Method for introducing heteroatoms into the framework of FER-type zeolite by intercalation of sub-zeolite of Lamellar precursor PLS-3

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Abstract

A method for introducing heteroatoms Al, Ti, and Sn into the framework of FER-type zeolite was provided. The incorporation of heteroatoms was achieved by intercalation of sub-zeolite of lamellar precursor PLS-3 that possessed disordered structure along layered direction using 4-amion-2,2,6,6-tetramentylniperidine together with salts containing a heteroatom. During intercalation, the molar ratio of Si and heteroatoms can be adjusted between 30 to ∞. Heteroatoms entered the material with the help of hydrothermal synthesis conditions used in the intercalation process, resulting in reordered layered metalosilicate structure. After mild acid treatment of these metalosilicates to remove extra-framework heteroatoms and further calcination, we obtained a three-dimensional zeolite of FER topology with framework Al, Ti, and Sn.

1. Introduction

Zeolites containing heteroatoms are a kind of functionally heterogeneous catalyst that can be used in a variety of industrial processes due to the heteroatom active sites they possess [1–3]. Many studies have been conducted on the application of metalosilicate zeolites, for example, aluminosilicate zeolites can be used for cracking [4], isomerization [5], and alkylation [6]; titanosilicate zeolites can be used for ammoximation [7] and epoxidation [8]; stanosilicate zeolites can be used for Baeyer-Villiger oxidation [9], Meerwein-Ponndorf-Verley reduction [10], isomerization of glucose to fructose [11], convert glyceraldehyde to alkyl lactates [12], and activate carbonyl groups efficiently [13]. Therefore, to further broaden the application of metalosilicate zeolites and create innovative heterogeneous catalysts with outstanding catalytic performance, it is critical to investigate a way of introducing heteroatoms into the framework of zeolites.

There are several methods for preparing zeolitic structures with heteroatoms, including direct hydrothermal synthesis and post-treatment modification [14]. The original synthetic systems of some zeolites already contain heteroatoms for direct hydrothermal synthesis; in fact, this is the case with many common aluminosilicate zeolite structures such as ZSM-5 [15], Beta [16], and FAU [17]. However, in intrinsic synthetic systems, heteroatoms are generally solitary, and the number of heteroatoms is likewise restricted [18]. Hydrothermal synthesis of heteroatom zeolites may also be achieved by adding heteroatoms and crystallization additives to the pure silicon synthesis system. However, because the ionic radius of heteroatoms differs from that of Si⁴⁺, it is difficult for heteroatoms to enter the zeolite framework. Furthermore, the inclusion of heteroatoms will result in a decrease in crystallinity or a phase change [18]. Post-treatment modification, on the other hand, is a rather easy process. Heteroatoms can be introduced by gas–solid or liquid–solid post-treatment [19]. In most cases, the materials must be pretreated to create vacancies that will allow the incorporation of heteroatoms. The process of creating vacancies usually causes damage to the structure of the material and reduces its stability; hence, acceptable conditions for this process must be found.

The zeolite of FER topology is composed of ferrierite sheets with unique 10 rings (10-R) intersected by 8-R two-dimensional channel system. Its Al-containing materials have already been proven to be an efficient...
Bronsted acid heterogeneous catalyst for 1-butene isomerization, and the unique pore system played an important role in its excellent catalytic activity in this reaction [20–22]. The synthesis of Al-containing FER zeolites has long been studied. It can be accomplished in an inorganic system using alkali cation to assist crystallization [23], transformation from layered precursor RUB-36 with CDO topology [24], or employing organic molecules as the structure-directing agents [25]. However, the adjustable range of Al content in aluminosilicate prepared by this technique is narrow, limiting the application of the material. There have also been reports on layered precursors of FER topology [26, 27]. However, all of these FER-type layered materials have rather broad morphology that is adverse for catalysis.

