Research Article GU J Sci, Part A, 11(1): 112-122 (2024) 10.54287/gujsa.1409513

Gazi University
Journal of Science
PART A: ENGINEERING AND INNOVATION
http://dergipark.org.tr/gujsa

Zeolite A Thin Film Growth on Silica Optical Fibers

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Keywords

Zeolite A
Thin Films
Nanoporous
Secondary Growth

Abstract

Thin films of zeolite A (Linde type A, LTA) were fabricated on silica optical fibers using dip coating method, followed by a secondary growth process. Zeolite A seed crystals with an average crystal size of 247.3 nm were synthesized through hydrothermal method. Then, the dip coating technique was applied to coat silica optical fibers. The one and two-time dip coating resulted in island-like growth, while three-time dip coating process led to the intergrowth of seed crystals, resulting in nearly continuous films on the optical fiber. The seed crystals, initially deposited as a monolayer, were grown by secondary growth method, leading to film thicknesses of 255.3 nm ± 10.1 nm (average ± standard deviation). Upon extending the secondary growth reaction time from 2 hours to 4 hours, the film thickness increased from 255.3 nm ± 10.1 nm to 649.6 nm ± 28.1 nm. Epitaxial growth was identified as the mechanism through which the seed crystals grow. The nanoporous zeolite A films formed on the optical fiber exhibit potential applications as gas sensors. These sensors function by detecting changes in optical reflection caused by the differential adsorption of gases.

Cite

Galioğlu Özaltuğ, S. (2024). Zeolite A Thin Film Growth on Silica Optical Fibers. *GU J Sci, Part A*, *11*(1), 112-122. doi:10.54287/gujsa.1409513

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Article Process

Submission Date	25.12.2023
Revision Date	19.01.2024
Accepted Date	05.02.2024
Published Date	15.02.2024

1. INTRODUCTION

Zeolites are preferred adsorbents, ion-exchangers, and catalysts for many reactions of industrial importance (Bennett et al., 2021). They have acidity with both Bronsted and Lewis acid sites, ion-exchange properties, and high specific surface area (Gumidyala et al., 2016; Sousa-Aguiar et al., 2019). Up to now, around 245 types of zeolites have been approved by the International Zeolite Association (Structural database of zeolites, 2023). Among other nanoporous materials, zeolites are the most important commercialized porous materials (Bennett et al., 2021). They are a crucial part of the heterogeneous catalysis industry, primarily due to their molecular size micropores (< 2 nm), and high thermal stability (650 - 900 °C) (Sousa-Aguiar et al., 2019).

Synthesized zeolites are obtained in powder form. They are typically processed into specific forms such as pellets or thin films to make use of them in advanced application areas. Having continuous thin films with preferred crystallographic orientation is an important task in the field of zeolites (Pham et al., 2011) to use them in advanced application areas such as sensing (Wales et al., 2015), catalysis (Hedlund et al., 2004; Kumar et al., 2020), nanofiltration (Kong et al., 2021) pervaporation (Cao et al., 2019; Shao et al., 2014) etc. Zeolite thin films are usually formed on porous substrates such as α-alumina (Al_2O_3). However, zeolite film growth is not thoroughly investigated for optical fibers because it is challenging to prepare zeolite thin films on cylindrical and non-porous substrates (Ji et al., 2007). Partial coverage of the seed layer and separation of the films from the fibers are the most encountered problems during the growth. Thin film formation of zeolite X and zeolite Y (FAU framework type) (Deng & Balkus, n.d.; Pradhan et al., 2000), silicalite-1 and ZSM-5 (MFI frame type) (Nazari et al., 2014; Zhang et al., 2005) and zeotype titanosilicate ETS-10 (Ji et al., 2007) on optical fibers was investigated in the literature. Among them, the potential of using silicalite-1 thin film

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prepared on optical fibers as optical chemical sensors for the detection of dissolved organics in water (Zhang et al., 2005) and selective sensing of alcohols in water (Nazari et al., 2014) was examined. It was shown that the formed films can be used as sensors by monitoring the optical reflection changes. The efficacy of a sensor based on Silicalite-1 zeolite thin film coated long-period fiber grating was examined for direct measurement of trace amount of organic vapors (Zhang et al., 2008). Optical fibers coated with Silicalite-1 zeolite thin film were employed as sensors for volatile organic compounds (VOCs) optical fiber sensors (Wu et al., 2017). In another approach, a chemical sensor for acetone vapors was developed using a tantalum pentoxide waveguide coated with hydrophobic MFI-type Silicalite-1 zeolite films with a thickness of 330 nm (Babeva et al., 2017).

