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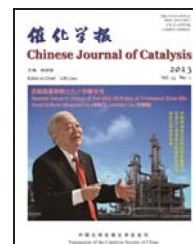
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Article

Preparation and formation mechanism of Al-YNU-1 using highly acid-treated Fe-YNU-1 molecular sieve as a silica source

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ABSTRACT

Al-YNU-1 molecular sieve was synthesized through the post-synthesis method from highly acid-treated Fe-YNU-1 in the presence of piperidine. The effects of silica sources, structure-directing agents, composition of raw materials, and crystallization conditions on the structure and Al content of Al-YNU-1 were investigated. Optimizing the Al and H_2O amounts in the synthesis mixture, as well as the crystallization time and the acid treatment conditions applied to the as-synthesized lamellar precursors, produced a large increase in the content of Al in the Al-YNU-1 framework, to nearly double that of a sample prepared using deborated MWW as the silica source. To form Al-YNU-1, it is essential to remove most of the template molecules and framework Al species from the lamellar Al-MWW precursor by acid treatment, and to have a large number of defect sites within the Si source.

1. Introduction

MCM-22 zeolite has a unique layered crystal structure, containing two independent non-intersecting pore systems accessible via 10-MR openings [1]. One system comprises two-dimensional sinusoidal channels with uniform, intralayer 10-MR openings throughout the structure, and the other system is formed by a series of supercages, 0.71 nm × 0.71 nm × 1.82 nm, accessible through the elliptic interlayer 10-MR windows. Such a pore system provides interesting structural characteristics, having potential applications in catalytic reactions like benzene alkylation [2], alkane cracking [3], isomerization [4,5], aromatization [6], and the conversion of methanol to hydrocarbons [7]. Nevertheless, the pore openings of MCM-22 are still not large enough to allow processing of bulky reactants. Much work has been done to improve the catalytic performance of MWW zeolites for large molecules by modifying the

pore systems through delaminating and pore expanding.

Because of the flexibility and structural diversity of layered zeolites, the precursor MCM-22 can be delaminated or interlayer pillared to obtain more accessible active sites in the interlayer supercages. By swelling the lamellar precursor with surfactant and then pillaring the layers with SiO_2 species, MCM-36 was synthesized by researchers at Mobil [8]. Compared with MCM-22, MCM-36 has larger interlayer pore openings, and shows potential for applications in the transformation of bulky reactant molecules. Corma et al. [9] developed a new delaminated material, ITQ-2, with a single layered sheet structure, by swelling and ultrasonic delaminating. ITQ-2 zeolite has a well-defined external surface area, and exhibits high catalytic activity in gasoline cracking. However, its hydrothermal stability is insufficient for practical application in industry, because of structural degradation. Recently, Fan et al. [10,11] proposed a new strategy to expanded the interlayer space from 10-MR to

12-MR by treating the MWW precursor in a hot acid solution to prepare YNU-1 zeolite. The new interlayer expanded zeolite Al-YNU-1 shows excellent catalytic performance in alkylation and acylation of anisole. However, the framework Al content of the zeolite prepared in this way was very low. On the other hand, through regulating the acid treatment and silylation of the MWW precursor, Wu et al. [12–14] and Inagaki et al. [15] obtained Al-YNU-1 with high framework Al content. However, this method also gave rise to a large amount of extra-framework Al species and Lewis acidic sites, which led to poor selectivity for certain reactions. In contrast, the expanded Al-YNU-1 synthesized by the methods of Fan et al. [11] had few Lewis acidic sites, and the ratio of strongly acidic sites to weakly acidic sites was up to 18, with gave this material unique catalytic performance in certain reactions. Nevertheless, it is still a great challenge to find a more effective way to prepare YNU-1 with a higher framework Al content.

In this work, Al-YNU-1 molecular sieve was synthesized through the post-synthesis method from highly acid-treated Fe-YNU-1 in the presence of piperidine. The effects of silica sources, structure-directing agents (SDA), composition of raw materials, and crystallization conditions on the structure and Al content of Al-YNU-1 were investigated. The synthesis mechanism was discussed based on characterization of the Al-MWW samples at different synthesis stages.

2. Experimental

2.1. Zeolite preparation

Al-MWW(P) was prepared using a post-synthesis method. Deborated MWW (DeB-MWW) or highly acid-treated Fe-YNU-1 (DeFe-YNU-1, used as the silica sources for the synthesis of Al-YNU-1) were synthesized by refluxing B-MWW or Fe-MWW samples in HNO_3 solution [10,16]. The silica source, Al source (aluminum isopropoxide), structure-directing agent (piperidine, PI or hexamethyleneimine, HMI), ammonium hydroxide (25 wt%), and distilled water were mixed and stirred at room temperature for 2 h until a homogeneous phase was obtained. The molar compositions of the gels were within the range SiO_2:

$(0–0.025)Al_2O_3$:$1.4PI$:$0.15NH_4OH$:$(7–30)H_2O$. After that, the gel was transferred to a Teflon-lined steel autoclave and rotated (20 r/min) at 150 °C for 1–7 d. The solid product of the precursor Al-MWW(P) was then treated in HNO_3 solution (100 ml liquid per g solid) under different temperatures and for different times. Subsequently, the solid Al-YNU-1 samples were then washed, dried, and calcined at 550 °C for 6 h. The obtained samples were named Al-YNU-1-x(B) or Al-YNU-1-x(Fe), where x was the ratio of Si/Al in gel. For comparison, a reference sample was also obtained through direct calcination of Al-MWW(P).

