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Crystal Growth Study of Nano-Zeolite by Atomic Force Microscopy

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1. Introduction

Mesoporous materials possess highly ordered periodic arrays of uniformly sized channels. Therefore, these compounds have attracted considerable attention for many researchers (Luo et al., 2000; Xu & Xue, 2006; Liu et al., 2009 a, Salehirad & Anderson, 1996; 1998a; 1998b; 1998c). Since the shape and texture of the materials strongly affect their properties, these materials due to their large surface areas, controllable pore size and easy functionalization have been used in separation science, drug delivery and various processes such as adsorption and catalysis (Liu et al., 2009a; Duan et al., 2008; Liu et al., 2009 b; Liu & Xue, 2008; Mohanty & Landskron, 2008; Salehirad, 2004; Alibouri, 2009a; 2009b).

Zeolites as crystalline aluminosilicates are microporous materials with well-defined channels and cavities have been used as ion-exchangers, adsorbents, heterogeneous catalysts and catalyst supports (Zhang et al., 2000; Zhang et al., 2000). Many parameters are found to be highly important in the physical appearance of final zeolite products (Aghabozorg et al., 2001). Morphology and crystal size of these compounds have an important role for their specific applications in industries (Zabala Ruiz et al., 2005). The ability to accommodate various organic and inorganic species in zeolites makes them ideal host materials for supramolecular organization (Bruhwiler & Calzaferri, 2004; Schulz-Ekloff et al., 2002; Sadegh Hassani et al., 2010a). In many cases, surface adsorption sites in zeolites lead to interesting photochemical properties for these compounds. (Zabala Ruiz et al., 2005; Hashimoto, 2003). Studying the surface structure of zeolites and dynamic phenomena occurring on the surface of these compounds under various conditions will accelerate the development of these compounds as catalyst or materials with versatile functions (Sugiyama Ono et al., 2001; Anderson, 2001; Sadegh Hassani et al., 2010a). Nucleation mechanisms and growth of zeolites are not well understood for many of the systems involved. In most cases, the problem is compounded with the presence of a gel phase. This gel also undergoes a continuous polymerization type reaction during nucleation and growth. Improved understanding of zeolite growth should enable a more targeted approach to zeolite synthesis in the future and may ultimately lead to the possibility of zeolite design to order. Numerous techniques have been used for study the structure of the zeolites. Among them, scanning probe microscopy (SPM) is an appropriate technique that can be applied in atmospheric condition. However, many SPM techniques can be used in essentially any environment, including ambient, UHV, organic solvent vapour and

biological buffer, making it possible to observe the system in states that are simply inaccessible to other techniques with comparable resolution and they can be also used over a wide range of temperatures (Hobbs, et al., 2009).

Scanning probe microscopy, such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), has become a standard technique for obtaining topographical images of surface with atomic resolution (Hyon et al., 1999; Klinov & Magonov, 2004; Giessibl, 1995, Sadegh Hassani et al., 2008 a,b; 2010b). In addition, they may be used in many applications such as investigation of mechanical, chemical, electrical, magnetic and optical properties of surfaces, study of friction and adhesion forces, modifying a sample surface, crystal growth study and process controlling (Sundararajan & Bhushan, 2000; Burnham et al., 1991; Aime et al., 1994; Sadegh Hassani & Ebrahimpour Ziaie, 2006; Ebrahimpour Ziaie et al., 2008; Sadegh Hassani & Sobat, 2011; Sadegh hassani & Aghabozorg, 2011; Magonov, et al., 1997; Hobbs, et al., 2009; Leggett, et al., 2005; Williams, et al., 1999; Cadby, et al., 2005). There are some disadvantages for these techniques because they are limited to a surface view of a sample. Hence, extreme care has to be taken for interpretation of data for achieving the bulk properties (Franke, 2008; Hobbs, et al., 2009). These nondestructive methods do not require complex preparation of the desired sample and allows processes to be followed in-situ (Hobbs, et al., 2009).

This technique enables very high resolution imaging of nonconducting surfaces (Fonseca Filho et al., 2004) with the ability to measure the height of the surface very accurately and observe zeolite growth features not detectable by conventional methods, i.e. SEM, TEM, etc. (Sadegh Hassani et al., 2010). AFM have been used to image the surface of zeolites such as scolecite, stilbite, faujasite, heulandite and mordenite, since 1990.

In addition, by this method it is possible to follow in situ processes such as crystallization which need non-destructive methods. In addition, the effect of changes in temperature on structures can be monitored at the nanometer scale (Hoobs et al., 2009).

In this chapter, it is focused on using AFM for current progress toward the elucidation of zeolite growth. In this regard, after introducing AFM technique, an overview about controlling of crystal growth of materials, especially zeolites, by AFM is presented.