Thin film formation of zeolite A (LTA framework type) on optical fibers has not yet been investigated. Zeolite A, which has both scientific and commercial importance, is frequently used both as a catalyst in petrochemistry and in detergent production technologies due to its ion exchange feature, and is considered one of the most commercially used zeolites (Mintova et al., 1999). The production of commercial zeolite A covers 73% of the total synthetic zeolite production (Antúnez-García et al., 2021). Zeolite A is also used extensively in sensor technologies (Vilaseca et al., 2007), membranes (Cao et al., 2019; Shao et al., 2014), thermal energy storage (Li et al., 2017), and water purification (Li et al., 2017).

Here we investigate the feasibility of forming zeolite A thin films on silica optical fibers. Mono-layer or double layer zeolite A thin films were formed on silica fibers to use them in potential gas sensors. These sensors function by detecting changes in optical reflection caused by the differential adsorption of gases. First, hydrothermal synthesis of nano-sized zeolite A crystals (average crystal size: 247.3 nm) was performed. Then, zeolite A seed layer coating on silica fibers was optimized. One-time, two-, three-, four- and five-time dip coating steps were examined to obtain mono- or double-layer seed layer formation. Then, seed layers deposited on silica optical fibers (diameter of 250 μm) were grown by the secondary growth method. Thin film thicknesses were altered and controlled by applying different secondary growth reaction times of 2 h, 3 h, 4 h, 6 h, and 7 h. Nearly continuous zeolite A thin films with different thicknesses were obtained via the intergrowth of seed crystals by applying the secondary growth method.

2. MATERIAL AND METHOD

2.1. Materials

Aluminium isopropoxide ($Al(iPro)_3$, > 98%, 220418, Aldrich), tetrapropylammonium hydroxide tetramethylammonium hydroxide (TMAOH, 25 wt. %, Aldrich), Silica sol (Ludox-HS 30, 30 wt. % SiO_2, pH=9.8, Aldrich), tetraethyl orthosilicate (TEOS, 98%, 131903, Aldrich), sodium hydroxide (NaOH, 99%, Merck), ethanol (EtOH, 99.99%, IsoLab), acetone (99.99 % Isolab). Corning specialty silica fibers were purchased from Fujikura Ltd., Japan. Deionized water (DI H_2O, resistivity = 18.2 MΩ) is used in synthesis and centrifugation.

2.2. Synthesis of Zeolite A (LTA Framework Type) Seed Crystals

$Al(iPro)_3 : 3\,TEOS : 7.36\,TMAOH : 0.33\,NaOH : 192.41\,H_2O$ molar formula was used for the synthesis of nano-sized zeolite A seed crystals (average crystal size: 247.3 nm). 0.95 g of DI water was added to 2.17 g of TMAOH and stirred for 20 min. Next, 0.17 g of $Al(iPro)_3$ was added gradually to the mixture and stirred for 1 h. Later, 0.53 g of TEOS was added to the mixture and stirred for 2 more hours. Simultaneously, 0.01 g NaOH and 0.23 g DI water were mixed in a different beaker and added to the final mixture dropwise. Lastly, the final mixture was stirred for 15 h at RT for aging. The hydrothermal reaction was carried out at 100 °C oven (Binder FD 115) for 8 h. The crystals were collected after centrifugation (14000 rpm, Eppendorf Centrifuge 5420), washed with DI water until the pH reached 7, and dried overnight under ambient air at 45 °C in an oven.