2.2. Characterization

X-ray diffraction patterns (XRD) were recorded on a Rigaku MiniFlexII X-ray diffractometer with Cu K_α radiation at 30 kV and 15 mA. Nitrogen physisorption measurements were performed at – 196 °C with a BELSORP-max instrument. Thermogravimetry and differential thermal analysis (TG/DTA) curves were acquired on a Rigaku Thermo plus Evo TG 8120 instrument under air atmosphere at a heating rate of 10 °C/min. FT-IR spectra was measured on a Bruker Tenson 27 spectrometer with a situ quartz cell. Self-supporting wafer (30 mg) was prepared and activated at 500 °C for 2 h under vacuum. After cooled to room temperature, the FT-IR spectra of the silanol groups were recorded.

3. Results and discussion

3.1. Al content

Figure 1 shows XRD patterns of as-synthesized Al-MWW(P), acid treated and further calcined samples obtained from synthesis gels having different Si/Al ratios (Si/Al = 20–70). These samples were synthesized with DeB-MWW as the Si source and hydrothermally crystallized at 150 °C for 1 d. The silica source, DeB-MWW, exhibits a typical 3D MWW structure (Fig. 1(a)). After crystallization, two new diffraction peaks at 2θ values of 3.3° and 6.5° appear in the XRD patterns of the precursors (Fig. 1(a)), suggesting that the 3D MWW structure has been changed to a 2D MWW layered structure in the present of PI as the SDA.
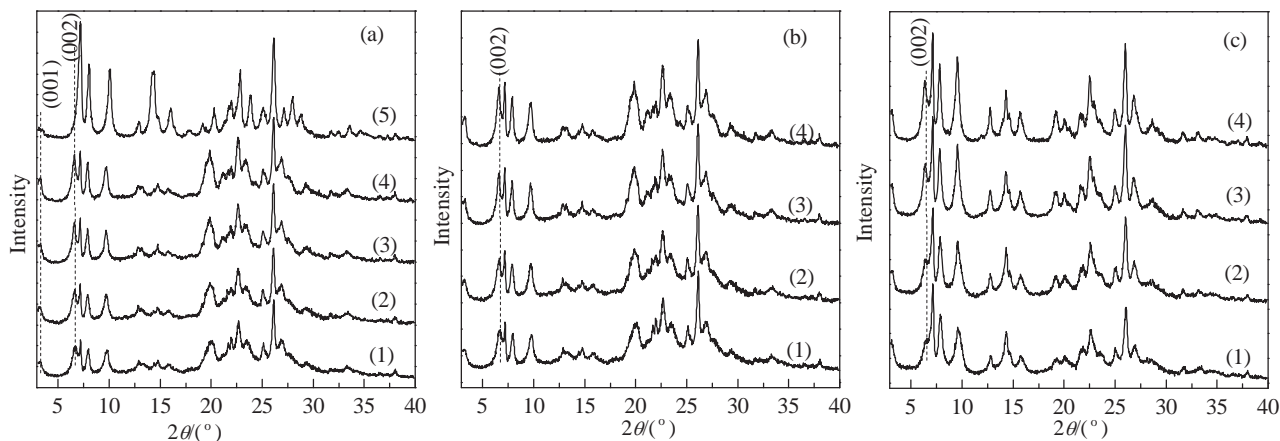

Fig. 1. XRD patterns of as-synthesized (a), acid-treated (b), and further calcined (c) samples obtained from synthesis gels having different Si/Al ratios. (1) Si/Al = 20; (2) Si/Al = 25; (3) Si/Al = 40; (4) Si/Al = 70; (5) DeB-MWW.

Table 1
Physical properties of Al-YNU-1 samples obtained from synthesis gels with different Si/Al ratios.

Sample	A_{BET}/(m²/g)	A_{ext}/(m²/g)	V_m/ml	Si/Al (ICP)
Al-YNU-1-20(B)	483	171	0.13	183
Al-YNU-1-25(B)	474	188	0.14	220
Al-YNU-1-30(B)	512	121	0.19	275
Al-YNU-1-40(B)	526	104	0.20	317
Al-YNU-1-75(B)	520	110	0.19	630

When HMI is used as the SDA in the synthesis of MWW precursor, our previous work suggested that a crystallization time of 4 d is necessary to obtain a 2D MWW layered structure [11]. This suggests that the smaller PI template molecule can be more easily inserted into the MWW interlayer to expand the interspaces under the crystallization conditions used here. After acid treatment, the layered structure is preserved (Fig. 1(b)). After further calcination at 560 ℃, the gel with Si/Al ratio of 20 gives a 3D Al-MWW structure, while the gels with higher Si/Al ratios have formed Al-YNU-1 (Fig. 1(c)). Moreover, the (002) line intensity increases with increasing Si/Al ratio in the synthesis gel.

Table 1 lists the physical properties of Al-YNU-1 samples obtained from synthesis gels with different Si/Al ratios. With increasing Si/Al ratio in the gel, the special surface area and micropore volume of the resultant Al-YNU-1 samples also clearly increase. Moreover, the Si/Al ratio of Al-YNU-1 is higher than that of the synthesis gel. These mean that the acid treatment removes a large amount of Al atoms from the precursor, allowing it to form Al-YNU-1 upon calcination [11].

