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COMMUNICATION

Fast synthesis of submicron aluminosilicate (low silica/alumina ratio) zeolites under solventless microwave radiation

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A promising strategy for synthesis zeolites has been reported in this paper. The method combines the advantages of both microwave heating and solventless synthesis. This method can generate zeolites under atmospheric pressure and is safe, highly efficient and environmentally benign.

Microwave radiation is a well-known energy source and has been employed in many chemical reaction studies. For many years, synthesis of molecular sieves via microwave (MV) dielectric heating has been regarded as a fast and efficient process. Similarly, microwave-assisted synthesis of zeolites is also simple, fast, cost-effective and an environmentally benign route, which is an example of green chemistry if carried out under solvent-free conditions.[1] The microwave synthesis of zeolites has many advantages over conventional heating methods, such as reduction in the synthesis time, and increased yields and purity of products.[2,3b] Moreover, microwave energy can heat the reaction mixture more uniformly, thereby leading to smaller particles with a narrow size distribution.[3]

Recently, Yan and co-workers have developed a new strategy for the preparation of MFI zeolite at ambient pressure via a dry-gel conversion using ionic liquid and microwave heating, making it a promising, safe, fast, and continuous process for industrial applications.[4] Because of the vanishingly low vapour pressure of ionic liquids, synthesis can be performed at ambient pressure, eliminating the safety concerns associated with high hydrothermal pressures.[5] Notably, Xiao and coworkers[6] reported a solvent-free synthesis of aluminosilicate and aluminophosphate-based zeolites. The main advantages of this method are reduction in water usage and use of a low pressure. Furthermore, microwave-assisted synthesis of zeolites in the absence of solvents and organic templates would be a more promising route in the synthesis of zeolite field.[1a] This has great significance on preparation zeolites with enhancing the synthesis productivity and reducing the energy

consumption for the thermal reaction.

Great attentions have been paid to prepare zeolites with small particle size. Generally, nanosize zeolite particles could enhance the adsorption capacity and catalytic activity due to higher surface area and shorter diffusion path length.[7] In addition, zeolite nanocrystals displayed impressive performance as seeds for zeolite powder and membrane, catalysts, chemical sensors, and ion exchangers.[8] Several strategies have been developed to synthesize nano zeolites with low silica/alumina ratio, that use organic amines and quaternary ammonium ions as structure directing agents.[9] Generally, the use of organic templates incurs high cost and causes environment hazards resulting from removing the organic templates by combustion at high temperature. It is a challenge to prepare sub-micron zeolites such as SOD, LTA, FAU, LTA/FAU zeolites in the absence of organic templates.

In this paper, we report, for the first time, a simple, fast and solventless route to prepare sub-micron zeolites with a low silica/alumina ratio (SOD, LTA, FAU, LTA/FAU) by mixing, grinding and heating the mixture of raw materials via microwave radiation (See the Supplementary Information for synthesis and characterization details). The synthetic processes and the zeolite properties were carefully investigated. Importantly, MS-NaX exhibits good ion exchange performance in Ca^{2+} exchange tests.

Fig. 1. shows X-ray diffraction (XRD) pattern, scanning electron microscope (SEM) image, N_2 adsorption isotherms, ^{29}Si MAS NMR spectra and transmission electron microscope (TEM) image of the as-synthesized sub-micron zeolite MS-NaX. The XRD pattern (Fig. 1A) showed a series of characteristic peaks corresponding to the FAU zeolite structure, indicating a successful synthesis of zeolite MS-NaX *via* microwave heating of the mixture of raw materials. The SEM image (Fig. 1B) shows the zeolite particle morphology to be roughly spherical in shape, 0.3-0.6 μ m in size. A small size of the particles could be obtained probably because of the fast heating by microwave dielectric radiation, high concentration of inorganic precursor, and presence of sodium chloride.[10] Zhu et al. claimed that NaCl plays the role of supplying the Na^+ cations, as well as acting as a salt affecting the crystallization and crystal morphology through its effect on the dielectric constant of the solution.[10b] The N_2 sorption isotherm (Fig. 1C) of the as-synthesized sample

