Synthesis of Zeolite ZSM-2 Using Zeolite NaX as Seeds

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A method is presented for the synthesis of zeolite ZSM-2 by adding zeolite X as seeds in the synthetic mixture containing both lithium and sodium. At the presence of zeolite X seeds, highly crystalline zeolite ZSM-2 with composition of $(0.3—0.7)Li_2O \cdot (0.7—0.3)Na_2O \cdot Al_2O_3 \cdot (2.5—4.0)SiO_2 \cdot nH_2O$ can be obtained in a wide range of SiO_2/Al_2O_3 ratios from 2.5 to 16, and the optimum $Li_2O/(Li_2O+Na_2O)$ fraction is between 0.3 and 0.7. The ZSM-2 products were characterized by XRD, SEM, IR, ^{29}Si MAS NMR and DTA/TG analysis *etc*. By ^{29}Si MAS NMR spectroscopy, it was found that ZSM-2 contained nearly equal FAU and EMT phase, and the Si/Al ratios in FAU were slightly lower than those in EMT domains in most cases. The lithium form zeolite ZSM-2 has comparable N_2 adsorption capacity with LiX.

Keywords   zeolite ZSM-2, zeolite X, seed, intergrowth, adsorption isotherm

Introduction

Oxygen and nitrogen have been produced traditionally by cryogenic distillation of air. Methods for the non-cryogenic separation based on selective adsorption have been developed and commercialized since the 1970s and have led to a cost-effective process for this important separation.[1] Low-silica zeolites are important materials for producing oxygen by selective adsorption of nitrogen. In 1989—1990, a new generation of lithium-based adsorbents was developed.[2,3] Highly lithium exchanged zeolite X (FAU) is the key component of pressure swing adsorption process (PSA) which was used to obtain oxygen from air. By ion-exchange, it is difficult to achieve high level of lithium content without using large excesses of expensive liuthium salts. In contrast, zeolite ZSM-2 contains high lithium content and complete exchange of Li^+ ions can be done more easily than in zeolite X.

Zeolite ZSM-2 in lithium form, which was originally reported by Ciric,[4] was thought of the first large pore zeolite related to faujusite to be prepared in the absence of sodium ions.[5] It was assumed as an intermediate structure of FAU/EMT similar to ZSM-3,[6] although the original work described it as a tetragonal lattice different from both the cubic lattice for FAU and the hexagonal lattice for EMT. Lithium containing ZSM-2 has N_2 and O_2 adsorption capacities similar to X-type adsorbents.[7]

In the synthetic prcedure described by Ciric,[4] a finely divided amorphous lithium aluminosilicate glass in the presence of water was used to prepare the reaction mixture. After hydrothermal treatment at relatively low temperature, for example, 55—60 ℃, for one month, a product consisting of equal amounts of ZSM-2 with particle size of 0.5 μm in diameter and un-reacted glass was obtained. Barrer and Sieber[5] obtained zeolite ZSM-2 from aluminosilicate gels containing Li^+ and Cs^+ together with TMA^+ cations. After crystallization at 90 ℃ for 46 h (without a proceeding aging step), fully crystallized zeolite ZSM-2 was recovered. The crystals had a platelet form and were about 0.75—1 μm in diameter and 0.15 μm thick. Another approach was reported by Schoeman *et al.*,[8] in which discrete colloidal particles of zeolite ZSM-2 with crystal sizes less than 100 nm, in the form of aqueous suspension, were synthesized in TMA-aluminosilicate gels in the presence of either lithium or a combination of lithium and sodium hydroxides.

In this paper, a novel route to produce fully crystallized is reported, TMA free zeolite ZSM-2 from the media with both Li^+ and Na^+ cations promoted by adding zeolite NaX as seeds.

Experimental

Sample preparation

An aluminate solution was prepared from sodium aluminate (41 wt% Al_2O_3), sodium hydroxide (96 wt%) and distilled water. A lithium hydroxide solution was prepared by dissolving lithium hydroxide (95 wt% $LiOH \cdot H_2O$) into distilled water. The previously dissolving of lithium hydroxide was to prevent forming undissolvable white sediment when lithium hydroxide was added to the sodium aluminate solution. A clear solution was obtained by mixing sodium aluminate solution and lithium hydroxide solution. Then a solium silicate solution (26.3 wt% SiO_2, 7.2 wt% Na_2O) or

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lithium silicate solution (18 wt% SiO_2, 2.6 wt% Li_2O, <0.2 wt% Na_2O), which was prepared as described by Schoeman *et al.*,[8] was added with stirring. The resulting hydrogel was continuously stirred for 30 min. At last, zeolite NaX seed crystals, previously reduced to a particle size of about 0.3 μm by grinding, were added with stirring. The amount of NaX seed crystals was 0.3 wt% with respect to the reaction mixture. The crystallization was carried out in a covered polypropylene bottle at 100 ℃ for about 5 h. The solid obtained was filtered, washed thoroughly with distilled water and then dried at 70 ℃ overnight.