2.3. Treatment of Optical Silica Fibers

Silica fibers with a cutoff wavelength of 870 - 950 nm and a diameter of 250 μm were used. Silica fibers were cut into 3 cm sections. Then, they are immersed in pure acetone for 20 minutes to remove the protective polymer coating on the silica fiber. After acetone treatment, the coatings were gently wiped off using lint-free Kimwipe tissues. The fibers were further rinsed with fresh acetone to ensure no polymer pieces were left and dried at room temperature.

2.4. Seed Layer Coating

The zeolite A thin film preparation on silica fibers consists of two steps: seed layer coating and secondary growth. In the first step, previously synthesized powder zeolite A was prepared in ethanol (5 wt. %) and sonicated for 1h. Clean polymer-free silica fibers were immersed in zeolite A ethanol solution for 30 s and dried for 20 s in each dip coating step. Depending on the experiment, each dip coating step was repeated two, three, four, and five times. The seed layer coated silica fibers were dried at 70 °C oven for 30 minutes. The seeded silica fibers were calcined at 450 °C rapid thermal annealing oven (ATV Technology Rapid thermal Processor, heating from 20 °C to 450 °C at 5 °C/min, isothermal heating at 450 °C for 1h and convective cooling to 20 °C).

2.5. Secondary Growth of Zeolite A Crystals

The seed crystals on silica fibers were formed by using a molar composition of $0.72\, Al_2O_3 : 5\, SiO_2 : 5.8\, (TMA)_2O : 0.12\, NaO_2 : 250\, H_2O$ (Mintova et al., 2001; Pradhan et al., 2000) in the following step of thin film preparation. In the formulation of the growth mixture, aluminum isopropoxide were mixed with TMAOH. Vigorous stirring was applied for 1h until clear suspension was obtained. NaOH and silica sol were added and 24 h RT aging was applied. The seeded silica fibers were diagonally placed in chromatography glass vials (Isolab), where they were completely immersed in the growth mixture. Depending on the experiments, after 2h, 3h, 4h, 6h, and 7h static hydrothermal treatment at 100 °C, the glass vials were cooled down to room temperature. The resulting zeolite A thin films on silica fibers were extracted from the growth mixture, rinsed several times with deionized water, and allowed to air-dry overnight at 45 °C.

2.6. Characterizations

The crystallographic structure of the zeolite powder samples was analyzed using an X-ray diffraction (XRD) spectrometer (Malvern Panalytical X'Pert Pro Multi-purpose Diffractometer), with a Cu K_α X-ray source (K_α = 1.54187 Å) operating at 45 kV and 40 mA, scanning between the 2θ angle range of 5° - 50°. The micrographs were taken using a Scanning Electron Microscopy (SEM) FEI Quanta 200F microscope operating at 30 kV after coating the samples with a 10 nm Au/Pd conductive layer using a Gatan 682 Precision Etching Coating system. SEM analyses were used to examine the morphology of zeolite seed crystals, particle size distribution, the coverage ratio of seed crystals on silica fibers, the growth behavior of thin films, and the thickness of the thin film.

3. RESULTS AND DISCUSSION

Being one of the important classes of nanoporous materials, zeolites have substantial scientific, technological, and commercial application areas. (Gumidyala et al., 2016; Wales et al., 2015). These materials are inorganic materials with pore size below 2 nm, a uniform and ordered pore structure throughout the crystal, and a large surface area. It is regarded as the integration of two systems. One of them is a negatively charged and covalently bonded aluminosilicate framework (Si, Al) and the other one is the ionically bonded extra framework cations (Na^+, K^+). They have extraordinary properties such as molecular pore size, high crystallinity, high surface area, gas adsorption sites, exchangeable ions, and selective gas penetration, which make zeolites good tools for gas sensor applications (Sasaki et al., 2002; Vilaseca et al., 2007; Wales et al., 2015; Zampieri et al., 2008). Among them, zeolite A, which has both scientific and commercial importance, is frequently used both as a catalyst in petrochemistry and in detergent production technologies due to its ion exchange feature, and is considered one of the most commercially used zeolites (Mintova et al., 1999). Zeolite A with an extra-framework cation of Na^+ has a nominal pore opening of 0.4 nm and different forms of zeolite A can be obtained by ion-exchange of extra-framework cations. K^+, Na^+, and Ca^{2+} form is considered as 3A, 4A, and 5A zeolites which have pore apertures of 0.3 nm, 0.4 nm, and 0.5 nm, respectively (Structural database of zeolites, 2023). The surface area of it provides available active sites for gas adsorption/desorption (Khoramzadeh et al., 2019; Valencia & Rey, 2020). It has high thermal stability and reversible gas adsorption/desorption behavior upon heating (Khoramzadeh et al., 2019; Valencia & Rey, 2020). The advantages above make zeolite A good candidate for gas sensor application which has been explored in our previous studies as well.