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exhibited a steep increase ranging from $10^{-6}<P/P_o<0.01$, which resulted from the filling of micropores. Additionally, at a relative pressure of 0.5-0.95, a hysteresis loop was observed, which indicated that mesopores were further generated from a tiny amount of residual aluminosilicate precursors. The Brunauer-Emmett-Teller (BET) surface area and the pore volume obtained were 542 m^2g^{-1} and 0.46 cm^3g^{-1}, respectively. Fig. 1D shows the ^{29}Si MAS NMR spectra of MX-NaX. The peaks at -85.1, -89.3, -93.9, -98.6, and -102.5 ppm were assigned to the various Si species, viz. Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al), respectively.[11] The molar ratio of Si/Al in the framework for MS-NaX was 1.42 by ^{29}Si MAS NMR spectra analysis. TEM images showed that some octahedral faceting of nanocrystals is apparent and the particle size is 300-600 nm (Fig. 1E).
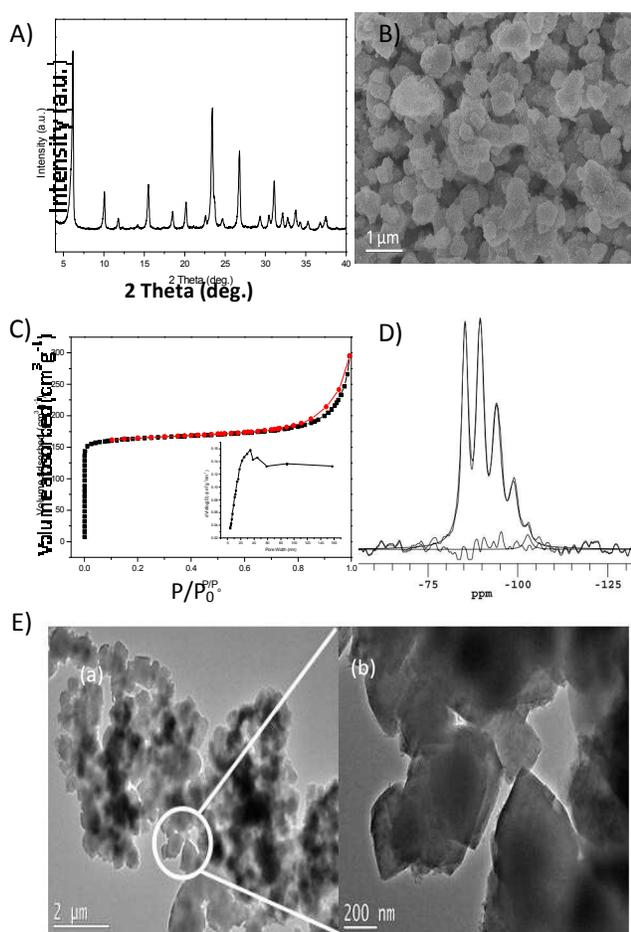
Fig. 1. As synthesized sub-micron zeolite MS-NaX. A) XRD pattern, B) the SEM image, C) N$_2$ adsorption isotherms (BJH pore distribution insert), D) ^{29}Si MAS NMR spectra and E) TEM images– (a) low, and (b) high magnifications.