2. AFM technique

Atomic force microscope is a kind of microscope in which a sharp tip is mounted at the end of a spring cantilever of known spring constant. This microscope employs an optical detection system in which a laser beam is focused onto the backside of a reflective cantilever and is reflected from the cantilever onto a position sensitive photo detector. An image can be obtained based on the interaction between a desired sample and a tip. As the tip scans the surface of the sample, variation in the height of the surface is easily measured as flexing of the cantilever, then variation in the photodiode signal. This gives a 3-D profile map of surface topography.

There are feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. AFM can be used not only for imaging the surfaces in atomic resolution but also for measuring the forces at nano-newton scale. The force between the tip and the sample surface is very small, usually less than 10^{-9} N. The detection system does not measure force directly. It senses the deflection of the micro cantilever (Ogletree et al., 1996; Sadegh Hassani et al., 2006; 2008c).

Imaging modes of operation for an AFM are dynamic and static modes. In the dynamic mode, including non contact and tapping modes, the cantilever is externally oscillated at or close to its fundamental resonance frequency. The oscillation amplitude, phase and resonance frequency are changed by tip-sample interaction forces. These changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. Using dynamic mode, it is possible to monitor both the phase of the drive signal oscillating the cantilever, and the cantilever's response. This phase signal gives access to material properties, a combination of adhesive and viscoelastic properties (Tamayo & Garcia, 1998; Tamayo & Garcia, 1998; Hoobs et al., 2009) with nanoscale resolution.

In non contact mode, the tip of the cantilever does not contact the sample surface. The cantilever is instead oscillated at a frequency slightly above its resonant frequency where the amplitude of oscillation is typically a few nanometers. The van der Waals forces, or any other long range force which extends above the surface acts to decrease the resonance frequency of the cantilever. This decrease in resonant frequency combined with the feedback loop system maintains a constant oscillation amplitude or frequency by adjusting the average distance between tip and sample surface. By measuring this distance at each point, a topographic image of the sample surface can be obtained.

In tapping mode, the cantilever is driven to oscillate up and down at near its resonance frequency similar to non contact mode. As the tip is approached to the surface the amplitude of oscillation is damped, and it is now the amplitude of the oscillation that is used as a feedback parameter.

In static mode, the cantilever is scanned across the surface of the sample and the topography of the surface are obtained directly using the deflection of the cantilever. In this operation mode, the static tip deflection is used as a feedback signal. Close to the surface of the sample, attractive forces can be quite strong, causing the tip to "snap-in" to the surface. Thus static mode AFM is almost always done in contact where the overall force is repulsive. Consequently, this technique is typically called "contact mode". In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection.

3. Monitoring processes with AFM

The advent of atomic force microscopy (AFM) (Binnig et al. 1986) has provided the new possibilities to investigate the nanometer-sized events occurring at crystal surfaces during crystal growth and recrystallization. This is possible under *ex situ* and often in *in situ* conditions as it can be suited to observe surfaces under solution. Under *ex situ* conditions a wide variety of synthetic parameters can be changed but some careful works such as quenching experiments must be performed before transferring the sample to AFM to prevent secondary processes caused by changing growth conditions.

Real-time images of growing crystals have provided the structural details revealing terrace growth, spiral growth, defect and intergrowth structure in a vast variety of growth studies (Mcpherson et al. 2000). The free energy for individual growth processes can be achieved by measuring real-time micrographs at a range of temperatures.

Over the last decade, the application of AFM to follow some processes in soft material has been reported. Hoobe et al. (2009) believed that scanning probe techniques have several capabilities that make them suitable for the investigation of soft materials, organic materials

as they pass through a transformation, and directly observe processes at a near molecular scale. For example, in a macromolecular system, such as semicrystalline polymer, phase transitions of large molecule sometimes are in metastable states. To follow these non-equilibrium states which often control the final material properties, is important and can be performed by AFM (Strobl, 2007; Hoobs et al., 2009).

In the early study of soft material using AFM, contact mode was used (Magonov et al., 1997). The development of dynamic modes of operation, such as tapping mode and the subsequent development of phase imaging, allowed a substantial growth in the possibilities of the technique (Garcia & Perez, 2002; Hoobs et al., 2009). For example, atomic force microscope with tapping mode was applied to study the surface morphology of as-grown (111) silicon-face 3C-SiC mesaheterofilms (Neudeck et al., 2004). Their observation showed that wide variations in 3C surface step structure are as a function of film growth conditions and film defect content. The vast majority of as-grown 3C-SiC surfaces consisted of trains of single bilayer height (0.25 nm) steps. They reported that Macrostep formation (i.e., step-bunching) was rarely observed. As supersaturation is lowered by decreasing precursor concentration, terrace nucleation on the top (111) surface becomes suppressed.

AFM technique also has been used for study the structure of the zeolites. In this chapter, it is focused on crystal growth processes in open framework, inorganic materials (i.e. zeolites) studied by AFM. The zeolite crystal growth experiment is important to enhance the understanding of growth of zeolite crystals and nucleation, and controlling the defects in zeolites.

