

Synthesis of beta zeolite with high levels of tetrahedral aluminium

Ramesh B. Borade and Abraham Clearfield

Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

A high substitution level of aluminium in the beta zeolite framework (Si:Al = 4.5:1) is achieved from a dense system containing a minimum of template with no evidence of the presence of octahedral Al in the ^{27}Al NMR spectrum.

Beta is a large pore 12-MR zeolite with a tridimensional channel system.¹ This zeolite acts as a strong acid catalyst for reactions such as cracking of paraffins and gas oil,^{2,3} C_8 alkyl aromatic isomerization,⁴ light paraffins isomerization⁵ and methyl *tert*-butyl ether (MTBE) formation from methanol and isobutene.⁶ Beta zeolite can be synthesized in a large variation of framework Si/Al ratios to obtain desired catalytic properties. The claimed range of Si/Al ratio was 5–100.⁷ Difficulties arise in the direct comparison of the acidic and catalytic properties of beta with the other large pore 12-MR highly successful commercial zeolite Y due to the large disparity in the Si/Al ratios of the synthesized materials. Zeolite Y crystallizes with an Si/Al ratio around three and zeolite beta crystallizes with an Si/Al ratio > 5.^{8,9} Therefore it is desirable to synthesize beta zeolite with an Si/Al ratio as close to the Si/Al ratio of zeolite Y as possible for better comparisons of catalytic behaviour. Here we report the synthesis of beta at higher substitution levels of aluminium than previously reported using a dense system containing a minimum of template.

The synthesized mixture was prepared using fumed silica (S-5130, Sigma), sodium aluminate (28.4% Na_2O , 46.8% Al_2O_3 , 24.8% H_2O), tetraethylammonium hydroxide (TEAOH; Johnson Matthey, 40% solution in H_2O) and demineralized water. Also in some experiments we used diethanolamine as a co-solvent.

The synthesis procedure was as follows. Sodium aluminate was added to tetraethylammonium hydroxide solution and stirred for 15 min. Then demineralized water was added and the mixture was stirred using a magnetic stirrer until a clear solution was obtained. To this solution was added a highly reactive fumed silica. Mixing was continued with a spatula for about 15 min and then with a mechanical stirrer. Initially, the mixture appears to be a dry powder. As stirring was continued for about 2 h the mixture turned into solid lumps which were transferred into a Teflon-lined stainless-steel autoclave of 100 ml or 1 l capacity and heated in an air oven at 120–170 °C at autogeneous pressure for a desired length of time. To stop the crystallization

process the autoclave was quenched in cold water. The resultant solid product was washed with demineralized hot water and then recovered by filtration. The samples were dried in an air oven at *ca.* 80 °C prior to characterization.

The effects of various reaction parameters such as $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{TEAOH}/\text{SiO}_2$, $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$, reaction temperature and time on the formation of final products were investigated.¹⁰ The water content and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the starting reaction mixture were found to be the critical parameters. When $\text{SiO}_2/\text{Al}_2\text{O}_3$ or $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ratios were in the range 6–8 or 25–35, respectively, the product was found to be gismondine or analcime or a combination thereof, depending upon the reaction temperature and time. A crystalline beta zeolite with Si/Al ratio as low as 4.5 was obtained, at 170 °C in 44 h, from a gel containing 1 Na_2O :1 Al_2O_3 :9 SiO_2 :1.6 TEAOH:60 H_2O (sample 4). Addition of 1.6 moles of diethanolamine to the same system produced amorphous material (sample 5). When the size of the autoclave was changed from 100 ml to 1 l capacity (samples 6 and 7) the product was associated with gismondine and/or analcime as impurity phases. The molar compositions of starting reaction mixtures, reaction conditions and final products obtained for selected batches are shown in Table 1.

The X-ray powder diffraction pattern of Al-rich beta zeolite of the present study (sample 4) is very similar to those reported

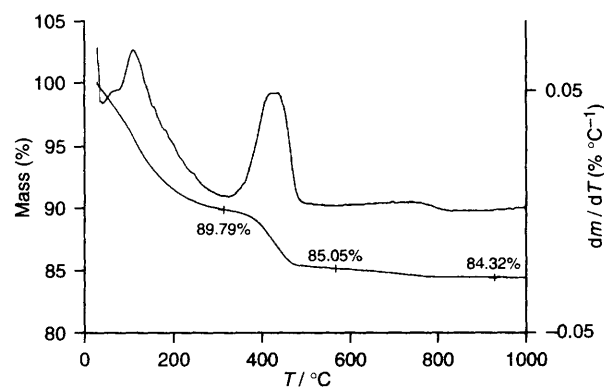


Fig. 1 TGA and derivative plots of as-synthesized beta zeolite (sample 4 of Table 1)

Table 1 Molar compositions, reaction conditions and products obtained

Sample	Na_2O	Al_2O_3	SiO_2	TEAOH	DEA ^a	H_2O	$T/^\circ\text{C}$	t/h	Product
1	1.0	1.0	10.0	1.6	—	55	170	20	Beta
2	1.0	1.0	10.0	1.6	—	55	170	19	Beta
3	1.0	1.0	10.0	1.6	—	55	170	23	Beta
4	1.0	1.0	9.0	1.6	—	60	170	44	Beta
5	1.0	1.0	9.0	1.6	1.6	55	170	105	Amorphous
6	1.0	1.0	9.0	1.6	—	55	170	16	Beta + G ^b + A ^c
7	1.0	1.0	9.0	1.6	—	60	170	40	Beta + A
8	1.0	1.0	8.0	1.6	—	49	165	30	Amorphous
9	1.0	1.0	8.0	1.5	—	61	120	264	Faujasite
10	1.0	1.0	8.0	1.3	—	49	170	39	Analcime