MS-NaA, MS-NaA/X and MS-SOD were also successfully prepared in a similar way *via* microwave heating of the mixture of solid raw materials. The XRD patterns displayed the characteristic peaks of each zeolite: MS-NaA (Fig. S1 A, ESI†), MS-SOD (Fig. S2 A, ESI†) and MS-NaA/X (Fig. S3 A, ESI†). Furthermore, both MS-NaA and MS-SOD zeolites had similar spherical morphologies along with some agglomerates (Fig. S1 B and Fig. S2 B, ESI†). On the other hand, MS-NaA/X exhibited a cubic structure with good dispersity, with increasing A/X ratio (Fig. S3 C, ESI†). The particle size of these three zeolites is ca. 200-500 nm. The synthesis that produced both MS-NaA and MS-NaX contains each phase in different proportion depending on the relative amount of the reaction mixture, *i. e.*, Si/Al ratio and alkali concentration. In general, the proportion of zeolite MS-NaX increased with decreasing alkali content of the starting solid mixture and enhancing Si/Al ratio in the initial composition. Considering the effect of adsorbents, there is a synergistic effect when using mixtures of these two zeolites on removal of Ca^{2+} and Mg^{2+} ions, and particularly suitable for application in detergent dealing with different concentrations of Ca^{2+} and Mg^{2+} ions in local water systems.[12,14,15c] Fig. S3 B, ESI† shows the N$_2$ sorption isotherms of MS-NaA/X with various ratios of NaA and NaX zeolite. The isotherm indicated that the microporous surface of the sample as well as micropore volume gradually increased with an increasing amount of zeolite X in MS-NaA/X (Table S1, ESI†). Compared with hydrothermal synthesis of nanoscale porous materials under microwave radiation, the distinguishing features of the microwave solventless synthesis of NaX is that a large reduction of reaction pressure resulting from absence of any solvents remarkably decreases the reaction pressure. Therefore, the requirement for the high pressure equipment could be avoided in the synthesis.[4b,6a]

Fig. 2. shows X-ray diffraction patterns, the transmission electron micrograph images and N$_2$ adsorption isotherms of the MS-NaX. Initially, the XRD patterns (Fig. 2A-b) showed no sharp peaks even after crystallization for 20 min, indicating that amorphous phase was dominant. However, after an exposure to microwave radiation for 45 min, the sample showed weak peaks associated with the FAU structure (Fig. 2A-c), indicating that Faujasite crystal were formed. Additionally, TEM images of this microwave-treated sample showed a large number of crystals along with some amorphous phase (Fig. 2C-c). By increasing the crystallization time to 55 min, the XRD signals gradually increased (Fig. 2A-f), as shown in the crystallization curve displayed in Fig. S4, ESI†. These typical FAU crystals were also examined under TEM (Fig. 2C-f). When the crystallization time was extended to 60 min, there was no further change in the XRD patterns (Fig. 2A-f). Furthermore, TEM images showed markedly well-defined octahedral shapes with a little amorphous phase (Fig. 2C-f). By contrast, pure SOD required 2 h of microwave heating to reach a similar level of crystallization. Fig. 2B shows the N$_2$ sorption isotherms of the MS-NaX samples crystallized at various time. Only a small amount of microporosity (17 m^2/g) could be obtained after a microwave radiation of 20 min (XRD pattern have no signals observed). When the crystallization time was between 45–60 min, there was a large increase in the crystallinity, and the micropore surface area also varied from 195 to 475 m^2/g (Table S1, ESI†). Furthermore, high magnification TEM micrograph in Fig. 2C, illustrate the process of growth of Faujasite crystals. The TEM images confirmed that the zeolite MS-NaX evolved from the nuclei inside the amorphous dense gel, and grew into larger crystals through consumption of the surrounding

amorphous phase.[13]

A)

B)