Many studies have been performed to investigate how zeolite crystals grow. Based on the results reported from these studies it is generally found that the growth linearly proceeds during the crystallization of most zeolites and this is applicable for both gel and clear solution syntheses (Subotic et al. 2003; Zhdanov et al. 1980; Bosnar et al. 1999; Iwasaki et al. 1995; Cundy et al. 1995; Bosnar et al. 2004; Cora et al. 1997; Kalipcilar et al. 2000; Schoeman et al. 1997; Caputo et al. 2000). Parameters such as gel composition, aging, stirring and temperature can affect on growth in zeolites (Subotic et al. 2003; Cundy et al. 2005). Imaging of zeolite surface by use of such a very powerful technique, has recently made possible the understanding the exact growth mechanism in the synthesis of these materials. The work performed on cleaved surface (0 0 1) of the natural zeolite scolecite (MacDougall et al. 1991) under ambient conditions has revealed the arrangement of 8-membered ring centers. Parameters such as lattice constants, angles and distances of the zeolite structure have been measured and compared favorably with its crystallographic structure. Feathered terraces with height $\sim 9 \text{ \AA}$, half the unit cell dimension of 17.94 \AA , have been reported on the cleaved surface (010) of natural zeolite heulandites (Scandella et al. 1993). The outer surface of this zeolite investigated by AFM (Binder et al. 1996) has also revealed growth spiral at screw dislocation with the pitch of $\sim 9 \text{ \AA}$ (sometimes double), which is consistent with the b-dimension of the zeolite. Further AFM works on heulandite (Yamamoto et al. 1998) crystals has revealed the presence of steps, suggesting a possible birth-and-spread mechanism.

The precipitated sodium aluminosilicate hydrogel has also been analyzed by AFM (Kosanovic et al. 2008). The obtained results have showed that predominantly true amorphous phase of the gel contained small proportions of partially crystalline (quasi-crystalline) or even fully crystalline phase. Some different methods such as FTIR, DTG, electron diffraction have confirmed this finding and also showed partially or even fully crystalline entities of the sample. AFM has also revealed that the particles of the partially or fully crystalline phase are nuclei for further crystallization of zeolite.

Anderson et al. (1996; 1998) have reported the first AFM study of synthetic zeolite Y and observed triangular (1 1 1) facet, revealing approximately triangular terraces. The height of the terraces is 15 Å which is consistent with one faujasite sheet and the step height observed by other techniques. By measuring the area of the terraces they showed that this area was growing at a constant rate which was consistent with a pseudo terrace-ledge-kink mechanism in comparison with the growth in dense phase structures.

Zeolite A due to water softening features is an industrially important zeolite. It has been studied to determine the mechanism of crystal growth, using AFM by some researchers (Agger et al. 1998; 2001; Sugiyama et al. 1999). This zeolite, similar to zeolite Y demonstrates a layer-type growth with terrace heights consistent with simple fractions of unit cell. The authors have reported terrace height of 12 Å, equivalent to half unit cell height consisting of a sodalite cage and double 4-ring (Agger et al. 1998; 2001). Sugiyama et al. (1999) have also reported values corresponding to the individual sodalite cage and double 4-ring with slight differences. Wakihara et al. (2005) have investigated the surface structure of zeolite A by AFM and compared their results with those obtained by the other techniques such as HRTEM and FE-SEM. They have found that the terminal structure of zeolite A is incomplete sodalite cages. These results support one of the terminal structures proposed by Sugiyama et al. (1999), although these findings may not be always applicable to all zeolites A synthesized by various methods.

Irregardless of these differences, the principal conclusions of both studies (Agger et al. 1998; Sugiyama et al. 1999) are the same and a layer-by-layer growth mechanism is operative for zeolite A (Agger et al. 1998). The area of the terraces in this zeolite grows at a constant rate confirmed by the parabolic cross-section of the surface. Agger et al. (1998) have also reported a detailed simulation of the growth features in zeolite A and suggested that the rate of growth at kink site is the fastest growth process. They also report that since the terrace edges run parallel to the crystal edges so the rate of growth at edge or ledge sites is considerably less than that at kink sites. These findings of the relative rates of growth processes help to understand and then affect the relative rates to control defects and structure.

Umamura et al. (2008) have presented a computer program that simulates morphology as well as surface topology for zeolite A crystals. They compared favorably the simulation results with those obtained from AFM images on the {1 0 0}, {1 1 0} and {1 1 1} faces of synthetic crystals.