The original samples were consecutively exchanged with 1 mol • L^{-1} solution of LiCl with a ratio solution to solid of 25 ∶ 1. The lithium ion-exchange solution was heated to a mild boil and then allowed to cool and settle down. Then the solution was decanted, and a fresh 1 mol •L^{-1} LiCl solution was added. The procedure above was repeated for a total of three times. After the final ion-exchange, it was filtered, washed with distilled water and dried to obtain LiZSM-2 samples.

Sample characterization

The chemical composition was analyzed by ICP-AES. X-ray powder diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer (Cu-Kα radiation). FT-IR spectra in the framework region from 400 to 900 cm^{-1} were recorded at room temperature on a Nicolet Nexus 470 FTIR spectrometer by using KBr pellets. Morphology was examined with a Philips XL 30 scanning electron microscope (SEM). ^{29}Si MAS NMR spectra of LiZSM-3 were obtained on a Bruker AVANCE DSX 300 NMR spectrometer. DTA/TG analysis was performed with Perkin Elmer instruments.

Adsorption tests

The adsorption isotherms were measured gravimetrically by using a homemade adsorption system. Highly purified nitrogen (99.999%) and oxygen (99.99%) were used as adsorbates. The isotherm measurements were found to be reproducible.

Results and discussion

Figure 1 shows the XRD patterns of the product synthesized by using zeolite NaX as seeds. Two broad and characteristic peaks of zeolite ZSM-2 in the region of 5°—8° (2θ) can be observed, which matchs well with those reported by Weigel *et al.*,[3] suggesting that the product is zeolite ZSM-2 without any impurity. This result means that ZSM-2 can be synthesized in the reaction mixture containing both lithium and sodium cations by adding structurally related zeolite NaX. TMAOH was used as base to avoid formation of opaque gels by inorganic bases under the same conditions.[5,8] It was considered that deposit formed by using inorganic bases

in this work highly crystalline ZSM-2 was obtained in the white slurry of aluminosilicate, implying that ZSM-2 can be obtained from either clear or opaque gels.
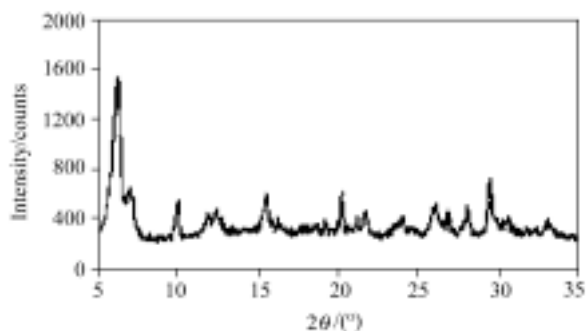

Figure 1 Powder X-ray diffraction of the as-synthesized ZSM-2 prepared using zeolite NaX as seeds.

Details of the syntheses are summarized in Table 1. As it is shown, zeolite ZSM-2 can be obtained in aluminosilicate gels with lithium and sodium cations by adding zeolite X as seeds. The optimum $Li_2O/(Na_2O+Li_2O)$ fractrion is in the range from 0.3 to 0.7 (smple 5 to 8). When the Li_2O/M_2O fraction is decreased to 0.2 (smple 5), the product obtained is not zeolite ZSM-2, but zeolite X, suggesting that lithium cations are necessary for crystallization of ZSM-2. However, in this work, high $Li_2O/(Na_2O+Li_2O)$ fraction does not benefit the growth of ZSM-2. As shown in smple 8, with a $Li_2O/(Na_2O+Li_2O)$ fraction of 0.7 it takes much more time to crystallize, and the product contains an unknown phase.