3.2. Silica source and crystallization time

Previous work has shown that the YNU-1 structure does not form even with a crystallization time of 6 d when preparing Fe-YNU-1 through the post-synthesis method. However, properly prolonging the crystallization time can promote the incorporation of the heteroatom into the framework of molecular sieves [11,16]. In this work, DeB-MWW and DeFe-YNU-1 samples were used as the silica sources to synthesize YNU-1, and the XRD patterns of the samples obtained using different
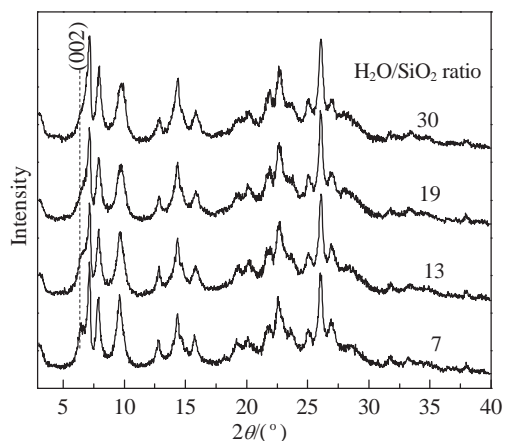

Fig. 3. XRD patterns of Al-YNU-1 samples synthesized from synthesis gels having different H_2O/SiO_2 molar ratios.

crystallization times are compared in Fig. 2. With DeB-MWW as the Si source, the structure of Al-YNU-1 is obtained when the crystallization time is 2 d (Fig. 2(a)). With increasing crystallization time to 4 d, the (002) line shifts gradually to higher angle, and merges with the (100) line, implying that the 3D Al-MWW structure has formed. When DeFe-YNU-1 is used as the silica source, the (002) line is clearly observed when the crystallization time is 2 d and changes little when the crystallization time is prolonged to 4 d. Furthermore, the Si/Al ratio of Al-YNU-1 using DeFe-YNU-1 as the Si source and a crystallization time of 4 d is 118, about half that of the Al-YNU-1(B) sample with DeB-YNU-1 as Si source crystallized for 1 d. All these results suggest that high framework Al content can be obtained in Al-YNU-1 by using DeFe-YNU-1 as the silica source.

3.3. H₂O content

The effect of H₂O content on the quality of Al-YNU-1 structure was investigated for gel compositions of SiO_2:0.02Al_2O_3: 1.4PI:0.15NH_4OH:(7–30)H_2O. The XRD patterns of the obtained Al-YNU-1 samples are shown in Fig. 3. The H₂O content has a significant effect on the formation of the Al-YNU-1 structure. With a H_2O/SiO_2 molar ratio of 7 in the synthesis gel, a well
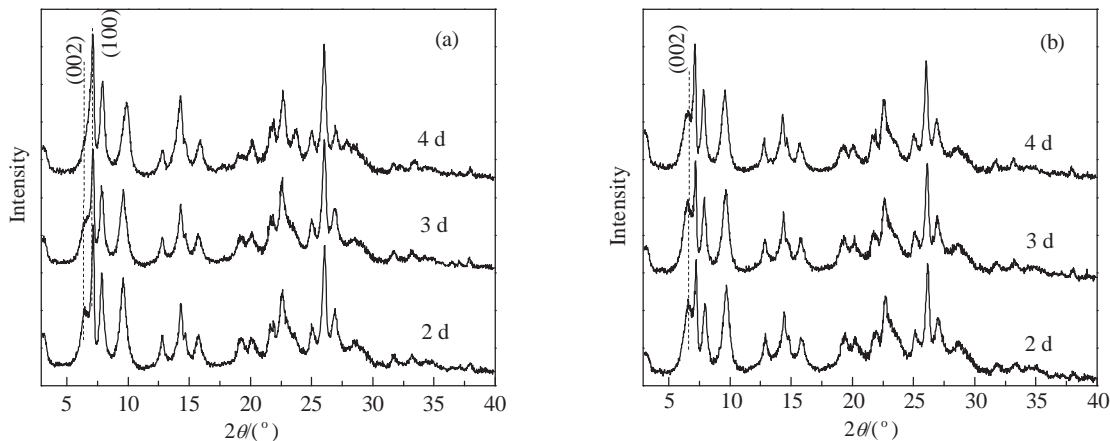

Fig. 2. XRD patterns of Al-YNU-1 samples synthesized using different crystallization times with DeB-MWW (a) or DeFe-YNU-1 (b) as the silica sources (the Si/Al ratio in the gel is 25).
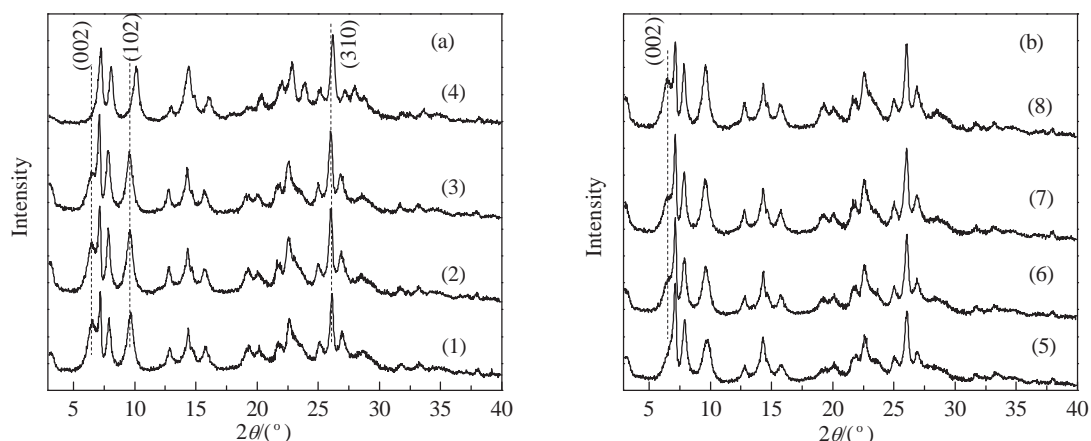
Fig. 4. (a) XRD patterns of the Al-YNU-1 samples obtained through treating with 2 mol/L HNO₃ (1), 1 mol/L HNO₃ (2), and 0.5 mol/L HNO₃ (3) for 1 d before calcination, and through direct calcination (4); (b) XRD patterns of the Al-YNU-1 samples obtained through treating with 1 mol/L HNO₃ for 4 h (5), 10 h (6), 16 h (7), and 24 h (8) before calcination.

separated (002) diffraction line is observed. With increasing H_2O content (> 13), the (002) diffraction line is shifted to higher angle, suggesting that we obtain a mixture of Al-YNU-1 and Al-MWW. Once the H_2O/SiO_2 molar ratio exceeds 30, only 3D Al-MWW structure zeolite is obtained.

