Catalysis Letters 26 (1994) 285–289

Synthesis of zeolite Beta from dense system containing a minimum of template

Ramesh B. Borade and Abraham Clearfield

Department of Chemistry, Texas A&M University, College Station, TX 77840, USA

Received 8 February 1994; accepted 1 March 1994

Zeolite Beta has been synthesized, in 24 h at 170°C, from an extremely dense system in which the weight ratio of solid (sodium aluminate and SiO_2) to liquid (tetraethylammonium hydroxide and H_2O) mixtures is 1 : 1.8; the product has comparable catalytic properties to those samples prepared by previous methods.

Keywords: zeolite Beta; synthesis

Recent patents and published literature suggest that zeolite Beta has potential technological applications in petrochemical processes and organic synthesis [1–5]. The structure of Beta was described by Treacy and Newsam [6] and Higgins et al. [7]. Zeolite Beta is an intergrowth hybrid of tetragonal and monoclinic structures. It is one of the large pore synthetic zeolites based on an aluminosilicate framework having a three-dimensional channel system with dimensions of 6.0 × 7.3 Å in the tetragonal system and 6.8 × 7.3 Å in the monoclinic system. Zeolite Beta has been synthesized from the system containing: $R–Na_2O–Al_2O_3–SiO_2–H_2O$, where R stands for tetraethylammonium hydroxide (TEAOH), diaza-1,4-bicyclo[2.2.2.] octane (DABCO) [8], dibenzyl-1,4-diazabicyclo[2.2.2.]octane [9] or benzyldimethylamine with a benzylhalide [10].

Now, we report a new method for the synthesis of zeolite Beta in which the amount of liquid (TEAOH) and H_2O) is just sufficient to wet all the solid particles and in some cases (especially at Si/Al ratio <10) the reaction mixture is in the form of small lumps. This method has great advantages in that it uses a much smaller proportion of TEAOH and shorter reaction time as compared to the usual synthetic methods. The reduction in the proportion of TEAOH required allows a decrease in the amount of water content. This change increases the weight ratio of solid to liquid in the systems from 1 : 9.1 to 1 : 1.8. The mole ratios of SiO_2/TEAOH increased from 0.53 to 6 and H_2O/SiO_2 decreased from 23 to 6.1. The consumption of organic compound could thus be reduced significantly, and the method does not require the separation of liquid mixtures before and after crystallization. In addition to this, the product yield is very high, i.e. 360 g of dry product per kg of the starting reaction mixture.

Sodium aluminate, TEAOH and water were mixed and stirred for about 15 min. Then, this solution was added to a highly reactive fumed silica and stirred with a spatula for about 15 min. Initially, the mixture appears to be a dry powder. As stirring continued for about 2 h the mixture turned into a very dense and thick solid (solid : liquid = 1 : 2), which was transferred into a stainless-steel autoclave and heated at 443 K and autogenous pressure for 24 h. The pH of the initial reaction mixture was in the range 13.2–13.8 and after crystallization it was in the range 11.4–12.0. After synthesis samples were dried at 120°C and then calcined at 540°C for about 15 h. The NH_4^+ form of zeolite-β was obtained by repeated ion exchange with 2 M NH_4Cl solution at 80°C. The protonated form was then obtained by calcining the NH_4^+ form at 450°C for about 15 h. The zeolite samples were characterized by X-ray powder diffraction, thermogravimetric analysis, bulk and surface analysis.

X-ray powder diffraction patterns were obtained with a Rigaku RU 200 automated powder diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). TGA analysis was carried out by using a Du Pont (model 951) thermal analyzer. The sample, about 30 mg, was placed in a quartz bucket and was heated at a rate of 10°C/min in the presence of N_2 (flow $\approx$ 60 ml/min). Total analysis of zeolite samples was carried out by dissolving the sample in hydrofluoric acid and then diluting with demineralized water to the desired volume. The resulting solution was analyzed for Si, Al and Na by an inductively-coupled plasma method using an ARL 3510 ICP spectrometer.