It was reported by Schoeman *et al.*[8] that ZSM-2 could be synthesized in the presence of a trace amount of sodium ions, which resulted not only in an increase in the crystal growth rate but also in a reduction in the reaction time. However, the product of ZSM-2, which was transformed to zeolite (Li, Na)-E in the presence of sodium ions in 8 h, and with increased sodium contents, resulted in no ZSM-2, but zeolite Na-A. The product of ZSM-2 prepared by this work is so stable that it maintains in phase pure ZSM-2 in the mother liquid with prolonged hydrothermal treatment (>2 d) at 100 ℃, except that the crystallinity is slightly decreased (Figure 2). It demonstrates that the presence of a great amount of sodium does not induce the transformation of ZSM-2 prepared in this condition.

The optimum SiO_2/Al_2O_3 ratios are in the range of 2.5—16.0. In a gel with a SiO_2/Al_2O_3 ratio of 2.0, only zeolite A is obtained. When the SiO_2/Al_2O_3 ratio is increased to 2.5, ZSM-2 is obtained at a crystallization temperature of 70 ℃, while at 100 ℃ an impurity of zeolite A is observed. The crystallization temperature is important but not very critical for obtaining zeolite ZSM-2. Higher temperature benefits to shorten the crystallization process and increase the crystallinity. By

Table 1   Details of representative syntheses

Sample	Reactant mixture (molar ratios)				$T/℃$	Time/h	Product
	SiO_2	Li_2O	Na_2O	H_2O			
1 [a]	2.5	1.5	1.7	375	70	18	ZSM-2
2 [a]	2.5	1.5	1.7	375	100	5	A+SM-2
3 [a]	3.0	2.3	1.7	450	70	18	ZSM-2
4 [a]	3.0	2.3	1.7	450	100	5	ZSM-2
5 [b]	4.0	1.4	5.6	600	70	18	X
6 [b]	4.0	2.1	4.9	600	70	18	ZSM-2
7 [a]	4.0	4.2	2.8	600	70	18	ZSM-2
8 [a]	4.0	4.9	2.1	600	70	36	ZSM-2 [c]
9 [b]	5.0	5.5	5.5	720	70	18	ZSM-2
10 [b]	10.0	6.2	4.7	1000	70	18	ZSM-2
11 [b]	10.0	6.2	4.7	700	70	18	ZSM-3 [d]
12 [b]	16.0	6.0	6.0	1500	70	18	ZSM-2 [e]

[a] Lithium silicate solution was used. [b] Sodium silicate solution was used. [c] A trace amount of unknown phase was observed. [d] Synthesized using an aged nucleus gel according to the method of Lechert *et al.*[9]   [e] A trace amount of unknown phase was observed.
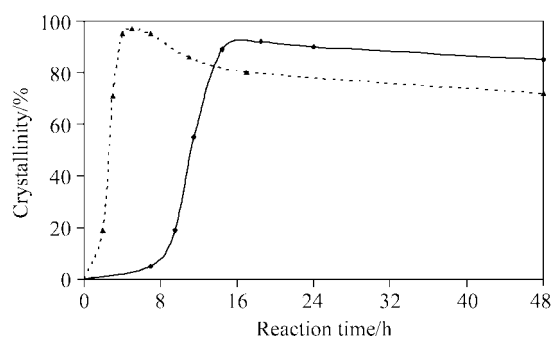

Figure 2   Crystallization curves at 70 ℃ (solid line, sample 3) and 100 ℃ (dashed line, sample 4).

100 ℃, the crystallization time decreased from 18 to 5 h.

The addition of zeolite NaX seeds is most important for crystallization of ZSM-2. It is found that all gels prepared without NaX seed crystals do not grow into ZSM-2 in an acceptable crystallization time. And there is a very interesting phenomenon that crystallization of ZSM-2 depends deeply on the addition of NaX seeds. It is shown that with the same reaction mixture except for the content of H_2O, ZSM-3 is formed in sample 11 by adding an aged sodium aluminosilicate gel according to Lechert *et al.*,[9] while in sample 10 ZSM-2 is obtained in the presence of NaX seeds. Even though both of ZSM-2 and ZSM-3 are thought of as intergrowths of FAU/EMT, there is difference in their XRD patterns. The main difference is that in the range of 5°—8° (2θ) ZSM-2 shows two diffraction peaks, while ZSM-3 announces three peaks between 5° and 7° (2θ).[10-12] It can be concluded that nuclei of ZSM-2 are formed by NaX seeds. However, the reason why NaX seeds induce formation of ZSM-2 while sodium aluminosilicate gel leads to crystallize ZSM-3 is unknown.

