Convenient Synthesis of Zeolite Beta in Basic Media without Alkali Metal Cations

Wanping Guo and Quanzhi Li*
Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

(Received November 22, 2001; CL-011182)

A convenient approach has been developed to synthesize zeolite Beta with SiO_2/Al_2O_3 ratios from 14.2 to infinity using tetraethylammonium hydroxide as the structure-directing agent (SDA) in absence of alkali metal cations.

Zeolite Beta is a high-silica and large-pore crystalline material initially synthesized by Wadlinger et al.[1] in basic media in the presence of tetraethylammonium hydroxide (TEAOH) and alkali metal cations. A lot of efforts have been made to synthesize it in a wide range of SiO_2/Al_2O_3 ratios using TEAOH as the structure-directing agent (SDA) since it is of great potential industrial interest as a good catalyst for hydrocarbon reactions.[2,3] Rao et al.[4,5] proposed the dry gel conversion technique to prepare it with SiO_2/Al_2O_3 ratios from 30 to infinity. However, a special autoclave had to be used in this method. Camblor et al.[6,7] reported its synthesis with various SiO_2/Al_2O_3 ratios ranging from $SiO_2/Al_2O_3 = 13$ to pure silica materials in the presence of TEAOH and HF at nearly neutral pH. But the major disadvantage of this synthesis route was the employment of HF. Up to now, zeolite Beta can not be synthesized with SiO_2/Al_2O_3 ratios above 250 using TEAOH as SDA in basic media without the use of seeds by the conventional hydrothermal method.[7,9] The synthesis of nanocrystalline zeolite Beta in basic media without alkali metal cations was previously reported.[8] However, the SiO_2/Al_2O_3 ratio of the product was restricted to a narrow range from 14.8 to 98. Now, we present a convenient approach[9] to prepare zeolite Beta with SiO_2/Al_2O_3 ratios from 14.2 to infinity using TEAOH as SDA in the absence of alkali metal cations.

The synthesis procedure was as follows: TEAOH (25 wt% aqueous solution) was diluted with deionized water. Then pseudoboehmite (51 wt% Al_2O_3, 49 wt% H_2O, Shandong Aluminium Factory) was added and the mixture was stirred for 15 min. Finally, fumed silica (Electrochemical Co., Shanghai) was added to the mixture with vigorous stirring. After stirring homogeneously, the slurry was heated to 343–353 K and kept for some time. The molar composition of the resulting gel mixture was $SiO_2 : x\ Al_2O_3 : y\ (TEA)_2O : z\ H_2O$, where $0 \leq x \leq 0.067$, $0.07 \leq y \leq 0.25$ and $4 \leq z \leq 10$. The reaction mixture was then charged into a PTFE-lined stainless-steel autoclave and heated at 413 K under autogenous pressure for 8–14 days. After crystallization, the product was recovered by filtration and washed with deionized water and dried at 373 K overnight. Calcination took place at 823 K for 6 h in air.

From the synthesis conditions shown in Table 1, it can be seen that the convenient synthesis of zeolite Beta ($SiO_2/Al_2O_3 = 14.2 - \infty$) has been achieved in basic media without alkali metal cations. Figure 1 exhibits the X-ray diffraction patterns of solid products typical of zeolite Beta with sharp and broad diffraction peaks. No other crystalline phase competing with zeolite Beta can be observed. There are two interesting features in our synthesis approach (see Table 1). One is that the yield of solid products except pure silica Beta is always in the range of 85–95%, which is quite different from the traditional synthesis in basic media where the yield of solid products remarkably decreases with the increase of SiO_2/Al_2O_3 ratio in the synthesis mixture.[8] The other is that the SiO_2/Al_2O_3 ratio in zeolite Beta sample is near to that in corresponding synthesis gel. These above features reveal the very effective synthesis of zeolite Beta in a wide range of SiO_2/Al_2O_3 ratios.

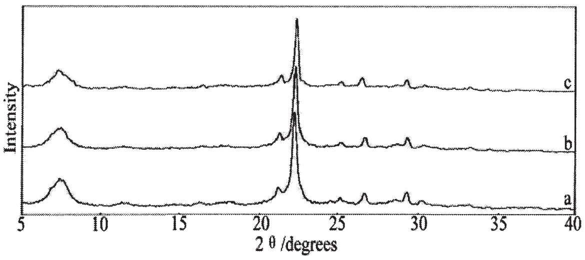


Figure 1. X-ray diffraction patterns of zeolite Beta synthesized in basic media without alkali metal cations starting from different SiO_2/Al_2O_3 ratio: (a) 30, (b) 200 and (c) infinity.

Table 1. Synthesis data of zeolite Beta samples obtained in basic media without alkali metal cations

	Chemical composition				Crystallization	Yield[a]	Relative
Sample	Gel			Zeolite	time/days	/%	crystallinity
	SiO_2/Al_2O_3	$(TEA)_2O/SiO_2$	H_2O/SiO_2	SiO_2/Al_2O_3			/%
S_1	15	0.25	9.7	14.2	14	94	55
S_2	20	0.23	8.5	17.9	14	92	70
S_3	30	0.10	6.2	27.7	10	88	100[b]
S_4	60	0.08	7.4	53.6	14	95	94
S_5	200	0.15	4.8	189	12	89	98
S_6	400	0.20	4.5	352	14	87	96
S_7	infinity	0.20	5.2	infinity	12	43	95

[a]Gram of solid per 100 g of fumed silica. [b]Reference zeolite.