3.4. Acid treatment

Figure 4 illustrates the influence of acid treatment conditions on the Al-YNU-1 structure. Direct calcination without acidic treatment transforms the precursor Al-MWW(P)(Fe) into 3D Al-MWW, as characterized by the three definite diffraction lines in the 2θ range of 6°–11° and the well separated lines in the 2θ range of 26.5°–30°, with no broad tails on the (310) peak (Fig. 4(a)(4)). However, treating the precursor with nitric acid before calcination leads to different diffraction lines for the calcined samples. Shifts to lower angles of the diffraction lines for (002) and (102) reflections were clearly observed (Fig. 4(a) (1–3)), indicating the formation of Al-YNU-1 structure [10,11]. These results imply that the acid treatment is indispensable for the synthesis of YNU-1 zeolite. Nevertheless, with increasing

HNO_3 content (Fig. 4(a)) and acid treatment time (Fig. 4(b)), the (002) peak intensity also increases gradually, because of an increase in the quantity of Al-YNU-1(Fe).

The effect of acid treatment on the amount of template molecule (PI) was investigated by TG tests, as shown in Fig. 5. The mass loss of Al-MWW(P)(Fe) precursor accounts for the change in mass of 15.5% observed between 140–700 °C, while the mass loss of the sample in this range after acidic treatment (1 mol/L HNO_3) is only 3.7%. This means that through acid treatment for 4 h, 76% of the PI in the Al-MMW(P)(Fe) was removed. With further increases in the acid treatment time, the amount of PI in the Al-MMW(P)(Fe) sheets does not reduce appreciably. However, increase in the acid treatment time will lead to a decrease in the Al content in the Al-MMW. The Si/Al ratio is increased from 30 at 4 h to 98 at 24 h. These findings are consistent with the report that when more framework Al is removed by acidic treatment, the formation of Al-YNU-1 becomes easier [11].

3.5. Morphology of sample

Figure 6 shows a SEM image of the DeB-MWW sample. DeB-MWW is present as typically round, lamellar particles of about 8 μm in diameter, made up of stacks of thin platelets (about 0.1–0.5 μm long and 0.05–0.1 μm thick). This morphol-
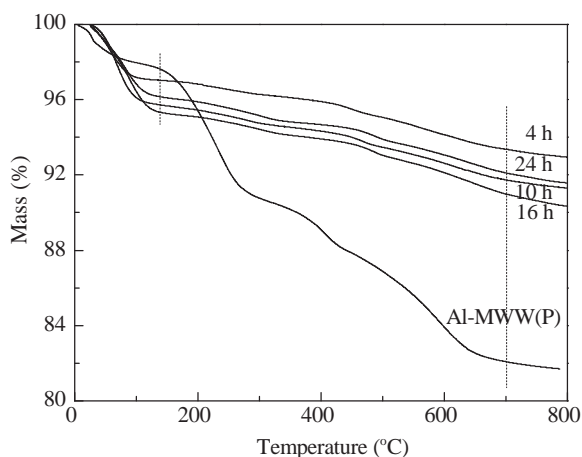

Fig. 5. TG profiles of Al-MWW(P)(Fe) samples treated with 1 mol/L HNO_3 for different times.
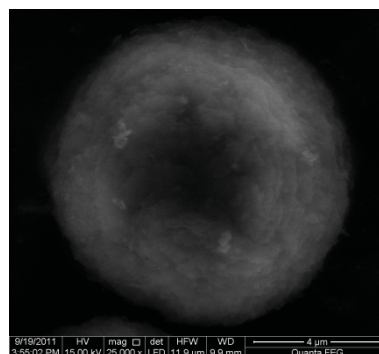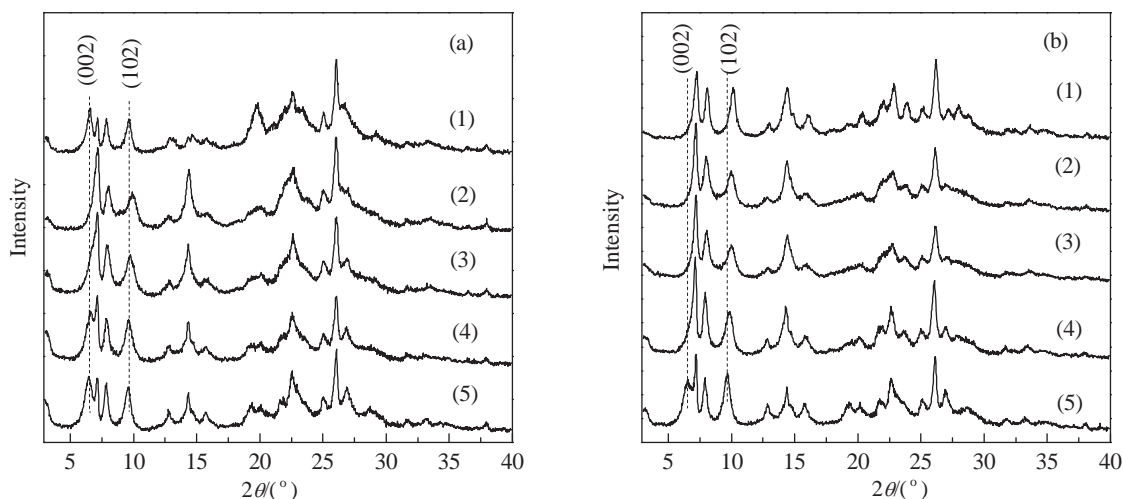

Fig. 6. SEM image of the DeB-MWW sample.