Figure 3 shows SEM photographs of the as-synthesized ZSM-2. It is shown that the products are polycrystals consisting of disorderly grown platelets without clear edges, about 0.2 μm thick. However, in those previous reports,[4,8,11] no twinning was observed, and each crystal was in a single platelet form. In this work, structurally related zeolite NaX was added into the reaction mixture. According to Lechert *et al.*,[9] a recrystallization process can be postulated involving at least the surface of the crystals or leading to a complete dissolution forming appropriate precursors. And the XRD pattern of the product taken out after a crystallization time of 1 h in this work shows no diffraction peak, suggesting the dissolution of NaX seed crystals. The polycrystalline mass formed over seed crystals can be postulated, the dissolution of NaX seeds are slower than growth of ZSM-2, and the dissolution of seed crystals forms nuclei with different growth directions for ZSM-2.

There are some differences between the IR spectra of the NaX seeds and ZSM-2. First, in the IR spectrum of zeolite NaX, there is a sharp band at 750 cm^{-1}, assigned to symmetric stretching and characteristic of zeolite NaX, while in the case of ZSM-2 only a shoulder-like band appears in the same region. Second, in the spectrum of ZSM-2, a doublet band at about 600 cm^{-1} is shown, not a sharp band at 563 cm^{-1}, which is assigned to the double-six ring of NaX.

The Langmuir surface area of the as-synthesized ZSM-2 is 720 m^2/g, and the BET surface area is 572 m^2/g, suggesting that it is fully crystallized. The original product of ZSM-2 loses its crystallinity on heating near 650 ℃ (Figure 4), and ecrystallizes to lithium alu-
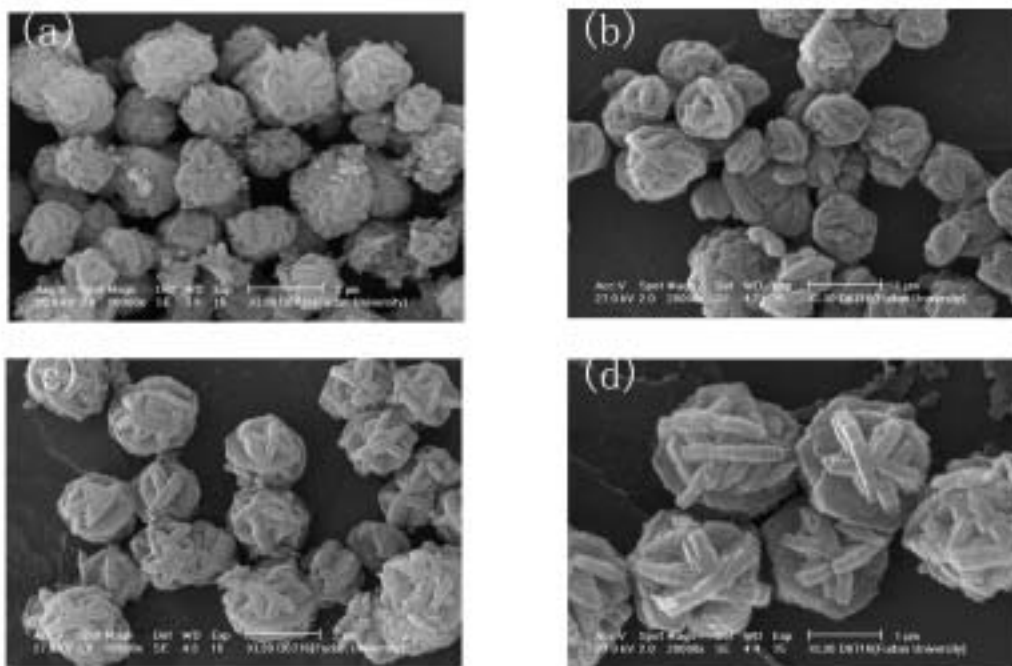
Figure 3   SEM photographs of the as-synthesized ZSM-3 in sample 10 (a), sample 7 (b) and sample 4 (c and d).