The ^{29}Si MAS NMR spectra of calcined zeolite Beta with SiO_2/Al_2O_3 ratio of 27.7 and pure silica Beta are given in Figure 2. The sample ($SiO_2/Al_2O_3 = 27.7$) exhibits the spectrum quite similar to that previously reported,[10] showing the peak maximum at -104.3 ppm assigned to the presence of Si atoms in Si (1 Al) environments and the other two peaks centered at -110.0 ppm and -115.2 ppm corresponding to non-equivalent silicon atoms in Si (0 Al) environments. The spectrum of calcined pure silica Beta exhibits the presence of connectivity defects [Q^3 sites: Si (3 Si, 1 OH)].[7,11] The peak at around -110.9 ppm is assigned to Q^4 sites while the peak at around -101.6 ppm can be assigned to Q^3 sites. The ratio of $Q^3/(Q^3 + Q^4)$ is 0.24.

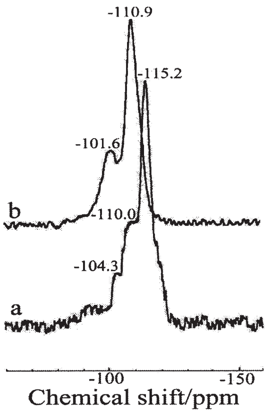
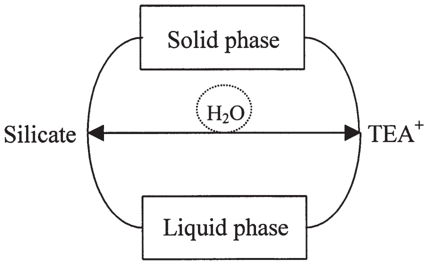


Figure 2. ^{29}Si MAS NMR spectra of calcined samples: (a) zeolite Beta with SiO_2/Al_2O_3 ratio of 27.7 and (b) pure silica Beta.

The marked difference between our synthesis approach and the reported method[8] is the water content in the reaction mixture. We think that the water content of synthetic hydrogel plays a vital role in preparing zeolite Beta with a wide range of SiO_2/Al_2O_3 ratios in basic media without alkali metal cations. The effect of H_2O/SiO_2 ratio in the starting reaction mixture on the formation of pure silica Beta was investigated. The final product from the gel with H_2O/SiO_2 ratio of 3.6 was amorphous while a clear solution instead of solid product was obtained from the gel with H_2O/SiO_2 ratio of 11. In this study, the molar composition of the gel mixture for preparing pure silica Beta was $SiO_2 : 0.18–0.25\ (TEA)_2O : 4–6H_2O$.

Considering the presence of Q^3 connectivity defects ($Si\text{-}O^-TEA^+$) in high silica or pure silica Beta obtained from basic media without alkali metal cations, it is believed that the water content of synthetic hydrogel can adjust the rational distribution of silicate and TEA^+ species in solid phase and liquid phase (see Scheme 1) to the formation of $Si\text{-}O^-TEA^+$, besides the liquid-phase transportation[12] of various species in the reaction mixture. It is TEA^+ species in solid phase that replenish continuously consumed TEA^+ species in liquid phase during the crystallization of high silica or pure silica Beta.



Scheme 1. Representation of the effect of the water content in synthetic hydrogel during the formation of high silica or pure silica Beta.

In conclusion, we have demonstrated that zeolite Beta with SiO_2/Al_2O_3 ratios from 14.2 to infinity can be conveniently prepared in basic media without alkali metal cations in the presence of TEAOH by restricting the water content of synthetic hydrogel. Our approach may be applied for the synthesis of other types of zeolites in a wide range of SiO_2/Al_2O_3 ratios.

Financial support from the National Natural Science Foundation of China is gratefully acknowledged (Grant No. 29733070).

References and Notes

1 R. L. Wadlinger, G. T. Kerr, and E. J. Rosinski, U. S. Patent 3308069 (1967); *Chem. Abstr.*, **67**, p 26245s.
2 A. Corma, V. Gomez, and A. Martinez, *Appl. Catal. A*, **119**, 83 (1994).
3 Y. Miyamoto, N. Katada, and M. Niwa, *Microporous Mesoporous Mater.*, **40**, 271 (2000).
4 P. R. Hari Prasad Rao and M. Matsukata, *Chem. Commun.*, **1996**, 1441.
5 P. R. Hari Prasad Rao, K. Ueyama, and M. Matsukata, *Appl. Catal. A*, **166**, 97 (1998).
6 M. A. Camblor, A. Corma, and S. Valencia, *J. Mater. Chem.*, **8**, 2137 (1998).
7 M. A. Camblor, A. Corma, and S. Valencia, *Chem. Commun.*, **1996**, 2365.
8 M. A. Camblor, A. Corma, A. Mifsud, J. Perez-Pariente, and S. Valencia, *Stud. Surf. Sci. Catal.*, **105**, 341 (1997).
9 W. Guo and Q. Li, C. N. Patent 01105643.6 (2001).
10 J. Perez-Pariente, J. Sanz, V. Fornes, and A. Corma, *J. Catal.*, **124**, 217 (1990).
11 T. Takewaki, S. J. Hwang, H. Yamashita, and M. E. Davis, *Microporous Mesoporous Mater.*, **32**, 265 (1999).
12 J. Perez-Pariente, J. A. Martens, and P. A. Jacobs, *Appl. Catal.*, **31**, 35 (1987).