Fig. 7. (a) XRD patterns of samples treated with H_2O at 100 °C for 1 h (1), 0.1 mol/L HNO_3 at 30 °C for 1 h (2), 2 mol/L HNO_3 at 30 °C for 1 d (3), 2 mol/L HNO_3 at 80 °C for 1 d (4), and 2 mol/L HNO_3 at 100 °C for 1 d (5); (b) XRD patterns of corresponding calcined samples.

ogy, including the particle size and stacking manner, exhibits little change after subsequent crystallization, acid treatment and calcination (not shown here), suggesting that although the crystallization and acid treatment for post-synthesis may change the microscopic MWW structure into that of DeFe-YUN-1 or Al-YNU-1(Fe), these steps have little influence on the macroscopic morphology.

3.6. Possible formation mechanism of Al-YNU-1

To elucidate the formation mechanism of Al-YNU-1, XRD patterns of the samples obtained by treating the Al-MWW(P) precursor under various conditions are displayed in Fig. 7. When the precursor is treated with hot water, little change in the XRD pattern is observed (Fig. 7(a)(1)). Correspondingly, the subsequently calcined sample shows a 3D Al-MWW structure (Fig. 7(b)(1)). However, after treating the Al-MWW(P) with 0.1 mol/L HNO_3 at 30 °C for 1 h, the (002) peak disappears or shifts to higher angle (Fig. 7(a)(2)), and about 71% of the total template PI is removed. The removal of PI molecules alters the parallel arrangement of the Al-MWW(P) sheets so that the in-

terlayer space is reduced. By increasing the degree of acid treatment, the (002) diffraction peak (which disappeared after very mild acid treatment) reappears, and its intensity increases with the strength of acid treatment (Fig. 7(a)(3–5)). After calcination of these samples, a mixture of Al-MWW and Al-YNU-1 is obtained (Fig. 7(b)(3,4)). Finally, pure YNU-1 structure is obtained after a deep acid treatment (Fig. 7(a)(5) and Fig. 7(b)(5)).

In addition, ICP results show that higher temperature, higher HNO_3 concentration and longer treatment time can remove more Al from the Al-MWW structure [10,11,16]. Thus, it can be inferred that the stepwise removal of interlayer templates and succedent Al atoms at the interlayer site occurs during the acid treatment stage. As a result, many interlayer framework defects are probably generated, and, at the next stage of calcination, the defect sites are then transformed into Si–O–Si bridges between the lamellar layers [17].

The effect of the framework defects on the Al-YNU-1 synthesis is demonstrated, as shown in Fig. 8, by comparing the IR spectra of the hydroxyl stretching vibration region of B-MWW treated with refluxing acid solution either once or three times.
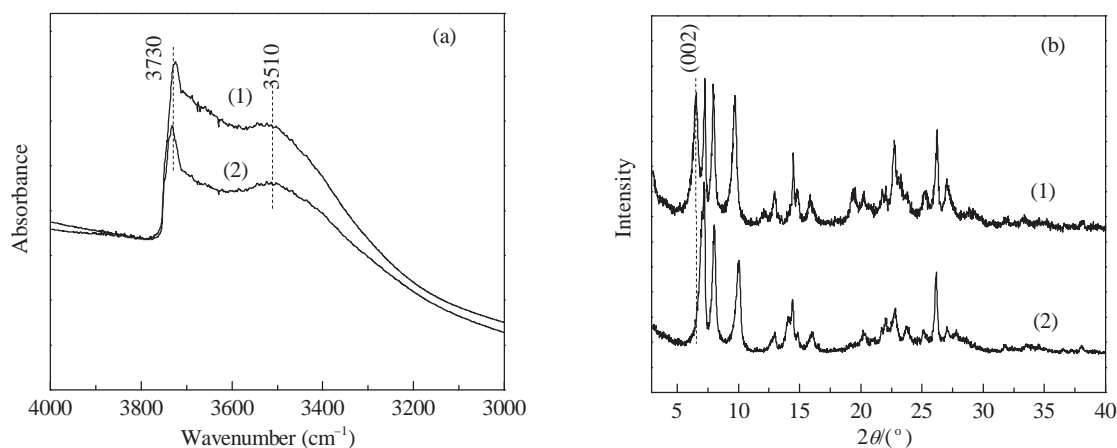

Fig. 8. (a) OH-region IR spectra of DeB-MWW obtained by treating B-MWW with acid once (1) and three times (2); (b) XRD patterns of corresponding YNU-1 samples synthesized from DeB-MWW obtained using B-MWW treated with acid once (1) and three times (2) as a silica source.

Graphical Abstract

Preparation and formation mechanism of Al-YNU-1 using highly acid-treated Fe-YNU-1 molecular sieve as a silica source

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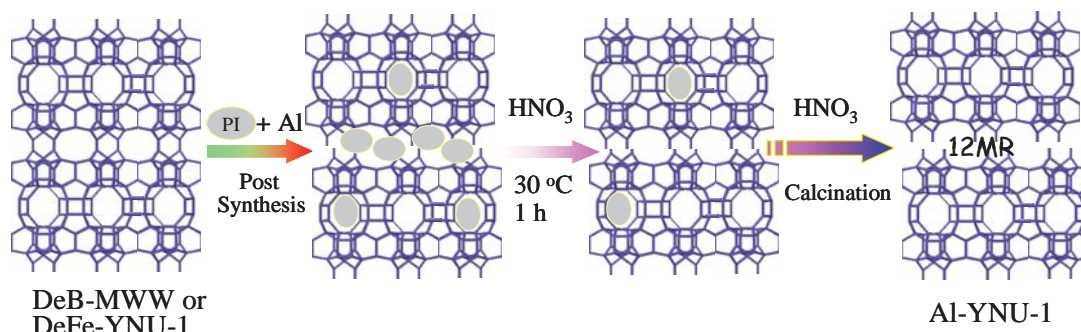
Al-YNU-1 zeolite was post-synthesized using DeFe-YNU-1 as a silica source. In this way, its framework Al content was significantly increased. The chemical composition of the synthesis gel and the acid-treatment conditions of the as-synthesized precursor have great effects on the formation of Al-YNU-1.