Silicalite is a siliceous form of zeolite ZSM-5 which is industrially important for catalytic properties, so the control of the synthesis of this inorganic solid is of great interest. An extensive AFM study of crystal growth has been fulfilled for this material (Agger et al. 2001; 2003; Anderson et al. 2000). In the low temperature synthesis of this material (similar to zeolites A and Y) terraced, layer-by-layer growth has been observed on both the (1 0 1) and (1 0 0) facets. The height of the terraces is 10 Å corresponding to half the unit cell dimension in the [0 1 0] direction (or the height of one pentasil chain). A constant-area-deposition mechanism, not dominated by addition at kink site, has resulted in the approximately circular shape of the terraces, indicating no preferential growth direction. Terraces in the high temperature synthesis, which produces large crystal (not similar to the low temperature synthesis, producing small crystals), grow towards the crystal edges and have the height of several hundred angstroms (up to 110 nm high on the (0 1 0) face and up to 20 nm high on the (1 0 0) face). Such terraces have no relation to any structural element of the silicalite. Assuming of a layer growth mechanism the authors have concluded that an

obstruction to terrace advance causes a build-up of the layers. They have suggested the defect inclusion mechanism to explain the relative terrace heights on the two faces.

4. Morphology study of Zeolite L by AFM

Zeolite L which was initially determined by Barrer et al. (1969) has hexagonal symmetry (Barrer et al., 1969; Baerlocher et al., 2001) with two-dimensional pores of about 0.71 nm aperture leading to cavities of about $0.48 \times 1.24 \times 1.07 \text{ nm}^3$ and the Si/Al ratio is typically 3.0 (Pichat et al., 1975; Sig Ko & Seung Ahn, 1999). The zeolite crystals consist of cancrinite cages linked by double six-membered rings, forming columns in the c direction. Connection of these columns gives rise to 12-membered rings with a free diameter varies from 0.71 nm (narrowest part) to 1.26 nm (widest part). The main channels are linked via non-planar eight membered rings forming an additional two-dimensional channel system with openings of about 0.15 nm. Studies have shown that the morphology of the crystals can be approximated by a cylinder, with the entrances of the main channels located at the base. The number of channels is equal to $0.265(dc)^2$, where dc is the diameter of the cylinder in nanometers (Zabala Ruiz et al., 2005; Bruhwiler & Calzaferri, 2005; Breck & Acara, 2005).

Brent and Anderson (2008) studied crystal growth mechanism in zeolite L and control the crystal habit by atomic force microscopy. They claimed that AFM was an excellent tool for determining crystal growth mechanisms in zeolites L and gave a snapshot in time as to how the shape of a crystal had developed, by imaging surface features. In their work, the surface features on both the (1 0 0) side walls, and the (0 0 1) hexagonal faces of zeolite L was investigated.

Sadegh Hassani et al. (2010a) reported synthesis and characterization of nano zeolite L. Nanosized zeolite L was synthesized from a gel mixture at 443 K with different aging times. The molar compositional ratio of the resulting gel was $7.6 \text{ Na}_2\text{O} : 7.2 \text{ K}_2\text{O} : 1.3 \text{ Al}_2\text{O}_3 : 40 \text{ SiO}_2 : 669 \text{ H}_2\text{O}$. This homogeneous gel mixture was transferred to a Teflon-lined autoclave and placed in an air-heated oven at 443K for different synthesis times (24, 45, 110, 160, and 200 h). The autoclave was removed from the oven at the scheduled times and quenched in cold water. The solid product was separated by centrifugation, washed thoroughly a few times with deionized water and oven dried at 353 K for 5 h.

The samples were characterized by XRD, XPS techniques and morphological changes investigated by TEM and AFM.

A commercial atomic force microscope (Solver P47 H, NT-MDT Company) operating in non-contact mode and equipped with a NSG11 cantilever was used to take images in nanometer scale. Samples were dispersed in ethanol by sonication and deposited on a suitable substrate to be applicable for AFM. Atomic force microscope was used to obtain detailed surface images, such as crystal dimensions, by zooming in on a fine particle.

The technique revealed the existence of a multitude of terraces with the height of either ≈ 1 or ≈ 2 nm. Figure 1.a shows a two dimensional image of the zeolite crystals after elapsing 24 h of the synthesis time. This image confirms again the hexagonal geometry of the zeolite crystal. Figure 1.b is a cross sectional profile of the image a. The terraces demonstrate growth direction; consequently, growth fronts develop a hexagonal profile. They are concentric, growing out to the crystal edge from a central nucleation point as shown in figure 1.c. It has been reported that the growth morphology is thermodynamically related to corresponding crystallographic structure, according to the chemical bonding theory of single crystal growth (Xu & Xue, 2006; Yan, 2007; Xue et al., 2009). Work carried out on

synthetic zeolite crystals to date suggests crystal growth occurs through deposition and subsequent expansion of layers (Xu & Xue, 2006; Anderson & Agger, 1998). Their findings are in good agreement with this suggestion and show that zeolite L crystals grow via a layer mechanism. Further observation of terraces at atomic level, using a single crystal will help this suggestion.