PLS-3 is a layered precursor of FER topology with a nanometer-scale crystal size of 50–150 nm [28]. The layered structure provides modifiability of the material, whereas the smaller crystal size enhances substrate diffusion during the catalytic reaction. Al-PLS-3, its Al-containing material, has previously been shown to be an effective catalyst for the isomerization of 1-butene [29]. However, the Si/Al ratio of Al-PLS-3 synthesized by this method cannot be less than 50; otherwise, the heterocrystals Beta would form. As a result, more research into the post-treatment approach of introducing heteroatom Al into PLS-3 is still required. Furthermore, if we can discover a way to incorporate other heteroatoms into the framework of PLS-3, we may be able to create novel heterogeneous catalysts with superior catalytic performance.

In this paper, we present a method for preparing FER-type zeolite containing framework heteroatoms Al, Ti, and Sn. We started with a sub-zeolite of layered zeolite PLS-3 that has a disordered structure along a layered direction. Intercalation of sub-PLS-3 with 4-amion-2,2,6,6-tetrametyliperidine and salts containing the appropriate heteroatom resulted in the introduction of Al, Ti, and Sn atoms. The disordered structure of the sub-zeolite made its interlayer structure more open, which assisted in the contact and entry of heteroatoms during the hydrothermal synthesis conditions of intercalation, and a 4-amion-2,2,6,6-tetrametyliperidine molecule inserted between the layers of sub-PLS-3, resulting in a reordered layered metasilicate structure. Extra-framework heteroatoms were also found in the resultant material, which may be eliminated by mild acid treatment. We may obtain a three-dimensional zeolite with FER topology and framework heteroatoms after calcination. UV–vis, vacuum infrared, pyridine adsorption, and 27Na NMR were used to characterize the state of the active sites of the products.

2. Experimental information

2.1. Preparing of pure silica PLS-3
Layered silicate PLS-3 was prepared according to the reference [28]. H-kaemite, TEAOH (25 wt% water solution), NaOH, and H2O were mixed uniformly (1.0 SiO2:0.04 NaOH:0.2 TEA+ :6.5 H2O in molar ratio). The starting mixture was reacted in a Teflon-lined autoclave at 443 K for 1 d. PLS-3 was obtained after filtering and washing with 200 ml of deionized water.

2.2. Sub-PLS-3
PLS-3 was post-treated for 30 min at 443 K in 1 M HCl aqueous solution with S:L = 1:30 [30]. We obtained Sub-PLS-3 with disordered structure along the layered direction after filtering and washing with 200 ml deionized water.

2.3. Al, Sn, or Ti-containing PLS-3
Sub-PLS-3 was treated in an aqueous solution of 4-amine-2,2,6,6-tetramethylpiperidine with Al, Sn, or Ti salts (SiO2:SiDEA:Al(NO3)3:9H2O, SnCl4:5H2O, or Tetraethyl titanate:H2O = 1:0.5:1/30–1/70:25 in molar ratio) for 20 h at 443 K. The product was filtered, washed with 500 ml deionized water, and dried for 24 h at 353 K to yield Intercalated-Al, Sn, or Ti-PLS-3-n, where n denotes the proportion of Si and heteroatom in the initial mixture. Pure silica intercalated material prepared without the addition of salt containing heteroatoms according to the method given above named Intercalated-PLS-3. The resultant material was then post-treated for 5 h at 333 K in 0.125 M HCl/H2O solution (S:L = 1:30). After filtering, washing with 500 ml deionized water, drying at 353 K for 24 h, and calcining at 823 K for 6 h, we obtained Al, Sn, or Ti-PLS-3-n with three-dimensional structure, where n denotes the proportion of Si and heteroatom in the initial mixture. Before active site characterization, all Al-containing materials required ammonium exchange. Conditions for ammonium exchange: Al-containing samples were stirred in 1 M NH4Cl solution for 2 h (S:L = 1:50, 3 times) and then calcined at 773 K for 5 h to generate the H+-form materials.