The two distinct bands at 3730 and 3500 cm^{-1} are attributed to external Si–OH and silanol nests. The silanol nests should originate from the defect sites formed as a result of the acidic deboronation. When B-MWW treated once with acid is used as the silica source, the resultant sample exhibits intense IR bands at 3730 and 3500 cm^{-1}, showing a large number of defect sites. After calcination, the YNU-1 structure is achieved (Fig. 8(b)(1)). In contrast, in the sample obtained using B-MWW subjected to three acidic treatments, the number of Si–OH, both external Si–OH and internal silanol nests, is reduced (Fig. 8(a)(2)), which can possibly be ascribed to the structure contraction from the harsh acidic treatment. When B-MWW subjected to three acidic treatments is the silica source, the resultant samples show only 3D MWW structure (Fig. 8(b)(2)). Hence, we may deduce that a large number of defect sites in the silica source, as a result of the acid treatment, are essential to obtain YNU-1 zeolite.

4. Conclusions

Al-YNU-1 molecular sieve was synthesized through the post-synthesis method from highly acid-treated Fe-YNU-1 in the presence of piperidine. We found that the gel ratio and the crystallization conditions strongly influence the synthesis of Al-YNU-1. High aluminum (Si/Al < 20) and water contents (H_2O/Si > 19) in the synthesis gel and long crystallization time (t > 4 d) are not favorable to the formation of Al-YNU-1. Through optimizing the synthesis conditions, the content of Al in the Al-YNU-1(Fe) framework is significantly increased (Si/Al = 98), to nearly double that in a sample prepared using deborated MWW as the silica source (Si/Al = 220). About 75% of the template molecules (PI) and a large amount of framework aluminum are removed in a stepwise way by acid treatment. To form Al-YNU-1, it is essential to remove most of the template molecules and framework Al species in the lamellar Al-MWW precursor during the acid treatment, and to have a large number of defect sites in the Si source.

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以深度脱铁Fe-YNU-1分子筛为硅源制备Al-YNU-1及其形成机理

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摘要: 主要研究了以哌啶为模板剂, 深度脱铁的Fe-YNU-1分子筛为硅源, 采用后合成法制备Al-YNU-1分子筛及其形成机理. 通过考察铝含量、水含量、晶化时间和酸处理条件对形成Al-YNU-1分子筛结构的影响规律, 发现Al-YNU-1分子筛骨架中的Al含量较以深度脱硼的B-MWW为硅源得到的样品提高了近一倍. 结果表明, Si源中存在大量晶格缺陷位、酸处理脱除Al-MWW层状前驱中大部分模板剂分子与大量骨架Al是形成Al-YNU-1分子筛的必要条件.

关键词: Al-YNU-1; 水热合成; 酸处理; 机理; Fe-YNU-1

1. 前言

MCM-22分子筛是一类层状结构的微孔材料, 具有两套独立的、彼此不相连接的10元环孔道体系. 一套是层间10元环孔道, 它与12元环超笼(0.71 nm × 0.71 nm × 1.82 nm)相连; 另一套为层内二维10元环正弦孔道, 与超笼并不相通[1]. 独特的孔道结构使MCM-22分子筛在苯烷基化[2]、烷烃裂解[3]、异构化[4,5]、芳构化[6]和甲醇制烯烃[7]等反应中显示出优异的催化性能. 但是, MWW分子筛较小的孔径限制了其在大分子反应中的应用. 为此, 许多研究者通过扩孔或层剥离以改善其在大分子反应中的催化性能.

MCM-22分子筛合成样品为二维层状结构, 为层间结构调变提供了可能. Mobil公司的研究者[8]发现, 该层状前驱体经碱性表面活性剂溶液溶胀、SiO₂交联可制备成层错堆积的MCM-36分子筛; 与MCM-22相比, 其层间孔口得到了一定程度的扩张, 在较大分子反应中, 其12元环超笼得到一定程度的利用. 为了进一步改善MCM-22分子筛在大分子反应中的催化性能, Corma等[9]通过对其层状前驱体进行溶胀、超声剥离处理, 得到具有单层结构的ITQ-2分子筛. 该分子筛在真空汽油裂解反应中显示出良好的催化性能. 但是, 这种分子筛含有大量的晶格缺陷位, 水热稳定性很差, 缺乏工业应用前景. 另外, 在制备过程中, 母体损失严重, 产物收率很低. 为了克服这些致命缺陷, Fan等[10,11]通过对层状前驱体进行酸处理和调变骨架Si/Al比, 成功将层间10元环孔道扩展为12元环孔道, 制得Al-YNU-1分子筛, 它在苯甲醚苯甲基化和酰化反应中具有较高的催化活性[11]. 遗憾的是, 这种分子筛骨架Al含量很低, 因而提高其骨架Al含量是一个挑战. 在此背景下, Wu等[12~14]和Inagaki等[15]通过改变酸处理路径, 借助硅烷化手段, 得到了骨架Al含量较高的Al-YNU-1分子筛. 但是, 这些方法得到的样品含有较多的非骨架Al, 产生大量的L酸, 从而造成它在某些反应中选择性很低, 而采用Fan等[11]的方法制备的样品不仅L酸量很少, 而且强酸量与弱酸量之比达到18以上, 使其具有独特的催化性能. 因此, 非常有必要发展一种新的制备Al-YNU-1分子筛的路径, 不仅可以提高其骨架Al含量, 而且能够避免非骨架Al的存在.