minium silicate ($Li_2Al_2Si_3O_{10}$) and nepheline ($NaAlSiO_4$), as a result from the XRD patterns. It is different from the report of Barrer and Sieber,[5] in which ZSM-2 recrystallized to β-eucryptite. The original products of ZSM-2 obtained by this method are more stable than those (Li, TMA) ZSM-2 synthesized by using TMAOH as an organic base.
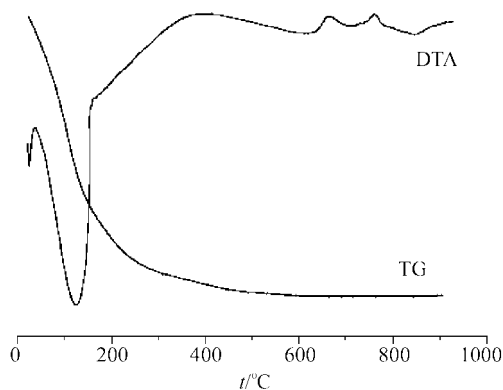

Figure 4   DTA/TG curves of as-synthesized ZSM-2.

The phase composition and SiO_2/Al_2O_3 ratios in the FAU and EMT domains of zeolite ZSM-2 products were measured by ^{29}Si MAS NMR according to the method reported by Martens *et al.*[13] After Li ion exchange of zeolite ZSM-2, a downfield shift of the FAU signals by $\delta = 2$—3 occurs and, consequently, partial resolution of the resonance signals is possible. Thus, we can decompose the ^{29}Si MAS NMR spectra of LiZSM-2 using 10 Gaussian components with predetermined position and intensity, and calculate the phase composition by simulated individual components. The results were summa-

rized in Table 2 together with the chemical analysis results. It shows that the products have nearly equal amounts of FAU and EMT, and the Si/Al ratios in FAU domains are slightly lower than those in EMT domains, except in sample 10.

Table 2   Phase composition and SiO_2/Al_2O_3 ratios of LiZSM-2 determined by ^{29}Si MAS NMR[a]

Sample	Phase composition/%		SiO_2/Al_2O_3 ratio	
	FAU	EMT	FAU	EMT
1	57	43	2.44	2.50
3	56	44	2.52	2.68
7	52	48	2.66	2.90
9	52	48	3.16	3.18
10	49	51	3.38	3.28

[a] According to the method of Martens *et al.*[13]

Figure 5 shows the adsorption isotherms measured at 25℃ for N_2 and O_2 for zeolite LiZSM-2 ($SiO_2/Al_2O_3 = 2.6$, 92% Li^+) after vacuum dehydration at 400 ℃. The isotherms in Figure 5 is compared with those on LiX ($SiO_2/Al_2O_3 = 2.5$, approximate 85% Li^+) fitted with the parameters available in reference 14 by the modified Langmuir isotherm and linear isotherm for N_2 and O_2, respectively. It clearly shows that the lithium form of ZSM-2 has N_2 and O_2 adsorption capacities similar to that of zeolite X. They also have a similar shape suggesting that the working capacities for a given process will also be comparable.

In conclusion, we have demonstrated a novel route to prepare highly crystallized zeolite ZSM-2 by using zeolite NaX as seeds in a short crystallization time without
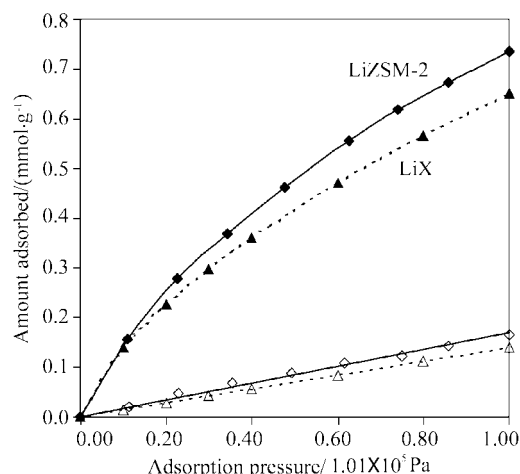
Figure 5   Adsorption isotherms at 25 ℃ on LiZSM-2 (SiO_2/Al_2O_3＝2.6, 92% Li$^+$) and LiX (SiO_2/Al_2O_3＝2.5, approximate 85% Li$^+$) for nitrogen (filled symbols) and oxygen (open symbols). The lines of LiX are fitted by parameters listed in the literature.[14]

TMA. The ZSM-2 products obtained by this method are polycrystals, with a reduced Si/Al ratio less than those reported before. The lithium form of ZSM-2 has nitrogen adsorption capability comparable to that of lithium exchanged zeolite X.

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