^a Diethanolamine. ^b Gismondine. ^c Analcime.

for beta zeolites.⁸ The X-ray crystallinity of the sample was *ca.* 92% when compared with the highly crystalline beta zeolite (Si/Al = 10.2) sample prepared using the 'normal' procedure. The Si, Al and Na content in the sample was determined by Galbraith laboratories. For as-synthesized Al-rich beta zeolite was found (mass%) 27.76 Si, 5.88 Al and 4.0 Na. The water and organic contents of the sample were obtained by TGA and found to be 10.2 and 4.75% respectively. The (Na⁺ + TEA⁺/Al) ratio is 0.98. The beta zeolite with Si/Al ratio 4.5 was subjected to thermal analysis using a Du Pont (Model 951) thermal analyser under a flow of N₂ at a heating rate of 10 °C min⁻¹ (Fig. 1). Three steps of mass losses were observed. The first step (25–300 °C) is due to the desorption of zeolitic water, the second step (300–575 °C) due to the decomposition of TEA⁺ cations interacting with the zeolite framework and the third step (575–850 °C) due to the decomposition/removal of organic

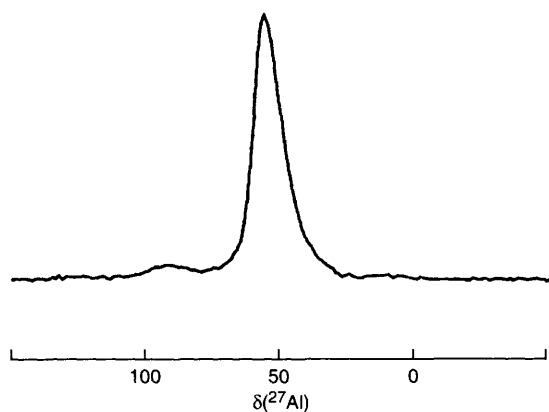


Fig. 2 ²⁷Al NMR spectrum of as-synthesized beta zeolite (sample 4 of Table 1)

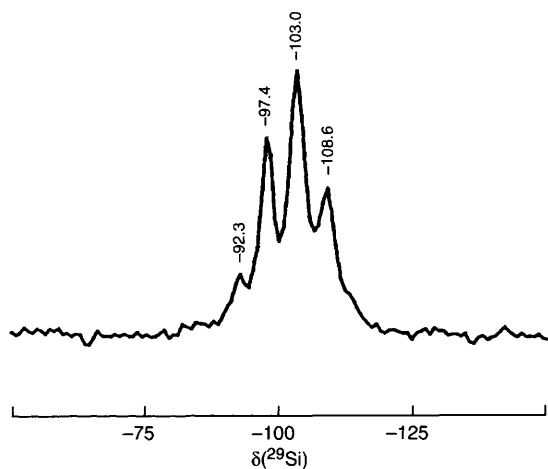


Fig. 3 ²⁹Si NMR spectrum of as-synthesized beta zeolite (sample 4 of Table 1)

residue. The low amount of mass loss due to TEA⁺ cations is consistent with our earlier findings.⁸

The strongest indication that Al belongs to the zeolite framework was provided by the ²⁷Al NMR study. Fig. 2 shows the ²⁷Al spectrum of as-synthesized Al-rich beta zeolite. The spectrum shows only one intense line at δ 56 from four-coordinate structural aluminium, indicating that the aluminium added into the gel mixture has been incorporated into the beta structure. Upon calcination at 540 °C for 4 h in air and then equilibrating the sample with water vapour at room temperature over saturated ammonium chloride solution, the ²⁷Al NMR peak at δ 54 remained unchanged. Surprisingly no new peak at δ 0 due to octahedral Al was seen. In earlier studies⁸ we observed a small peak at δ 0 corresponding to octahedral aluminium in the ²⁷Al NMR spectrum of beta zeolite calcined at 540 °C for 15 h. This may mean that longer calcination of beta zeolite, to remove organic template, produces an octahedral Al species.

The incorporation of aluminium in the beta zeolite framework is also reflected in the ²⁹Si NMR spectrum (Fig. 3). The beta samples with Si/Al ratio in the range 5–9 showed the presence of three peaks^{8,9} whereas the Al-rich sample of the present study showed four peaks. These peaks at δ -109, -103, -98, -93 could be assigned to Si(0Al, 4Si), Si(1Al, 3Si), Si(2Al, 2Si) and Si(3Al, 1Si), respectively.^{9–12} The main difference is that the sample of the present study shows a well resolved additional peak at δ -93. This confirms the aluminium richness of the sample.

In conclusion, beta zeolite with a Si : Al ratio as low as 4.5 : 1 has been synthesized. The ²⁷Al NMR study confirmed that all aluminium species are in the zeolite framework positions and removal of template by air calcination at 540 °C for 4 h does not produce octahedrally coordinated aluminium.

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