The XRD pattern shown in fig. 1 is very similar to that reported for Beta. The product contains an average 14.2 wt% organic as shown by the TGA analysis. The surface area determined by the N_2 BET method was 490 m^2/g which was roughly 5% lower than the Beta sample synthesized using the regular conventional method. In table 1 we have reported chemical analysis, XPS and IR data for three samples synthesized using the present method. The details of the experimental procedure for acidity determination using FTIR and N 1s XP spectra of chemisorbed pyridine are available elsewhere [11]. It is clearly seen that the bulk and the surface Si/Al ratios are close to each other for all samples indicating that there is a homogeneous distribution of Al species from the bulk to the surface of the crystallites. The XPS data of pyridine chemisorbed on protonated zeolites indicated that there exist three N_{1s} component peaks corresponding to three types of acid sites. The N_{1s} XP spectra of pyridine chemisorbed on Beta zeolite are well characterized [11]. The N_{1s} component peak at lower binding energy value (peak I) is assigned to the nitrogen of pyridine associated with Lewis acid sites and medium (II) and high binding energy value (III) to the nitrogen of pyridine to the relatively weak and strong Brønsted acid sites, respectively. The binding energy values of N_{1s} component peaks are quite comparable to the N_{1s} component peaks of pyridine chemisorbed on Beta zeolites synthesized using previous methods [11]. The Brønsted to Lewis

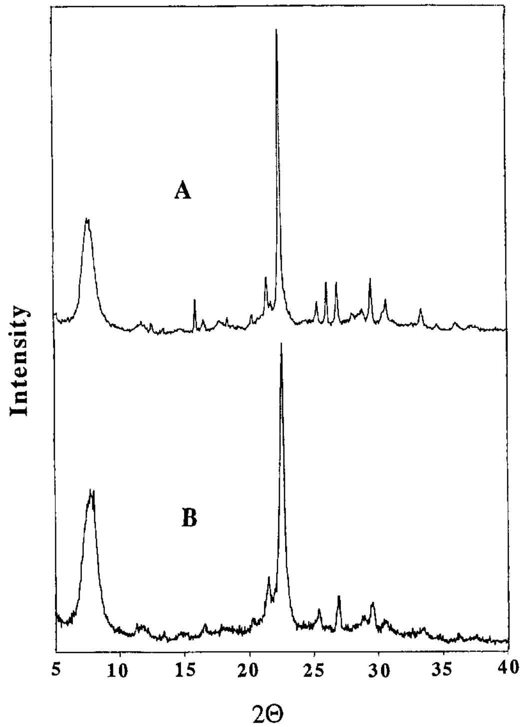

Fig. 1. X-ray powder diffraction patterns of Beta zeolites synthesized using: (A) (SiO_2/TEAOH= 1.2) at 170°C for 96 h, and (B) (SiO_2/TEAOH= 6) at 170°C for 24 h.

ratios determined by the XPS and IR methods using pyridine as a probe molecule are in excellent agreement confirming that all Al species present in three different samples are associated with either Brønsted and or Lewis acid sites.

The *n*-hexane cracking activity was determined using a quartz reactor with an internal diameter of 5 mm. 40 mg of the zeolite sample, in the form of 20–45 mesh size chips, was placed in the reactor and the remaining part was filled by glass wool. Prior to the reaction, the zeolite samples were activated carefully under flowing nitrogen (27 ml/min) 450°C for 1 h. After activation the catalyst temperature was reduced to 350°C and then the reactor was bypassed but kept at same temperature for 30 min while the nitrogen was directed through a hexane saturator maintained at 0°C. The temperature of the saturator was controlled within ±0.1°C by using a Haak model G controller. The hexane flow (ca. 27 ml/min total flow) was then passed through the reactor with the catalyst at 350°C. After 5 min on stream a gas sample was injected into the GC. A Varian 3400 gas chromatograph equipped with flame ionization detector (FID) and connected with an alumina PLOT fused silica capillary column was used for the analysis of the *n*-hexane reaction products. The activity based on the weight of hydrated zeolite, was determined from the weighed sum of the products, including small amounts of C_6 isomers. The catalytic behavior for *n*-hexane cracking of the sample of the present study and that synthe-

Table 1
Physicochemical characteristics of Beta zeolites synthesized from dense system containing a minimum of template

Sample	Si/Al		N/Al	N_{1s} binding energy (eV) [a]		
	chemical	XPS		I	II	III
beta(A)	16.2	15.5	0.91	400.0	401.8	403.0
beta(B)	13.9	12.1	0.87	400.1	401.9	402.9
beta(C)	6.7	9.2	0.82	400.0	401.9	402.9

	Relative intensity			B/L	
	I	II	III	XPS [b]	IR [c]
beta(A)	30.8	44.5	25.2	2.2	2.03
beta(B)	19.5	61.2	19.4	4.13	4.17
beta(C)	21.2	48.0	30.8	3.70	3.30

[a] N_{1s} binding energy of chemisorbed pyridine after deconvolution with reference to Si_{2p} = 103.3 eV. For peak assignment and other details see ref. [11].

[b] Brønsted-to-Lewis ratio determined from the N_{1s} relative intensity data.

