

Aging time effect on the synthesis of small crystal LTA zeolites in the absence of organic template

S. Alfaro ^{a,*}, C. Rodríguez ^a, M.A. Valenzuela ^a, P. Bosch ^b

^a Lab. Catálisis y Materiales, ESIQIE-Instituto Politécnico Nacional, Zacatenco, 07738, México D.F., México

^b Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, 04510, México D.F., México

Received 13 November 2006; accepted 1 March 2007

Available online 12 March 2007

Abstract

Crystals of LTA zeolites were obtained in absence of organic templates using a crystallization temperature of 373 K. The as-synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-Transform Infrared (FTIR) spectroscopy. The aging time was found to be a crucial factor for the control of the crystal size. Samples aged between 72 and 144 h presented an average crystal size of ca. 200 to 500 nm.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Crystal growth; Nanomaterials; Hydrothermal synthesis; Zeolite LTA; Aging time

1. Introduction

Zeolites are crystalline aluminosilicate or silicate materials, which have a highly regular and open microporous structure formed by a three-dimensional network of SiO₄ and AlO₄ tetrahedra. The tetrahedra are linked together to give cages connected by pore openings of defined size; depending on the structural type, the pore sizes range from 0.3 to 1 nm approximately [1]. These exceptional properties have led to numerous technical applications as bulk powder form (catalysts, adsorbents and ion exchangers) [2–4]. The synthesis of small or nanocrystal like zeolites is crucial to prepare new materials [5–8] as ultra-thin zeolite films in membranes among other examples [9–11]. In addition, the reduction of the crystal size to the nanometer scale is the basis for unique applications in micro-electronics devices [12].

The synthesis of zeolite nanocrystals in the form of stable colloidal suspensions has been one of the most important research lines in zeolite science during the past decade. Several microporous materials, among others MFI-, LTA-, FAU-, BEA-type materials, have been prepared in the form of colloidal

suspensions with narrow particle size distribution [13]. The synthesis of zeolite crystals with narrow particle size distribution requires homogeneous distribution of the viable nuclei in the system. Therefore, the homogeneity of the starting system and simultaneity of the events leading to the formation of precursor gel particles, and their transformation into a crystalline zeolitic material, are of primary importance [14]. In general, very diluted systems containing abundant amounts of tetraalkylammonium hydroxides have been used in the synthesis of zeolite nanocrystals with narrow particle size distribution. The alkaline cation concentration in such systems has to be very limited in order to avoid the flocculation of gel particles. All these factors together with the careful choice of the silica source allow the stabilization of “clear” starting solutions where only discrete gel particles are present. Another important factor that influences zeolite crystal size is the temperature. The crystallization of zeolite nanoparticles has been usually performed at the lowest possible temperature for a particular zeolite, which results in a relatively long synthesis [15]. Therefore, a reduction of the crystallization time and optimization of the conditions yielding zeolite nanoparticles is highly desirable. Several authors have already reported on the synthesis of nanocrystalline zeolite A [16–20]. However, the drawback of these synthesis procedures is generally that large amounts of the comparatively expensive organic template tetramethylammonium hydroxide (TMAOH)

* Corresponding author. Tel.: +52 55 57296000x55112; fax: +52 55 5586 2728.

E-mail address: salfaroh@ipn.mx (S. Alfaro).

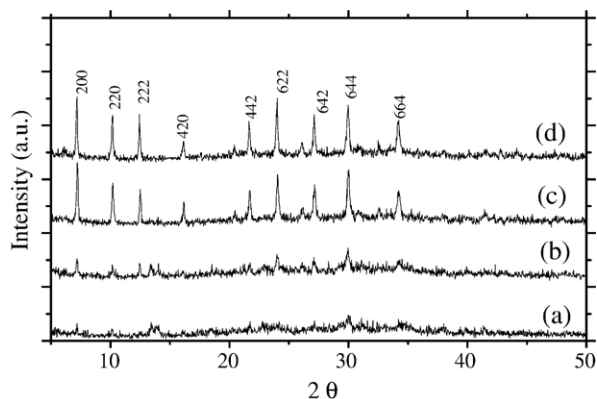


Fig. 1. XRD patterns of LTA zeolites obtained by hydrothermal method, using variable aging time. a) 24 h, b) 48 h, c) 72 h, d) 144 h.

have to be employed in order to promote nucleation and, thus, the formation of nanocrystals [13].