As synthesized zeolite powders are typically processed into specific forms, such as pellets or thin films, to be used in advanced application areas such as sensing (Wales et al., 2015). Having continuous thin films with preferred crystallographic orientation is an important task in the field of zeolites Pham et al., 2011). The preparation of thin zeolite films on the optical fibers is challenging due to the difficulties of preparing thin films on cylindrical and non-porous supports andremains to be elucidated. To the best of our knowledge, the thin film formation of zeolite A (LTA framework type) on optical fibers has not been investigated up to now. In the scope of this study, the feasibility of forming zeolite A thin films on silica fibers was examined. The films were produced using a two-step method. First, zeolite A seed layer coating was prepared via the dip coating procedure. Then, the growth of the seed layer deposited film was conducted via the secondary growth method (Figure 1a). Mono- or double-layer zeolite A thin films were formed on silica fibers to use them in potential gas sensors that function by monitoring the optical reflection changes caused by the selective adsorption of gas molecules (Figure 1b). To obtain a high response from the gas sensor, reflection changes due to the adsorption of gas molecules should be significant because the response increases as the thickness of the thin film decreases.

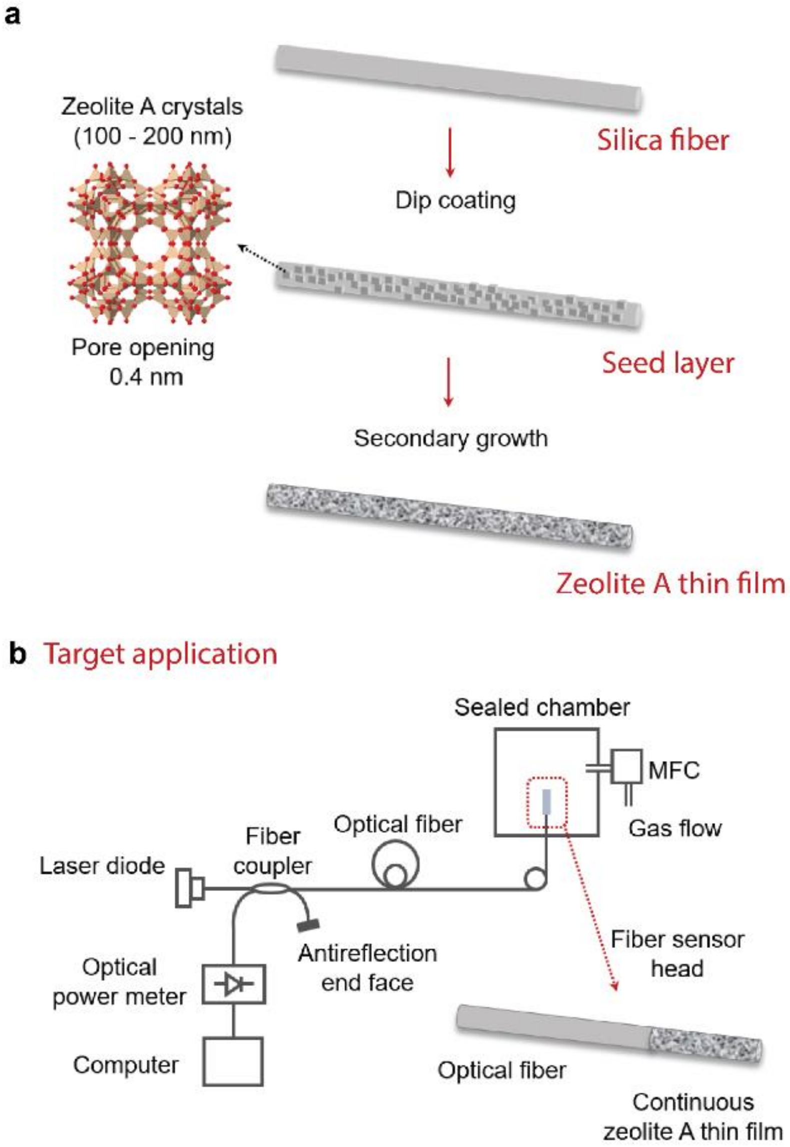