本文通过系统研究硅源种类、模板剂结构、原料配比和晶化条件等对合成产物结构的影响规律, 发现深度脱铁的Fe-YNU-1分子筛(DeFe-YNU-1)为硅源不仅可以在一定程度上提高Al-YNU-1分子筛骨架的Al含量, 而且能够对Al-YNU-1分子筛进行可控合成.

2. 实验部分

2.1. 样品的制备

将一定量的哌啶(PI, 99%, 国药集团化学试剂有限公司)、去离子水和氨水(25%)混合均匀后, 加入深度脱硼的DeB-MWW (Si/B > 200)或脱铁的DeFe-YNU-1 (Si/B > 1500, Si/Fe > 2000)样品, 待搅拌均匀后再加入异丙醇铝(AR, 国药集团化学试剂有限公司), 并搅拌1 h, 然后移入内衬聚四氟乙烯的合成釜中, 于150 °C转动晶化. 凝胶摩尔配比为SiO₂:(0~0.025)Al₂O₃:1.4PI:0.15NH₄OH:(7~30)H₂O. 产物经过滤、洗涤和干燥后得到Al-MWW(P)前驱体样品. 再经不同浓度的HNO₃(液固比为100 ml/g)处理和550 °C焙烧, 得到Al-YNU-1-x(B)或Al-YNU-1-x(Fe)分

子筛(x为凝胶的Si/Al比). DeB-MWW和DeFe-YNU-1分子筛的制备方法分别详见文献[10,16].

2.2. 样品的表征

样品的粉末衍射(XRD)谱在Rigaku Mini flexⅡ X射线衍射仪上测试,Cu $K_α$射线源,管压30 kV,管流15 mA,扫描步长0.02°,扫描速率4°/min. 样品的热性质在Rigaku Thermo Plus Evo 8120型热重差热(TG-DTA)分析仪进行考察,空气气氛,室温到800 °C,升温速率10 °C/min. 样品组成在电感耦合等离子光谱仪(CP-AES, TJA Autos-can16)上分析. 样品的红外光谱用Bruker Tenson 27仪器测试,30 mg的样品自支撑片在原位红外池中经500 °C真空处理2 h,室温采谱.

3. 结果与讨论

3.1. Al含量的影响

图1(a)为以DeB-MWW为硅源、添加不同Al量、150 °C水热晶化1 d得到样品的XRD谱. 由此可见,样品在6.54°处出现了对应于(002)晶面的衍射峰,表明具有3D结构的DeB-MWW在不同Al含量体系中均可转变为2D层状前驱体Al-MWW(P);而同样条件下,以六次亚甲基亚胺(HMI)为模板剂时,需晶化4 d才能形成这样的结构[11],表明分子直径较小的PI分子更易插入MWW分子筛层间结构中. 这些2D Al-MWW(P)样品经HNO$_3$(2 mol/L)处理后,仍保留层状结构(见图1(b)),但再经560 °C焙烧后,Si/Al比为20的凝胶得到样品的(002)衍射峰强度大幅减弱,表明其转变为3D Al-MWW结构,而其它样品则转化为Al-YNU-1分子筛(见图1(1)),说明Al含量较低时有利于Al-YNU-1分子筛的形成.

表1为不同Al含量凝胶合成样品的物性参数. 由表可见,增加凝胶中Al含量可以适度提高Al-YNU-1分子筛骨架中的Al含量,但孔体积减小,比表面积略有下降,而外比表面积增加. Al-YNU-1分子筛的层间孔道为12元环,而3D Al-MWW层间孔道为10元环,由图1可见,较高Al含量凝胶合成的样品中含有的Al-YNU-1分子筛量较少,因此,孔体积较小. 研究表明[11],Al-MWW(P)前驱体只有经过较为苛刻的酸处理,除去大部分模板剂分子和骨架Al后才能转化为Al-YNU-1分子筛.

3.2. 晶化时间和硅源的影响

前期研究表明,采用后合成法制备Fe-YNU-1分子筛时,当其晶化时间达到6 d时,不能形成YNU-1结构[16],但适度延长晶化时间有利于杂原子进入分子筛骨架[11,16]. 图2为分别采用DeB-MWW和DeFe-YNU-1为硅源,Si/Al

= 25时,凝胶在不同晶化时间得到样品的XRD谱. 由图可见,以DeB-MWW为硅源时,晶化时间少于2 d时,可以得到Al-YNU-1分子筛;若晶化时间延长到4 d时,样品(002)晶面衍射峰向高角度移动,逐渐与(100)晶面衍射峰重叠,形成3D Al-MWW结构. 但当用DeFe-YNU-1作为硅源时,晶化4 d仍可得到Al-YNU-1分子筛,其骨架Si/Al比降至118,约是Al-YNU-1-25(B)的1/2,表明以DeFe-YNU-1分子筛为硅源可以大幅提高Al-YNU-1分子筛骨架的铝含量(见表1).

3.3. 水量的影响

图3是凝胶组成为SiO$_2$:0.02Al$_2$O$_3$:1.4PI:0.15NH$_4$OH:(7~30)H$_2$O时,水含量对所制Al-YNU-1样品结构的影响. 结果表明,合成原料中添加的水量虽然对前驱体Al-MWW(P)(Fe)的形成没有明显影响,但对Al-YNU-1分子筛结构的形成影响很大. 当凝胶中H$_2$O/SiO$_2$ = 7时,产物的(002)衍射峰清晰;增加合成原料中的水量至H$_2$O/SiO$_2$ > 13时,所得样品(002)晶面衍射峰逐渐变弱,说明其中Al-YNU-1分子筛的含量逐渐减少;当H$_2$O/SiO$_2$ = 30时,只能得到3D Al-MWW分子筛.