C)
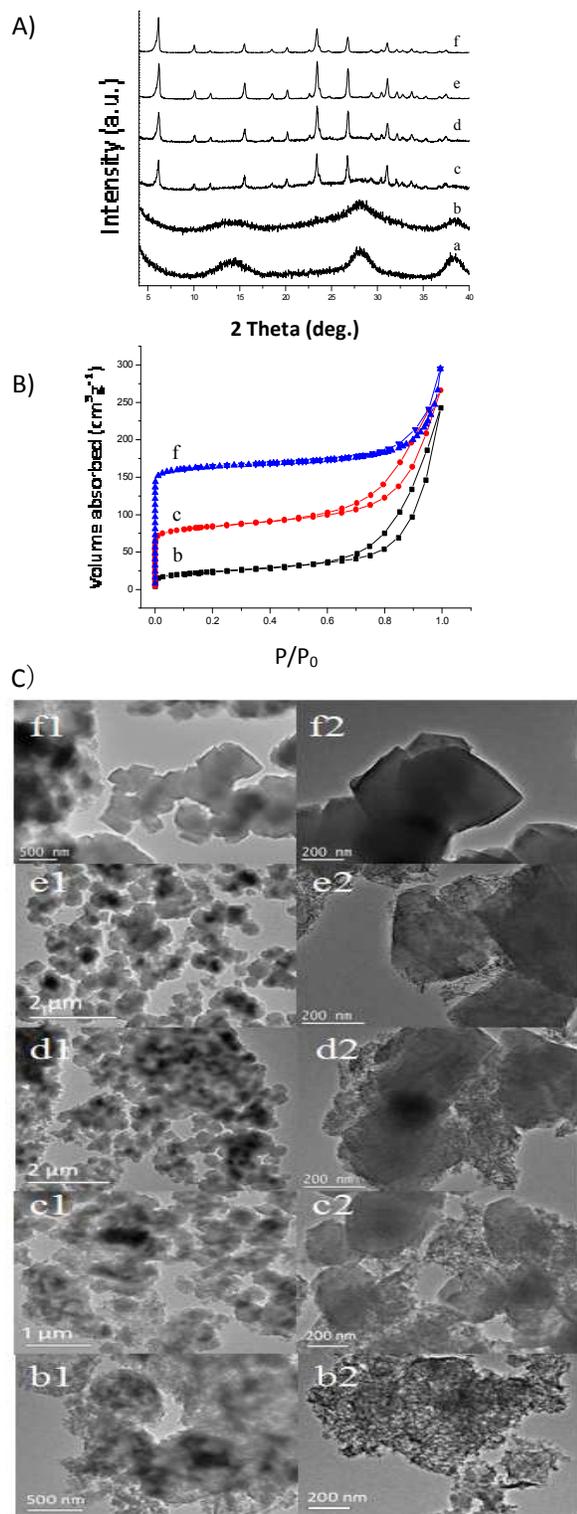
Fig. 2 A) XRD patterns, B) N_2 sorption isotherms and C) TEM images of the MS-NaX samples under microwave radiation for different times (a) 15, (b) 20, (c) 45, (d) 50, (e) 55, (f) 60 min.
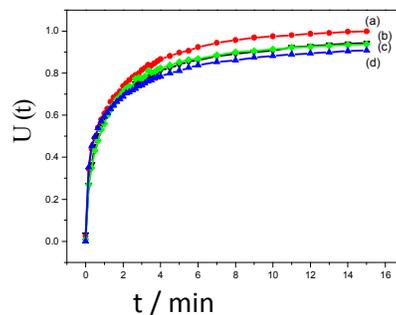
Fig. 3. The sodium ion-exchange curves of (a) MS-NaX zeolite(●), (b) conventional NaX zeolite(▼) and low quality MS-NaX with different crystallization time, (c) 55 min (◆) and (d) 50 min (▲)

Calcium ion-exchange rate is important for practical application of zeolite as detergent builders. The rapid replacement of the calcium ions in water with sodium ions contained in zeolites convert hard water to soft water, thus enhancing the washing power of detergents.[14] The Ca^{2+} exchange kinetics of zeolite MS-NaX was monitored by sodium ion selective electrodes.[15] Fig. 3 shows the exchange rate curves of Na^+ by Ca^{2+} at 294 K, the $C_{t\ min}$ and $C_{15\ min}$ indicate the amount of exchange at time t and 15 min, $U(t)=C_{t\ min} / C_{15\ min} \times 100\ \% / t$, denotes the exchange rate at a certain time, which also represent calcium exchange capacity (CEC) at certain time. Compared to NaX (ca. 4 μm in size, Fig. S5, ESI†), the excellent exchange rate of Na^+ by Ca^{2+} in MS-NaX can probably be attributed to small particle size or the presence of mesoporosity[16] (Fig. 1C), which are favorable for the diffusion of ions in the aqueous solution. Furthermore, we contrast less well-crystallized MS-NaX , fully crystallized MS-NaX with NaX prepared by conventional hydrothermal synthesis method, both the samples (MS-NaX-55$_{min}$ and MS-NaX-55$_{min}$) showed the same (Fig. 3c) and slightly low (Fig. 3d) ion-exchange rates compared with the conventional zeolite NaX, even though MS-NaX is poorly crystalline. An ICP-MS analysis revealed that amount of Ca^{2+} exchanged in conventional zeolite NaX and MS-NaX were 158 and 172 mg $CaCO_3$ per gram hydrous zeolite, respectively. Therefore, submicron MS-NaX probably have many advantages commercially as detergent builders at a large scale, and it is expected that our methodology will favor the development of soft detergent additives.