AFM allowed the detailed observation of nanometer-size events at crystal surfaces. In addition, the images showed layer growth of the zeolite crystal and the height of terraces. Two-dimensional AFM images (Fig. 1.a) showed hexagonal structure which is in good agreement with the TEM results (Fig. 2). Furthermore, Three-dimensional structure of the zeolite crystal (Fig. 1.c) obtained by AFM (not possible by TEM) indicated hexagonal layers. In addition, Figure 3 exhibits the aggregation of zeolite L crystals.

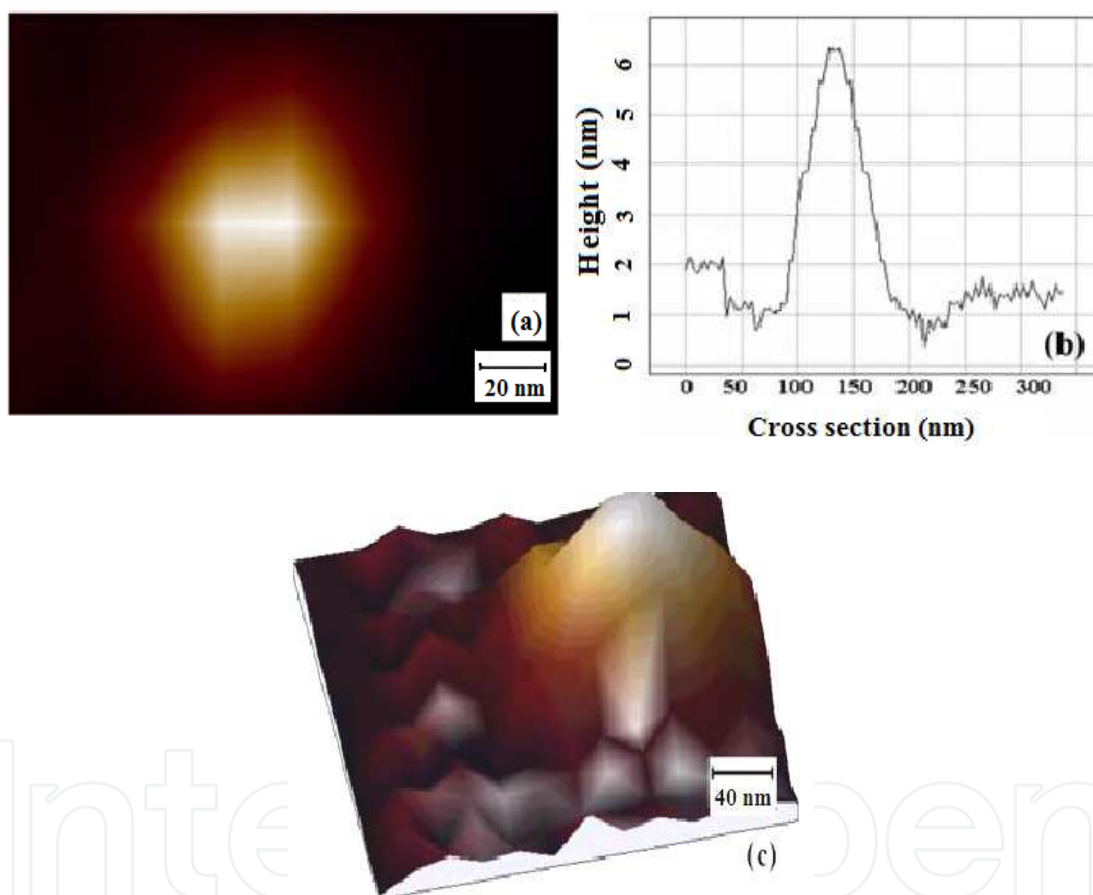


Fig. 1. AFM images of synthesized zeolite L. (a) two dimensional image of the crystal after 24 h and (b) its cross section, (c) three dimensional image of the crystal after 160 h (Sadegh Hassani et al., 2010a).

TEM images of the samples were recorded on CM260-FEG-Philips microscope and samples dispersed in acetone by sonication and deposited on a microgride. Figure 2 shows TEM images of the synthesized samples with various magnifications. These images indicate the average size of the sample crystallites (about 50 nm) possessing hexagonal geometry. A detailed surface image of the zeolite particles (Fig. 2c-d) indicated the parallel one dimensional channels arranged in a uniform pattern with hexagonal symmetry.