Figure 1. a) *Schematic figure shows the growth of zeolite A (LTA framework type) thin films on silica optical fibers. Zeolite A seed layer coating was performed via dip coating procedure and growth of seed layer deposited film was conducted via secondary growth method,* ***b****) The nanoporous zeolite A thin films formed on the optical fiber exhibit potential applications as gas sensors. These sensors function by detecting changes in optical reflection caused by the differential adsorption of gases*

Accordingly, the growth of a multi-layer seed layer is not desired for the potential gas sensor application. The proposed principle can be explained detecting changes in optical reflection caused by the differential adsorption of gases. The light from the laser diode can be sent into optical silica fiber. Then, a fiber coupler can be used to divide to two paths. A splicer can be used to splice zeolite-coated 3 cm long fiber to the main fiber. A sealed chamber and mass flow controller (MFC) can be used to load the chamber with a single gas or gas mixture at the specified rate. An optical power meter and a computer can be used to detect changes in optical reflection caused by the differential adsorption of gases on zeolite A thin film coated fiber part.

First of all, hydrothermal synthesis of zeolite A crystals was performed to obtain seed crystals. SEM analysis revealed that the morphology of the seed crystals with an average crystal size of 247.3 nm was cubic (Figure 2a). The biggest crystals within the population did not surpass a size of ~ 250 nm. The nano size of the seed crystals ensures uniform coating of the crystals on optical silica fibers. The crystalline nature of zeolite A is confirmed by XRD compared with reference XRD data of zeolite A data taken from the IZA web page (Figure 2b) (Structural database of zeolites, 2023).