2.4. Characterization
The type of x-ray diffractometer was Χ’Pert PRO MPD (Cu-Kα radiation, λ = 1.5405 Å). The type of SEM instrument was Quanta200 microscope. N2 adsorption measurements were carried out on a BEL-MAX gas/
vapor adsorption instrument at 77 K (All the samples were evacuated at 573 K for 10 h before characterization). The $S_{BET}$ and $V_{total}$ were calculated by the Brunauer–Emmett–Teller method. UV–vis spectra were carried out on a PerkinElmer Lambda 35 spectrophotometer (190–500 nm, interval of 2 nm). The type of FT-IR instrument was Nicolet Nexus 670 (absorbance mode, resolution 4 cm$^{-1}$). Samples were pressed into self-supported wafer (4.8 mg cm$^{-2}$) and set in a quartz cell sealed with CaF$_2$ windows to connect to vacuum system (723 K, 2 h). Pyridine adsorption spectra were taken by exposing the evacuated wafer to a pyridine vapor at 298 K for 0.5 h. Then the adsorbed pyridine was evacuated at different temperatures from 423 to 723 K (1 h). Spectra were collected after the samples cool to room temperature.  

$^{27}$Al solid-state MAS NMR spectra were given by a VARIAN VNMRS-400WB equipment, chemical shift reference material was KAl(SO$_4$)$_2$$\cdot$12H$_2$O. Al, Sn, and Ti content was tested by ICP on a VISTA-MPX atomic emission spectrometer.

3. Results and discussion

The XRD patterns of PLS-3, sub-PLS-3, and intercalated structures are shown in figure 1(A). PLS-3 precursor shows good crystallinity, and the peak positions of characteristic diffraction match those reported in the literature [28]. The long-range order of the PLS-3 structure is lost after short-time acid treatment. The diffraction peak intensity of sub-PLS-3 is decreased, and its shape is also broadened, indicating that its structure has partially collapsed. This result was caused by the partial removal of organic molecules occluded between the layers during acid treatment [30]. Sub-PLS-3 has a disordered structure along the layered direction, resulting in more exposed surface area. The structure of sub-PLS-3 is reformed after intercalation with 4-amine-2,2,6,6-tetramethylpiperidine as organic molecules entered between the layers, yielding a new layered precursor with an ordered structure (figure 1(c)). The structure of the product will not change if we introduce heteroatoms through metal salts during intercalation (figures 1(d)–(f)). Resultant crystallinity does not change significantly, indicating that the addition of heteroatoms does not affect the intercalation process. The diffraction pattern shows no heterocrystalline peaks, indicating that the introduced heteroatoms do not exist as aggregates. The XRD patterns of intercalated materials after calcination are similar to those of PLS-3 (figure 1(B)), indicating that the intercalated derived lamellar precursors have FER topology.

The amount of heteroatoms introduced can be varied over a relatively wide range. The XRD patterns of intercalated materials prepared with different amounts of heteroatoms are shown in figure S1 (available online at stacks.iop.org/MRX/9/055001/mmedia). They all exhibit intense and sharp peaks, indicating high crystallinity. This behavior suggests that the amount of heteroatoms introduced by this method may be regulated. There has been a report on the direct addition of Al atoms into the PLS-3 synthetic system to prepare its Al-containing materials; however, the Si/Al ratio of the initial mixture cannot be less than 50; otherwise, heterocrystalline Beta would occur [29]. As a comparison, we also conducted direct addition of Sn or Ti atoms into the PLS-3 synthetic system to prepare its corresponding Sn or Ti-containing materials (figure S2). However, the crystallinity of the resulting products was very poor. This finding indicates that our strategy of introducing heteroatoms via intercalation is relatively efficient.

SEM was used to characterize the crystalline morphology of the materials. Figure 2 shows the SEM images of PLS-3 and its modified samples. The intercalation samples exhibit the same crystalline morphology as the original sample PLS-3. The intercalated materials have a uniform morphology with no amorphous phase. This finding suggests that the intercalation products have excellent crystallinity, and that throughout the intercalation
process, only organic molecules inserted between the layers of sub-PLS-3 and the heteroatoms enter into the laminates; no recrystallization occurs.