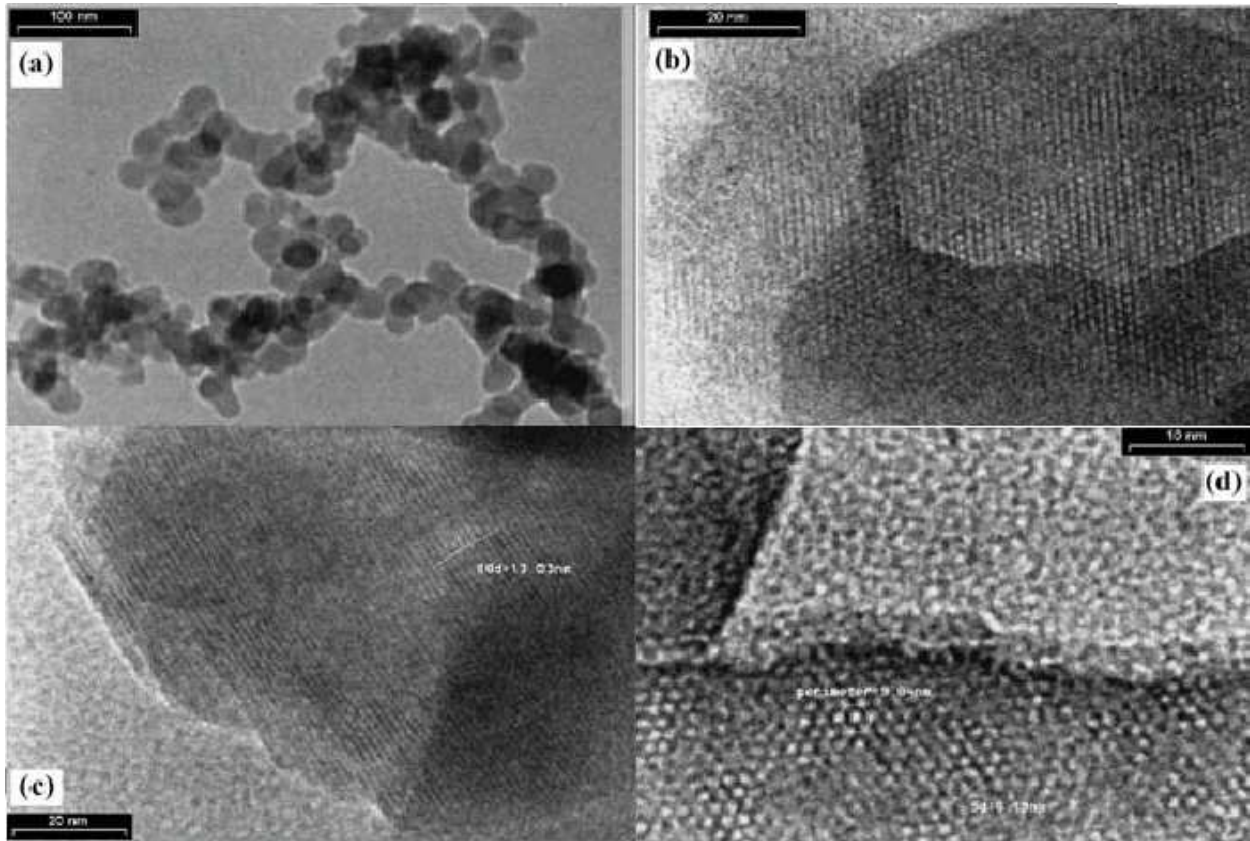


Fig. 2. TEM images of as-synthesized zeolite L with different resolutions for (a) the particle size and (b) morphology of the sample and (c) and (d) detailed surface images of the zeolite (Sadegh Hassani et al., 2010a).

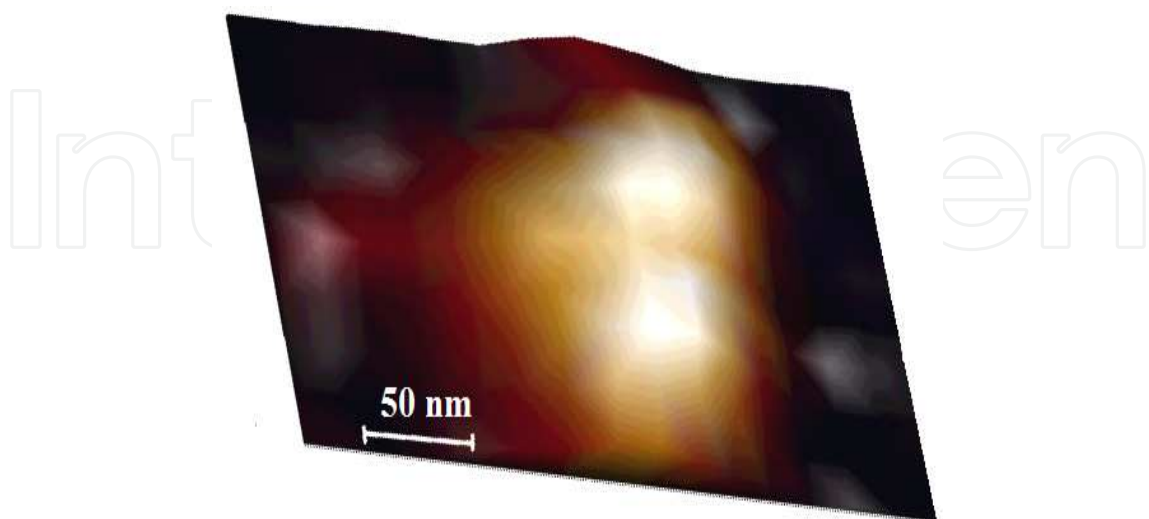


Fig. 3. Three dimensional AFM image of as synthesized zeolite L prepared in 160 h exhibiting aggregation of crystals.