In this work, we present the resulting LTA zeolites prepared by hydrothermal synthesis without the presence of organic template at low temperature of crystallization (373 K) and the study of the aging time effect.

2. Experimental

2.1. Synthesis

The precursor gels were prepared in two steps. First, an aqueous sodium hydroxide solution (NaOH, Fluka) was mixed with an aluminum isopropoxide ($\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$, Aldrich) solution using a vigorous stirring (magnetic stirring: 1500 rpm) during 1 h to avoid a rapid gelling. Second, a diluted solution of colloidal silica (LUDOX AS-40, DUPONT) was added into above suspension under stirring. The final composition of the gels was: $\text{Al}_2\text{O}_3:1.2\text{SiO}_2:2.5\text{NaOH}:145\text{H}_2\text{O}$. The gels were aged from 24 to 144 h, then the mixture was transferred to a teflon-lined stainless steel autoclave and the hydrothermal reaction was carried out for 24 h under static conditions in a convection oven preheated at 373 K. The obtained zeolite powder was rinsed with distilled water and calcined for 4 h at 623 K to remove the water excess occluded in the zeolite pores.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were collected on a Siemens D500 diffractometer coupled to a copper anode tube

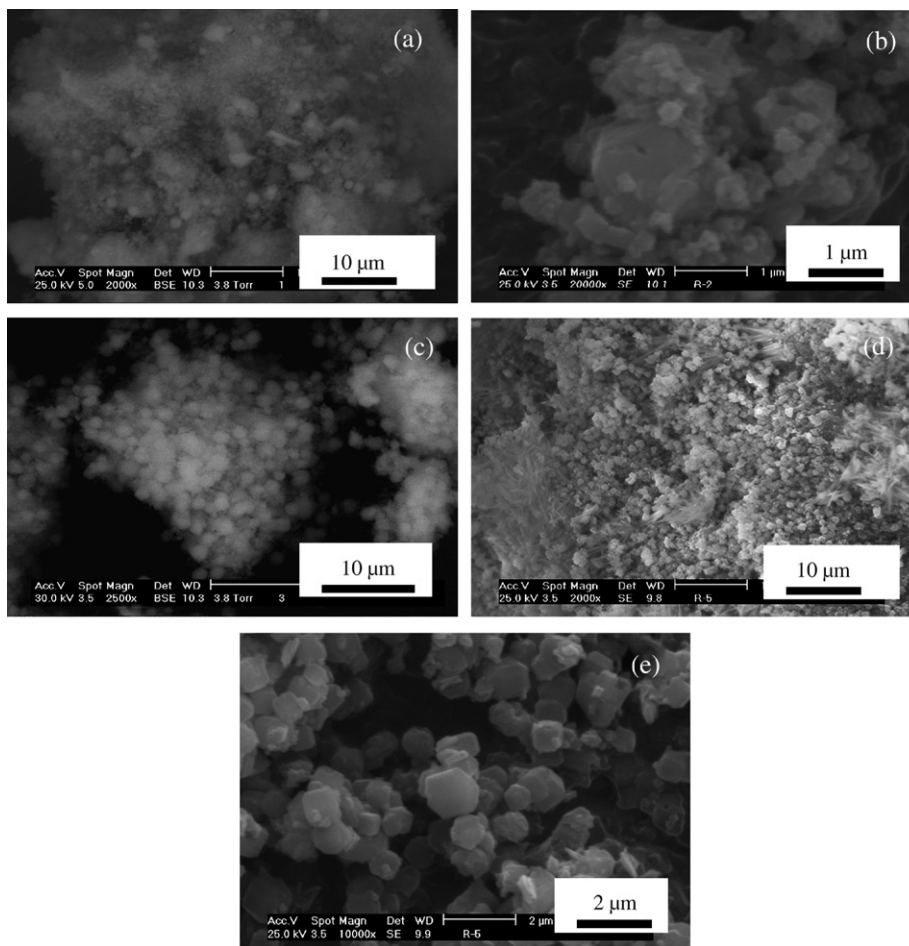


Fig. 2. SEM images showing small crystals of LTA zeolites obtained by hydrothermal method, using variable aging time. a) 24 h, b) 48 h, c) 72 h, d) 144 h, e) 144 h at a higher magnification.

