using imidazole as the template. The thermal stability of as-synthesized FeAPO-LAU has been investigated with *in situ* temperature-dependent X-ray diffraction. The removal of template has been conducted carefully using stage-temperature-programmed calcination with lower heating rate in $O_2$ atmosphere. $N_2$ adsorption and $NH_3$-TPD analysis show the calcinated FeAPO-LAU has BET surface areas of ca. 105 $m^2/g$ and a weak acidity.

## 2. Experimental sections

### 2.1. Synthesis of FeAPO-LAU

The compound was synthesized under solvothermal conditions by using imidazole as the template. Typically, iron(II) chloride tetrahydrate (0.524 g) and orthophosphoric acid (1.36 mL, 85 wt%) were first added into triethylene glycol (7.5 mL) and water (1.5 mL) with stirring for half an hour, followed by the addition of aluminum triisopropoxide (1.0 g). The mixture was stirred for 4 h and imidazole (1.683 g) was added to give a gel with overall molar composition of 0.54 $FeCl_2$/1.0 $Al(^iPrO)_3$/4.1 $H_3PO_4$/5.1 imidazole/11.0 triethylene glycol/29.0 $H_2O$. The gel was stirred until it was homogeneous and then sealed in a 25 mL Teflon-lined stainless steel autoclave at 180 °C for 7 days. The colorless tetragonal prism crystals of FeAPO-LAU were washed with water and dried in air at room temperature.

### 2.2. Preparation of detemplated FeAPO-LAU

To eliminate the influence of physisorbed water inside the channels of as-synthesized FeAPO-LAU, finely ground sample was first treated under the vacuum of $10^{-3}$ mbar at 373 K for 3 h. Then the sample was treated under stage-temperature-programmed calcination and gases (ultra high purity grade) with a flow (60 $cm^3\ min^{-1}$) passed parallel to the crystal layer. The sample was first heated from 300 K to $T_1$ at a temperature ramp of 1.0 K/min and kept at $T_1$ for 1.5 h, followed by further heating to $T_2$ at a rate of 0.5 K/min and kept 3 h at this temperature. The $T_1$ temperature in the heating progress was set as 593, 613, 623, and 633 K, whereas $T_2$ temperature was 723, 738, 753, 763 and 773 K, respectively. The twenty calcination runs were carried out and the resulting calcinated sample was designated FeAPO-LAU ($T_1$, $T_2$). In addition, the sample without grinding was also studied to testify whether grinding is essential for the detemplation.

### 2.3. Characterization

X-ray powder diffraction (XRD) data were collected on a Rigaku X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscopy (SEM) image was taken on a JSM-6700F electron microscope operating at 5.0 kV. Thermogravimetric analysis was performed on a Perkin–Elmer TGA7 unit with a heating rate of 10 K/min in air (ultra high purity grade) over a temperature range from ambient to 1073 K. Inductively coupled plasma (ICP) analysis was carried out on Perkin–Elmer Optima 3300 DV ICP instrument. Elemental analyses were conducted on Perkin–Elmer 2400 elemental analyzer. The infrared (IR) spectrum was recorded within the 400–4000 $cm^{-1}$ region on a Bruker-IFS 66 V/S spectrometer using KBr pellets. Temperature-dependent magnetic susceptibility data was recorded on a Quantum-Design MPMSXL SQUID magnetometer. Sample was loaded into gelatine capsules at room temperature and data were collected over the range from 4 to 300 K after cooling the sample in zero applied field (zfc) and cooling under an applied field of 5 kOe. The $^{57}Fe$ powder absorption Mössbauer spectra were recorded on an OXFORD MS-500 instrument with a $^{57}Co/Pd$ source at room temperature with α-Iron foil as a standard.

*In situ* temperature-depended X-ray diffraction experiments were performed under oxygen flux which ensured the same environmental atmosphere with the template removal. Nonisothermal runs were carried out, using a temperature ramp of 5.0 K/min from 323 to 1000 K and adopting an equilibration time 1.0 min at each temperature before starting measurements. Diffraction data were collected with a scan speed of 6°/min at the 2θ region 4°–40°.

$N_2$ adsorption was performed at 77 K on Micromeritics ASAP 2020 instrument. Sample was outgassed at 200 °C for 10 h under He. Liquid nitrogen was used as a coolant over a $P/P_0$ range of 0.00025–1.0. Acidity of calcined sample was characterized by a temperature programmed desorption of ammonia ($NH_3$-TPD), which was performed in a micromeritics AutoChem II 2920 Chemisorption Analyzer with a heating rate of 3 °C $min^{-1}$ from 373 to 873 K.

## 3. Results and discussion

### 3.1. Synthesis and characterization of as-synthesized FeAPO-LAU

Pure sample of as-synthesized FeAPO-LAU was solvothermally synthesized in the reaction mixture of $FeCl_2{\cdot}4H_2O/Al(^iPrO)_3/H_3PO_4$/imidazole/triethylene glycol/$H_2O$ with the molar ratio of 0.5–0.7: 1.0: 3.9–4.1: 5.1: 11.0: 29.0 at 180 °C for 7 days. Many synthetic factors affect the formation of FeAPO-LAU, as shown in Table 1. First of all, the amount of iron is crucial for the crystallization of FeAPO-LAU. The absence of iron ions or Fe/Al molar ratio less than 0.5 in the synthesis result in the formation of a layered aluminophosphate $[C_3N_2H_5]_2[Al_3P_4O_{16}H]$ [40]. When Fe/Al molar ratio is more than 0.7, an iron containing dense phase [41] is obtained. Secondly, the amount of $H_3PO_4$ also influences the phase selectivity of FeAPO-LAU. If $P_2O_5/Al_2O_3$ molar ratio is less than 2.0 in the reaction gel, only an amorphous phase is obtained. Increasing the $P_2O_5/Al_2O_3$ molar ratio to 2.0–2.3 leads to the formation of the open-framework compound FeAPO-CJ50 [42]. Further increasing this value to 2.3–3.2, a mixture of FeAPO-LAU and FeAPO-CJ50 is formed. Pure FeAPO-LAU can be produced when the molar ratio of $P_2O_5/Al_2O_3$ is of 3.9–4.1. In addition, when ethylene glycol, water, or 2-butanol is used as the solvent instead of triethylene glycol, while keeping other conditions unchanged, FeAPO-LAU can not be formed.

Fig. 1 shows the SEM image of the as-synthesized FeAPO-LAU, and large single crystals in the form of tetragonal prism can be

**Table 1**
Molar composition of different synthetic batches[a] and the resulting products.

| $FeCl_2$ | $Al(^iPrO)_3$ | $H_3PO_4$ | Imidazole | Products |
|---|---|---|---|---|
| 0.5–0.7 | 1.0 | 3.9–4.1 | 5.1 | FeAPO-LAU |
| 0–0.5 | 1.0 | 4.0 | 5.1 | Layered $[C_3N_2H_5]_2[Al_3P_4O_{16}H]$ [40] |
| >0.7 | 1.0 | 4.0 | 5.1 | Iron-containing dense phase [41] |
| 0.5–0.7 | 1.0 | <2.0 | 5.1 | Amorphous |
| 0.5–0.7 | 1.0 | 2.0–2.3 | 5.1 | FeAPO-CJ50[42] |
| 0.5–0.7 | 1.0 | 2.3–3.2 | 5.1 | FeAPO-LAU and FeAPO-CJ50 |

[a] Solvent: 11.0 triglycol.