In addition, AFM results exhibited bigger size of the crystal by increasing the synthesis time up to 160 h. Beyond this synthesis time, the size of the crystal decreased (Fig. 4). However, X-Ray diffraction patterns of the samples indicated that the synthesis times up to 110 h maintain almost the same crystallinity, whereas the synthesis times longer than that cause to decrease the crystallinity (89% for 160 h and 63% for 200 h). The apparatus used for XRD study was the powder X-ray diffractometer, Philips PW-1840, with a semi conductor detector and a Ni-filtered $K\alpha$ (Cu) radiation source attachment.

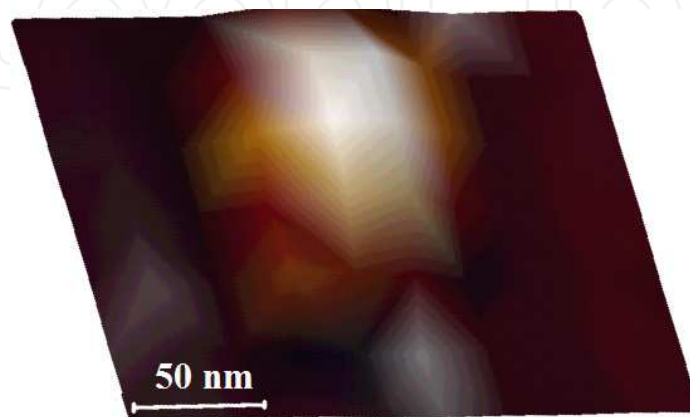


Fig. 4. Three dimensional AFM image of as synthesized zeolite L prepared in 200 h.

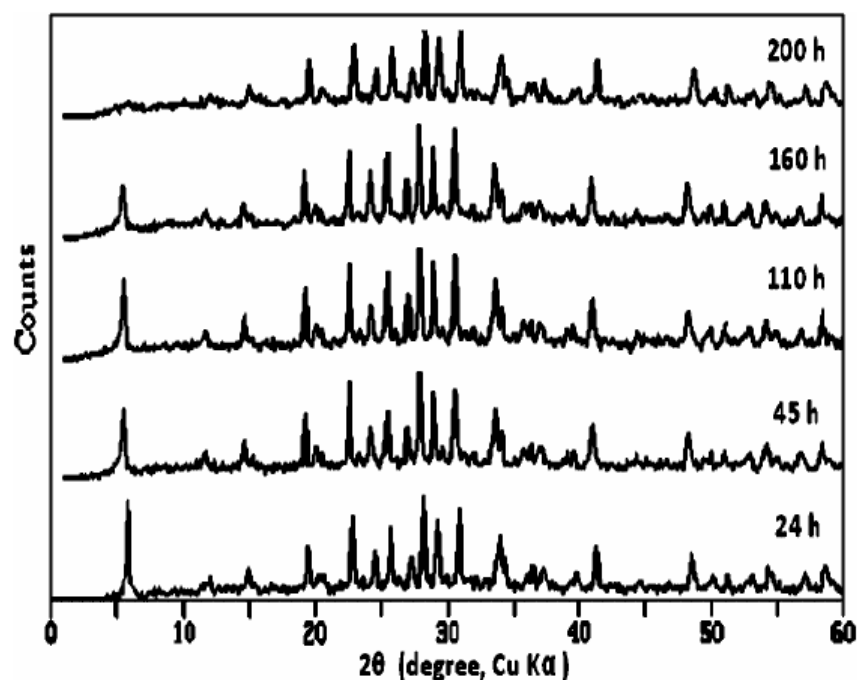


Fig. 5. X-ray diffraction patterns of the synthesized zeolite L obtained at different crystallization time at 443 K (Sadegh Hassani et al., 2010a).

Figure 5 shows the X-ray diffraction patterns of the as synthesized zeolite L samples obtained with different crystallization times. Characteristic XRD peaks showed that the fully crystalline phase (97% crystallinity) was obtained after 24 h. Reflections located at $2\theta \approx 5.5$,

19.4, 22.7, 28.0, 29.1 and 30.7 were used to calculate crystallinity. Results show that the synthesis times up to 110h maintain almost the same crystallinity, whereas the synthesis times longer than that cause to decrease the crystallinity (89% for 160 h and 63% for 200 h).