Conclusions

To summarize, submicro zeolites with the structure of FAU, LTA, FAU/LTA and SOD have been successfully synthesized via a solventless route by microwave radiation heating. The zeolites were obtained by facile mixing of hydrated form of solid silica and alumina source and heating the mixture in a modified household microwave oven. For example, the FAU zeolite, synthesized in this work, had a particles size of 200~600 nm versus 4 μm in conventional products. Furthermore, the synthesis time in this work was much shorter (50 min) than the conventional one (5 h).

Compared to the microwave method, the hydrothermal synthesis of zeolite is a time-consuming process. The advantages of the solventless synthesis are directly using the starting raw materials and reducing the pollute water for without adding extra water. Moreover, the MS-NaX exhibited excellent calcium ion-exchange rate higher than that of the conventional hydrothermally synthesized zeolite NaX. Overall, the current method of preparation of zeolites by microwave heating via a solventless route is convenient, efficient, and saves both energy and cost. Thus, this method has potential application in large-scale industries in the future.

Notes and references

1 (a) X. Meng and F. S. Xiao. *Chem. Rev.,* 2014, **114**, *1521*; (b) G. A. Tompsett, W. C. Conner, and K. S. Yngvesson, *ChemPhysChem,* 2006, **7**, 296; (c) M. Inada, H. Tisujimoto, Y. Eguchi, N. Enomoto, J. Hojo, *Fu*el, 2005, **84,** 1482

2 (a) G. Kühl, Robson, H. (Ed.) 2nd Edition Elsevier Science B.V. 19-20; (b) L. Bonaccorsi, E. Proverbio, *Journal of crystal growth,* 2003, **247**, 555; (c) Melkon Tatlier, K. Baris Cigizoglu, Begum Tokay etc, *Journal of crystal growth,* 2007, **306**, 1463; (d) Y. S. Li, W. S. Yang, *J. Membrane Sci.,* 2008, **316**, 3

3 (a) H. J. Kitchen, S. R. Vallance, J. L. Kennedy ect. *Chem. Rev.,* 2014, **114**, 1170; (b) B. Panzarella, G. Tompsett, W. C. Conner, K. Jones, *ChemPhysChem,* 2007, **8**, 357

4 (a) A. Anna Jawor, B. H. Jeong, E. M. V. Hoek, *J Nanopart Res.,* 2009, **11**:1795-1830; (b) R. Cai, Y. Liu, S. Gu, Y. S. Yan, *J. Am. Chem. Soc.,* 2010, **132**, 12776; (c) Y. Xu, Z. Tian, S. Wang, Y. Hu, L. Wang, B. Wang, Y. Ma, L. Hou, J. Yu, L. Lin, *Angew. Chew. Int. Ed.,* 2006, **45,** 3965.

5 E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald, R. E. Morris, *Nature,* 2004, **430**, 1012.

6 (a) L. Ren, ,Q.Wu, C. Yang, L. Zhu,, C. Li; P. Zhang,, H. Zhang, X. Meng, F. Xiao, *J. Am. Chem. Soc.,* 2012, **134**, 15173; (b) Q. Wu,, X. Wang, G. Qi, Q. Guo, S. Pan, X. Meng, F. Deng, F. Fan,Z. Feng, C. Li, S. Maurer, U. Müller, *J. Am. Chem. Soc.,* 2014, **136**, 4019; (c) J. Y. Jin, Q. Sun, G. D. Qi, C. G. Yang, J. Xu, F, Chen, X. J. Meng, F. Deng, F. S. Xiao, *Angew. Chem. Int. Ed.* 2013, **52**, 9172.