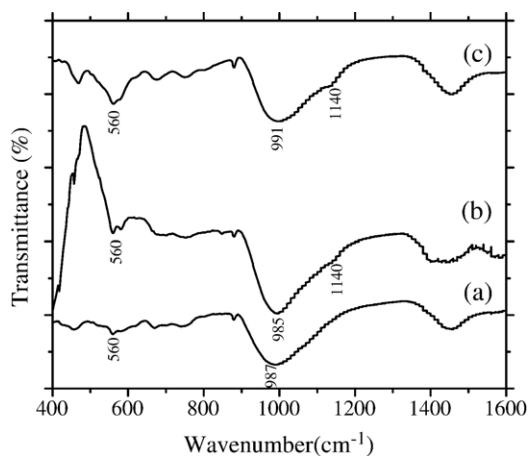


Fig. 3. IR spectra of LTA zeolites obtained by hydrothermal method, using variable aging time a) 48 h, b) 72 h, c) 144.

($K\alpha$, $\lambda = 1.5405 \text{ \AA}$). The particle size and the morphology were determined by scanning electron microscopy (XL30, ESEM, Philips). FTIR spectra in the region $1600\text{--}400 \text{ cm}^{-1}$ were obtained with a Nexos-470 Nicolet spectrometer.

3. Results and discussion

3.1. XRD

X-ray diffractograms of the 623 K treated samples, aged at different times, are compared in Fig. 1. The patterns of the 24 and 48 h aging time (Fig. 1(a) and (b)) samples present a few broad peaks, which are due to small crystallites with undefined phase composition. This means that, for an aging time of 24–48 h, the zeolite crystals do not grow. However, samples aged for 72 and 144 h (Fig. 1(c) and (d)) clearly show sharp and intense peaks which can be attributed to LTA zeolite (JCPDS = 89-5422 card).

3.2. SEM

Results obtained by XRD were confirmed with those of SEM. This technique was used to determine the morphology and the particle size. Fig. 2 compares the SEM images of the samples treated at 623 K. Images of samples aged at 24 and 48 h (Fig. 2(a) and (b)) consist of small crystals, ca. 1000 nm, embedded in amorphous aggregates. However, increasing the aging time to 72 and 144 h (Fig. 2(c) and (d)) edged and well-defined small crystals of LTA zeolite appeared with a size less than $1 \mu\text{m}$. Note that sample with the higher aging time (144 h, Fig. 2d) presents the smallest crystal size compared with those at 24, 48 or 72 h of aging time. In addition, the 144 h aging time sample has a morphology similar to the 72 h sample with the characteristic cube shape of the LTA zeolites [2] and with a higher dispersion. Note that no aggregates are present. Fig. 2e corresponds to an expanded zone of Fig. 2d, which shows more clearly the LTA zeolites crystal morphology with an average size of 500 nm approximately, although some particles with sizes ranging from 200 to 300 nm can be observed.

3.3. FTIR

Fig. 3 displays the FTIR spectra of the samples treated at 623 K. Vibrations of the zeolites framework give rise to the typical bands in the mid and far infrared. A distinction is made between external and

internal vibrations of the TO_4 tetrahedra. The original assignments of the main IR bands [2,21] were as follows: internal tetrahedral $1250\text{--}920 \text{ cm}^{-1}$, pore opening vibrations; $1150\text{--}1050 \text{ cm}^{-1}$, double ring $650\text{--}500 \text{ cm}^{-1}$. The most important peak in the region from 500 to 600 cm^{-1} is related to the presence of the double ring (D4R) that is characteristic in the A zeolite.

According to these results, it seems that the formation of small zeolitic crystals depends on the amount of aluminosilicate nuclei present in the precursor gel. As mentioned in the experimental section, the silica source was slowly added to an aqueous solution of sodium hydroxide with a high concentration of aluminum ions, followed by a long aging time. During the last step the adsorption of Al reduces the rate of silica dissolution and this slow dissolution of the silica releases monomeric silica anions that rapidly react with aluminate anions to form an aluminosilicate precipitate leading to a better control of the nuclei formation rate as well as the nuclei growth [22,23]. On the other hand, Zhdanov and co-workers [24] showed that room temperature ageing of aluminosilicate Na-X gels resulted in both an acceleration of the crystallization and a crystal size diminution of the product, thus linking the ageing process directly to the number of formed nuclei. The product-promoting effect of aging was attributed to the action of polycondensation reactions in the formation of groups facilitating crystallization.