The state of the active sites introduced into the materials was then characterized using appropriate methods. The UV–vis spectra of Intercalated-Sn-PLS-3–50 and Intercalated-Ti-PLS-3–50 are shown in figure 3(A). They all exhibit the main characteristic peaks of tetra-coordinated metal ions at 210 nm, as well as the characteristic peaks of hexa-coordinated metal ions at 260 nm. This result implies that in intercalated Sn or Ti-containing materials, there exist not only tetra-coordinated framework heteroatoms but also hexa-coordinated extra-framework heteroatoms [31–33]. Using $^{27}$Al NMR, we were able to characterize the state of heteroatoms in Al-containing materials. Figure 3(B) depicts the $^{27}$Al NMR spectrum of Intercalated-Al-PLS-3–50, which, similar to Sn and Ti-containing materials, has a framework Al peak at 54 ppm and a non-framework Al peak at 0 ppm. According to literature [6], non-framework heteroatoms can harm the catalytic performance of catalysts; thus, we need to find a way to remove them.

Acid treatment has been proven to be effective for removing the non-framework heteroatoms from zeolites [31]. However, the framework heteroatoms will also be eliminated as well during the acid treatment. As a result,
to prevent the loss of framework active sites, we should adopt mild acid treatment conditions with low concentration and low temperature. We treated as-prepared Intercalated-Sn, Ti, and Al-PLS-3–50 samples with 0.125 M HCl/H2O solution for 5 h at 333 K. Following additional calcination, the resultant materials were characterized. The UV–vis spectra of Sn and Ti-PLS-3 following acid treatment and calcination are shown in figure 4(A). The absorbance at 260 nm associated with the hexa-coordinated non-framework heteroatoms vanishes for both of them, indicating that extra-framework Sn and Ti atoms are successfully removed. According to ICP analysis, the heteroatom content in Sn and Ti-containing materials decreased by 20% and 21%, respectively (table S1). This suggests that acid treatment also results in the loss of active sites while eliminating non-framework heteroatoms. The Ti active sites were also characterized by FT-IR (figure 4(B)), and Ti-PLS-3–50 exhibits an obvious absorbance at 960 cm$^{-1}$, demonstrating the presence of tetra-coordinated Ti ions. Pyridine adsorption was used to identify the Lewis acid sites in Sn-containing materials. Sn-PLS-3–50 exhibits characteristic absorbance at 1490 cm$^{-1}$ for both Lewis and Bronsted acid sites, 1450 cm$^{-1}$ for Lewis acid sites, and 1600 and 1440 cm$^{-1}$ for hydrogen-bonded pyridine, as shown in figure 5(A(b)). The presence of Lewis acid sites can be used to prove the presence of framework Sn atoms. The material after acid treatment Al-PLS-3–50 has only tetra-coordinated framework Al atoms, according to the $^{27}$Al NMR spectra (figure 3(B)), since it exhibits only one characteristic signal at 54 ppm. Vacuum infrared and pyridine adsorption were also used to characterize the state of Al active sites. The vacuum infrared spectrum of Al-PLS-3–50 exhibits an obvious absorbance at 3600 cm$^{-1}$, which is attributed to the presence of Bronsted acid sites (figure 5(B)). Bronsted acid sites in aluminosilicate zeolites are created by a charge imbalance caused by the introduction of framework Al atoms in a tetra-coordinated state. The negative charge on the framework of zeolites caused by the introduction of tetra-coordinated Al atoms must be balanced by protons, resulting in the formation of Bronsted acid sites. Thus, the appearance of the characteristic peak at 3600 cm$^{-1}$ may be used to indicate the incorporation of tetra-coordinated Al atoms by intercalation. Pyridine adsorption was used to assess the acid sites of Al-containing materials after acid treatment. Unlike Sn-PLS-3–50, Al-PLS-3–50 exhibits another characteristic peak at 1540 cm$^{-1}$ that is attributable to Bronsted acid sites except for Lewis acid sites and hydrogen-bonded pyridine.

Figure 4. (A) UV–vis spectra of Sn-PLS-3–50 (a) and Ti-PLS-3–50 (b). (B) FT-IR spectra of Intercalated-PLS-3 (a) and Ti-PLS-3–50 (b).