It was reported that Si/Al molar ratio in zeolites structure could affect on morphology and crystal size of these compounds (Shirazi et al., 2008; Mintova et al., 2006; Celik et al., 2010). Therefore, Sadegh hassani et al. (2010a) using AAS and XPS performed the elemental analyses of the bulk and surfaces of the as synthesized nanozeolite L, respectively. Elemental surface analysis of the zeolite sample was carried out on the X-ray Photoelectron Spectroscopy (XR3E2 Model-VG Microtech; Concentric Hemispherical Analyzer, EA 10 plus Model-Specsis).

Figure 6 shows the XPS spectrum of the sample. The spectrum depicts the surface analysis of the as synthesized nanozeolite L. The Si/Al ratios of the gel mixture, bulk and surface of the sample are shown in table 1.

The slight difference in Si/Al ratios (0.5) was observed between bulk and surface of the zeolite sample.

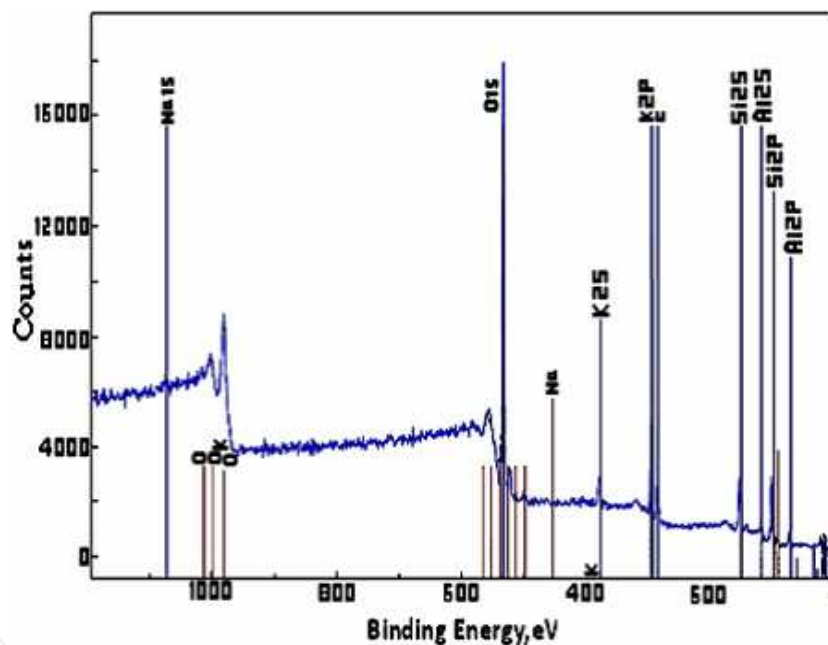


Fig. 6. Surface analysis results of synthesized zeolite L crystal by X-ray photoemission spectroscopy. (Sadegh Hassani et al., 2010a).

Sample	Si/Al
Gel mixture	15.4
Zeolite L (bulk)	3.5
Zeolite L (surface)	3.0

Table 1. Si/Al molar ratios of samples (Sadegh Hassani et al., 2010a).

5. Conclusion

This chapter is focused on the crystal growth study of various samples especially zeolites using AFM. Studies are revealed that atomic force microscopy is a powerful technique to follow in situ processes such as zeolite crystallization. In this regard, a study of crystal growth of nano-zeolite L is focused using atomic force microscopy (AFM). The results are compared with those of obtained from X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) techniques.

TEM and two-dimensional AFM images indicate that the zeolite particles are in a nano-range and they have hexagonal structure. In addition, the AFM images show layer growth of the zeolite crystal and reveal the existence of a multitude of terraces with the height of either ≈ 1 or ≈ 2 nm.

The terraces demonstrate growth direction; consequently, growth fronts develop a hexagonal profile. They are concentric, growing out to the crystal edge from a central nucleation point. In addition, the AFM images exhibit layer growth, the height of terraces and the aggregation of zeolite L crystals. A detailed surface image of the zeolite particles indicate the parallel one dimensional channels arranged in a uniform pattern with hexagonal symmetry. AFM results also show bigger size of the crystal by increasing the synthesis time up to 160 h, beyond this synthesis time, the size of the crystal decrease.

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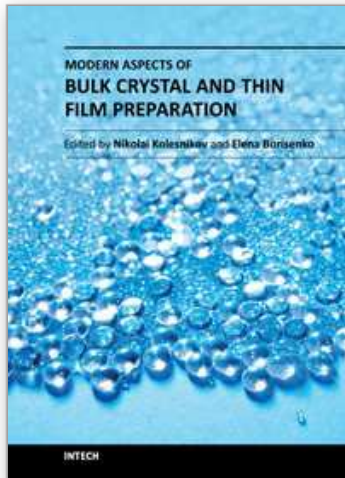
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