3.4. 酸处理条件的影响

图4为酸处理条件对Al-YNU-1分子筛形成的影响. 由图可见,直接焙烧Al-MWW(P)(Fe)后,样品于2$θ$ = 6°~11°处出现3个清晰的尖峰,且在26.5°~30°区间的峰也清晰可辨,说明直接焙烧形成3D结构的Al-MWW分子筛. 而先经酸处理再焙烧所得样品(002)晶面衍射峰清晰可见,且(102)面衍射峰等略向低角度方向偏移,形成Al-YNU-1分子筛[10,11]. 且随着酸浓度和处理时间的增加,样品(002)晶面衍射峰逐渐增强,表明Al-YNU-1(Fe)量显著增加.

样品的TG-DTA曲线如图5所示,在140~700 °C之间,前驱体样品Al-MWW(P)(Fe)的失重量为15.5%,酸处理4 h样品的失重量为3.7%,说明用硝酸处理Al-MWW(P)(Fe)前驱体4 h,即可脱除其76%的模板剂. 进一步延长酸处理时间,样品的模板剂脱除量不再显著增加,但Si/Al从30 (1 mol/L, 4 h)增加到98 (1 mol/L, 24 h). 研究表明[11],酸洗除去的骨架Al量越多,越利于形成Al-YNU-1分子筛.

3.5. 晶粒形貌

图6为合成样品的SEM照片.母体DeB-MWW样品由长约0.1~0.5 μm、厚约0.05~0.1 μm的薄片状小晶粒堆积成直径约为9 μm的中心凹型的圆饼状大晶粒组成. 经脱B、水热晶化、酸处理和焙烧得到的DeFe-YUN-1和

Al-YNU-1(Fe)样品晶粒大小与堆积方式基本没有发生变化(照片未给出),说明这些处理过程虽然改变了DeB-MWW的层间结构,但对其晶粒形貌影响不大.

3.6.　Al-YNU-1分子筛形成机理探讨

TG/DTA测试表明, Al-MWW(P)(Fe)在水中沸腾处理并不能脱除模板剂,因此,处理后的样品仍保持前驱体结构, 焙烧后形成3D Al-MWW结构. 但经硝酸(0.1 mol/L)在30 ℃处理1 h可脱除约71%的模板剂,并导致层间结构发生明显变化, 2D Al-MWW(P)(Fe)前驱体转变成3D Al-MWW. 只有逐渐增加酸处理温度,并进一步延长酸处理时间,二维层间前躯体结构才会逐渐得以保留,因此在560 ℃空气气氛中焙烧10 h后,仍保留这样的层间结构,从而形成YNU-1分子筛.

ICP和TG结果表明,增加酸浓度和酸处理时间能够脱除较多的骨架Al和大部分、特别是层间模板剂分子. 这是形成YNU-1分子筛的两个必要条件[10,11,16]. 大量骨架Al的脱除导致形成大量的晶格缺陷位,大量模板剂分子的脱除使层间孔道变得空旷,从而为无定形SiO_2碎片在层间T1位发生交联反应提供了可能,结果造成层间10元环孔道转变为12元环孔道[17]. 该孔道结构虽然水热稳定性较差,但热稳定性较高,因此,焙烧后仍可保留下来,转为YNU-1结构. 而用低浓度酸处理或处理时间较短时,虽然Al-MWW(P)(Fe)前驱体中大部分模板剂分子得以脱除,但骨架中Al的脱除量较少,因此,形成的晶格缺陷位较少,不利于SiO_2物种在T1位发生交联反应,导致焙烧后得到3D Al-MWW分子筛.

晶格缺陷位的作用可以通过下面的实验得到间接证实. 图8(a)为B-MWW样品分别经一次酸处理和三次

酸处理后得到DeB-MWW样品的羟基FT-IR谱. 3730和3500 cm^{-1}处吸收峰分别对应于外表面孤立Si–OH和以氢键相互连接的OH巢振动吸收峰. 由图可见,与脱B三次得到的DeB-MWW (记为DeB-MWW-3)相比较,酸处理脱B一次得到的DeB-MWW (记为DeB-MWW-1)的羟基吸收峰明显增强,表明其骨架中存在较多的晶格缺陷位. 如图8(b)所示,以DeB-MWW-1为原料可以制备出结构完美的Ti-YNU-1;而以DeB-MWW-3为原料则只能得到3D Ti-MWW. 这表明采用后合成法制备YNU-1分子筛时,其Si源(如DeB-MWW和DeFe-YNU-1)须有或者在酸处理层状前驱体过程中创造大量的晶格缺陷位,才能形成YNU-1结构.

4.　结论

采用后合成法制备了Al-YNU-1分子筛,发现合成原料的配比和晶化条件对形成Al-YNU-1分子筛的影响很大,凝胶中高铝含量(Si/Al < 20)、高水量(H_2O/Si > 19)及长的晶化时间($t > 4$ d)等不利于合成Al-YNU-1分子筛. 通过优化合成原料中的铝含量、水量及晶化时间和前驱体的酸处理条件,与DeB-MWW作为硅源相比,以DeFe-YNU-1分子筛为Si源合成的Al-YNU-1(Fe)分子筛中的Al含量增加一倍. 对不同酸处理程度样品的分析表明,层状前驱体中的模板剂分子和骨架铝在酸处理过程中被逐步脱除. 具有3D MWW结构的硅源在水热晶化转变为2D层状前驱体和后续酸洗与焙烧过程中其形貌没有发生明显变化. 酸处理脱除层状前驱体中大部分模板剂分子和骨架铝及Si源中存在大量晶格缺陷位是形成YNU-1结构的必要条件,三者缺一不可.