4. Conclusion

Small crystals of LTA zeolites were obtained from diluted solutions without organic template at low temperature of crystallization (373 K). This work shows that the structural and morphological properties of LTA zeolites depend strongly on the synthesis aging time. Using an aging time of 144 h and vigorous stirring during the crystallization step, the agglomeration of the particles is avoided and then a higher dispersion of the particles is obtained with crystal size ranging from 200 to 500 nm.

Acknowledgments

The authors are grateful to the financial support of Project SIP 2006-0099, and COFAA, IPN. The technical work of L. Baños and J. Guzmán from IIM-UNAM and E. Terrés and V. Menéndez from IMP is gratefully acknowledged.

References

- [1] R. Szostak, *Molecular Sieves — Principles of Synthesis and Identification*, 1st ed.; Van Nostrand Reinhold: New York, 1989; 2nd ed.; Blackie: London, 1998.
- [2] D.W. Breck, *Zeolite Molecular Sieve, Structure, Chemistry and Use*, E. Krieger Publishing Co, USA, 1994.
- [3] M. Stöcker, *Microporous Mesoporous Mater.* 82 (2005) 257.
- [4] E.E. McLeary, J.C. Jansen, F. Kapteijn, *Microporous Mesoporous Mater.* 90 (2006) 198.
- [5] Y. Cheng, L.-J. Wang, J.-S. Li, Yu-C. Yang, X.-Y. Sun, *Mater. Lett.* 59 (2005) 3427.
- [6] S.D. Kim, S.H. Noh, K.H. Seong, W.J. Kim, *Microporous Mesoporous Mater.* 72 (2004) 185.
- [7] R.M. Mohamed, O.A. Fouad, A.A. Ismail, I.A. Ibrahim, *Mater. Lett.* 59 (2005) 3441.
- [8] S.S. Hayrapetyan, H.G. Khachatryan, *Microporous Mesoporous Mater.* 78 (2005) 151.

- [9] M. Vilaseca, J. Coronas, A. Cirera, A. Cornet, J.R. Morante, J. Santamaría, *Catal. Today* 82 (2003) 179.
- [10] S. Mintova, T. Bein, *Microporous Mesoporous Mater.* 50 (2001) 159.
- [11] J. Coronas, J. Santamaría, *Chem. Eng. Sci.* 59 (2004) 4879.
- [12] Y.S.S. Wan, J.L.H. Chau, A. Gavriilidis, K.L. Yeung, *Microporous Mesoporous Mater.* 42 (2001) 157.
- [13] L. Tosheva, V.P. Valtchev, *Chem. Mater.* 17 (2005) 2494.
- [14] C.S. Cundy, P.A. Cox, *Chem. Rev.* 103 (2003) 663.
- [15] B.A. Holmberg, H. Wang, J.M. Norbeck, Y. Yan, *Microporous Mesoporous Mater.* 59 (2003) 13.
- [16] G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu, O. Terasaki, *Chem. Mater.* 10 (1998) 1483.
- [17] J.E. Otterstedt, P.J. Sterte, B.J. Schoeman, WO 94/05597, 1994.
- [18] R. Rakoczy, A. Traa, Y., *Microporous Mesoporous Mater.* 60 (2003) 69.
- [19] S. Mintova, N.H. Olson, V. Valtchev, T. Bein, *Science* 283 (1999) 958.
- [20] C.S. Cundy, P.A. Cox, *Microporous Mesoporous Mater.* 82 (2005) 1.
- [21] E.M. Flanigen, H. Khatami, H.A. Seymenski, in: E.M. Flanigen, L.B. Sand (Eds.), *Adv. Chemistry Series*, 101, American Chemical Society, Washington, D. C., 1971, p. 201.
- [22] A.E. Persson, B.J. Schoeman, J. Sterte, J.E. Otterstedt, *Zeolites* 15 (1995) 611.
- [23] D.M. Ginter, A.T. Bell, C.J. Radke, *Zeolites* 12 (1992) 742.
- [24] S.P. Zhdanov, N.N. Samulevich, L.V.C. Rees, *Proc. 5th Int. Conf. Zeolites*, Heyden, London, 1980, p. 75.