[c] $B/L = (A_B/A_L)(\varepsilon_L/\varepsilon_B)$, where A_B/A_L is the absorbence ratio and $\varepsilon_L/\varepsilon_B$ the extinction coefficient ratio which is taken as 1.5 for samples having Si/Al ratio >7.5 and 1.15 for Si/Al ratio <7.5.

sized by the method in ref. [11] are compared in fig. 2. The activity data of the sample of the present study compares well with those samples. Both preparation methods involve use of TEAOH but in the case of previous methods (ref. [11] and references therein) the weight ratio of solid to liquid was 1 : 9.1, whereas for the sample of the present study it was 1 : 1.8 and the SiO_2/TEAOH ratios were 0.53 : 1 and 6 : 1, respectively. This confirms that Beta zeolite samples prepared by the present method are equally active compared to those samples prepared by previous

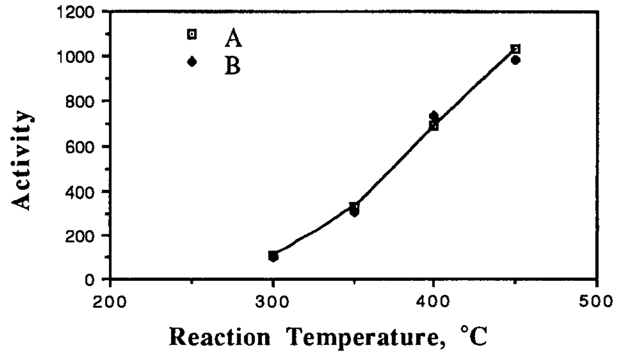

Fig. 2. Comparison of *n*-hexane cracking activity of Beta zeolites. (A) Samples prepared using (SiO_2/TEAOH= 1.2) at 170°C for 96 h, (B) (SiO_2/TEAOH= 6) at 170°C for 24 h. Activity in μmoles of *n*-hexane molecules converted per min per gram of the zeolite. Reaction conditions: sample weight = 40 mg; (N_2 + *n*-hexane) total flow = 27 ml/min. $P_{n\text{-hexane}}$ = 46.6 Torr.

methods. In using the present method of synthesis the SiO_2/Al_2O_3 ratio of the starting reaction mixture can be varied from 10 to 60.

Recently, Cannan and Hinchey [12] synthesized zeolite Beta using a reaction mixture containing 1.5 M Na_2O–6 M TEAOH–0.6 M diethanolamine–1 M Al_2O_3–25 M SiO_2–300 M H_2O. Though the amount of TEAOH with respect to SiO_2 is comparable to our method their procedure requires not only addition of 0.6 M diethanolamine but also about 10% by weight (based on total SiO_2 content) crystals of zeolite Beta as a seed. During the course of this work we were informed that a similar method of "in situ surface moistening" was used to prepare zeolite Beta with minimal use of TEAOH [13].

The marked reduction in the use of TEAOH in the present method (2.5 versus 10–28 moles of TEAOH with reference to 1 mole of Al_2O_3), shorter crystallization time (24 h versus 4–10 days) and increased productivity (per batch) should lead to a lower synthesis cost of zeolite Beta. The product obtained also has comparable catalytic properties at least with reference to the cracking of hexane.

References

[1] B.J. Arena and P.R. Kurek, US Patent 633873 (1990).
[2] N.Y. Chen and S.B. McCullen, Eur. Patent Appl. 325053 (1989).
[3] R.B. Lapierre and R.D. Patridge, Eur. Patent Appl. 94872 (1983).
[4] B. Coq, V. Gourves and F. Figueras, Appl. Catal. 97 (1993) 69.
[5] J. Pardillos, D. Brunels, B. Coq, P. Massianni, L.C. de Menorval and F. Figueras, J. Am. Chem. Soc. 112 (1990) 1313.
[6] M.M.J. Treacy and J.M. Newsam, Nature 332 (1988) 249.
[7] J.B. Higgins, R.B. Lapierre, J.L. Schlenker, A.C. Rohrman, J.D. Garwood, G.T. Kerr and W.J. Rohrbaugh, Zeolites 8 (1988) 446.
[8] P. Caullet, J. Hazm, J.L. Guth, J.F. Joly, J. Lynch and F. Raatz, Zeolites 12 (1992) 240.
[9] M.K. Rubin, Eur. Patent Appl. 149847 (1985).
[10] M.K. Rubin, Eur. Patent Appl. 149846 (1985).
[11] R.B. Borade and A. Clearfield, J. Phys. Chem. 96 (1992) 6729.
[12] T.R. Cannan and R. Hinchey, US Patent 5,139,759 (1992).
[13] L.H. Zuo, private communication.