7 (a) F. Pan, X. C. Lu, Q. S. Zhu, Z. M. Zhang, Y. Yang, T. Z. Wang, S.Chen, *J. Mater. Chem. A,* 2014, **2**, 20667; (b) K. Shen, N. Wang, W. Z. Qian, Y. Cui, F. Wei, *Catal. Sci. Technol*, 2014, **4**, 3840; (c) T. F. Chaves, H. O. Pastore, D. Cardoso, *Micro. Meso. Mater.,* 2012, **161**, 67.

8 (a) Z. L. Cheng, E. Gao, H. L. Wan, *Chem. Comm,* 2004, 1718; (b) L. Tosheva, V. P. Valtchev, *Chem. Mater.,* 2015, **17**, 2494; (c) T. L. Cui, X. H. Li, L. B. Lv, K. X. Wang, J. Su, J. S. Chen, *Chem. Comm*. 2015, **51**, 12563.

9 (a) B. A. Holmberg, H. Wang, J. M. Norbeck,Y. Yan, *Micro. and Meso. Mater.,* 2003, **59**, 13; (b) W. Fan, S. Shirato, F. Gao, M. Ogura, T. Okubo, *Micro. Meso. Mater.,* 2006, **89**, 227; (c) O. Larlus, S. Mintova, T. Bein, *Micro. Meso. Mater.,* 2006, **96**, 405; (d) M. Jafari, A. Nouri, M. Kazemimoghadam, T. Mohammadi, *Powder, Technol.* 2013, **237**, 442.

10 P. Sharma, J. Yeo, D. K. Kim, C. H. Cho J., *Mater. Chem.,* 2012, **22**, 2838; (b) G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu. O. Terasaki, *Chem. Mater.,* 1998, **10**,1483.

11 G. Engelhardt, E. Lippmaa, M. Tarmak, M.A. Magi, Z. *Anorg. Allg. Chem.,* 1981, **482,** 49.

12 (a) A.Zatta,R. Clerici ,E. Faccetti, P. D. Mattioli. M. R. Rabaioli, P. Radici, R. Aiello, F.Crea, *JORNADAS-COMITE ESPANOL DE LA DETERGENCIA,* 1997, **27**: 71; (b) Y. Rraa and R. W. Thompson, *J. Mater. Chem.,* 2002,**12**, 496.

13 (a) S. Mintova, N. H. Olson, V. Valtchev, T. Bein, *Science,* 1999, **283**, 958, (b) P. M. Slangen, J. C. Jansen, H, Bekkum, *ja.,* 1997, **9**,259; (c) J. F. Yao, D. Li, X. Y. Zhang, C. H. Kong, W. B. Yue, W. Z. Zhou, H. T. *Wang, Angew. Chem. Int. Ed.,* 2008, **47**, 8397.

14 (a) Y. Yu, J. Zhao, E. B. *Andrew, Chin. J. Chem. Eng.,* 2008, **16**, 517; (b) R. L. B. Mao, N. T. Vu, S. Xiao, A. Ramsaran, *J. Mater. Chem.,* 1994, **4**, 1143; (c) S. H. Park, J. K. Yang, J. H. Kim, C. B. Chung, C. Seo, *Green Chem.*, 2015, **17**, 3571.

15 (a) Y. Wang, L. Fu, Y. Liu, Q. Xu, Chin. J. Ana. Chem. 1999, **27**; (b) S. Fang, Y. Fu and P, Lin, *Talanta,* 1994, **41**, 155; (c) Y. Traa, R. W. Thompson, *J. Mater. Chem.,* 2002, **12**, 496; (d) Z. Wang, W. Wang, *China Surfactant Detergent & Cosmetics, 1*993, **3** , 41; (e) Z. T. Xue, Z. L. Lin, J. H. Ma, X. Bai, Y. H. Kang, W. M. Hao, R. F. Li, *Desalication,* 2014,**341**,10

16 S. Liu, X. Cao, L, Li, C. Li, Y. Ji, F. Xiao, Colloids and Surf. A: *Physicochem*. *Eng. Aspects,* 2008, **318**, 269.

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