Figure 5. (A) FT-IR spectra of pyridine adsorbed on Intercalated-PLS-3 (a), Sn-PLS-3–50 (b), and Al-PLS-3–50 (c). (B) Vacuum infrared spectra of Intercalated-PLS-3 (a) and Al-PLS-3–50 (b).
Figure 5A(c), showing the presence of both Brønsted and Lewis acid sites in the Al-containing materials. According to the ICP analysis (table S1), acid treatment results in a 31% reduction of Al content.

Figure S3 gives N₂ adsorption isotherms of calcined pure silicon intercalation material Intercalated-PLS-3 together with calcined acid-treated heteroatom-containing intercalated material Sn-PLS-3–50, Ti-PLS-3–50, and Al-PLS-3–50. From the perspective of adsorption isotherms, the introduction of heteroatoms did not affect the structure of the material, since their N₂ adsorption isotherms are almost uniform. The textural property S_{BET} and V_{total} of these heteroatom-containing materials are also at the same level without significant change (see table S1).

Figure 6 shows a schematic diagram of the process of introducing heteroatoms into FER-type zeolite by intercalation. As illustrated, the sub-zeolite must first be prepared with a more open interlayer structure by a short-time high-temperature acid treatment. The sub-zeolite is then intercalated using 4-amion-2,2,6,6-tetrametylperidine together with salts containing a heteroatom; the heteroatoms can insert into the framework of sub-PLS-3 using hydrothermal synthesis conditions of intercalation. We obtained zeolites with FER topology, Sn, Ti, or Al-PLS-3, with framework heteroatoms as active sites after mild acid treatment of the intercalated materials to remove extra-framework heteroatoms and further calcination.

4. Conclusions

The methodology for incorporating framework atoms Al, Ti, and Sn into FER-type zeolites is provided. The introduction of heteroatoms was conducted by intercalation using 4-amion-2,2,6,6-tetrametylperidine together with salts containing heteroatom of sub-PLS-3 that was a post-modified material of lamellar precursor PLS-3. Sub-PLS-3 has a disordered structure along the layered direction, which favors the incorporation of heteroatoms during intercalation by hydrothermal synthesis. The three-dimensional zeolite of FER topology with framework heteroatoms was thus prepared after mild acid treatment of these metalosilicates generated by intercalation. This method may be extended to another sub-zeolite to obtain new types of zeolites with heteroatoms as active sites.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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References

[1] Davis M E 2002 Nature 417 813
[2] De Baerdemaeker T, Gies H, Yilmaz U, Feyen M, Xiao F S, Zhang W, Yokoi T, Bao X and De Vos D E 2014 J. Mater. Chem. A 2 9709
[3] Bian C, Wu Q, Zhang J, Pan S, Wang L, Meng X and Xiao F S 2015 J. Energy Chem. 24 642
[4] Zhao Y, Ye Z Q, Zhang H B, Zhang Y H and Tang Y 2019 Ind. Eng. Chem. Res. 58 13174
[5] Ushiki R, Akada Y and Matsukata M 2018 Chem. Lett. 47 1428
[6] Cundy C S and Cox P A 2003 Chem. Rev. 103 663
[7] Nie X W, Ren X X, Ji X J, Chen Y G, Janik M J, Guo X W and Song C S 2019 J. Phys. Chem. B 123 7464
[8] Li Y and Yu J H 2014 Chem. Rev. 114 7268
[9] Silva L L, Cardoso D, Sievers C and Martins I 2020 J. Phys. Chem. C 124 2439
[10] Kots P A, Zabilnik A V, Khramov E V, Grigoriev Y V, Zubavichus Y V and Ivanova I I 2018 Inorg. Chem. 57 11978
[11] Moteki T, Nakada D, Murakami Y, Moriyama S and Okubo T 2014 J. Phys. Chem. C 118 23664
[12] Ji X Y, Wang Y N, Fujii T, Otomo R, Kondo J N and Yokoi T 2019 Chem. Lett. 48 1130
[13] Yang B T, Cui T X, Zhou Y Y, Chen H M and Qin J H 2020 Mater. Res. Express 7 045501