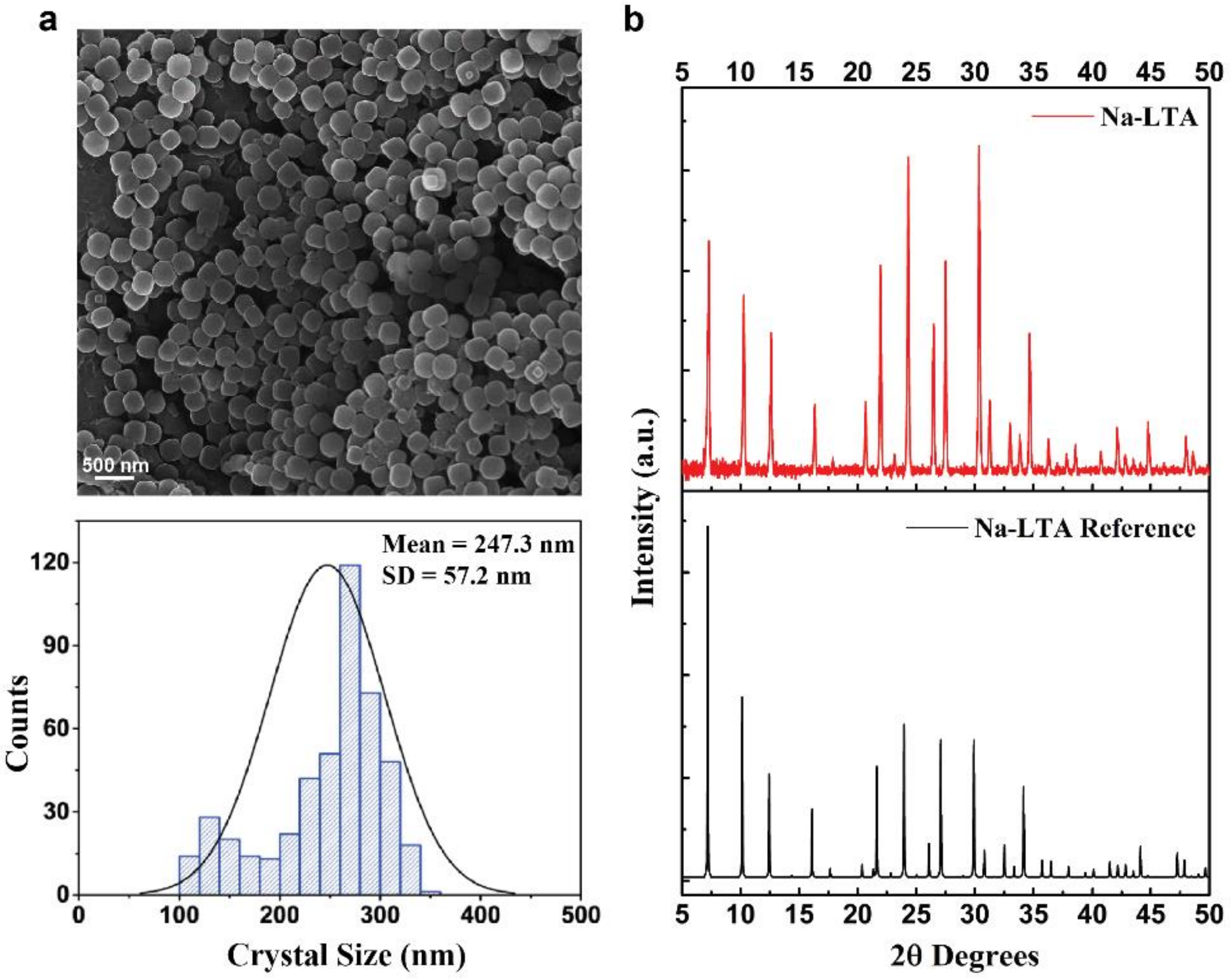

Figure 2. ***a****) SEM image of zeolite A seed crystals synthesized via hydrothermal method. The morphology of the seed crystals with an average crystal size of 247.3 nm was cubic (SD: standard deviation),* ***b****) XRD data of synthesized zeolite A compared with reference XRD data taken from IZA web page (Structural database of zeolites, 2023)*

3.1. Effect of the Seed Layers

To obtain thin film of zeolite A, first of all, zeolite A seed layer coating on silica fibers was optimized. 5 wt. % nano-sized zeolite A, synthesized previously, in ethanol suspension was used to dip coat silica optical fibers.

One-time, two-, three-, four- and five-time dip coating steps were examined to obtain mono- or double-layer seed layer formation. Figure 3a shows bare optical silica fiber surface and Figure 3b indicates one-time dip coating step was not adequate to coat the surface of silica fibers. As can be seen from the SEM images, island-like coverages were formed with spacing > 15 µm and the uncovered silica fiber surface was clearly observed. A similar trend was observed for two-time dip coating (not shown). One-time or two-time dip coating steps were not sufficient to obtain full coverage of silica fibers. Although island-like coverages were observed, mono-layer seed formation was seen when one-time and two-time dip coating steps were applied. Three-time dip coating of the seed layer was found to be optimum to obtain mono- or double-layer zeolite A crystals on silica fibers (thicknesses of the mono-layer seed layers ~ 200 nm) (Figure 3c) while four-time (Figure 3d) or five times dip coatings (not shown) were resulted in multi-layer seed formation not desired for potential gas sensor applications.

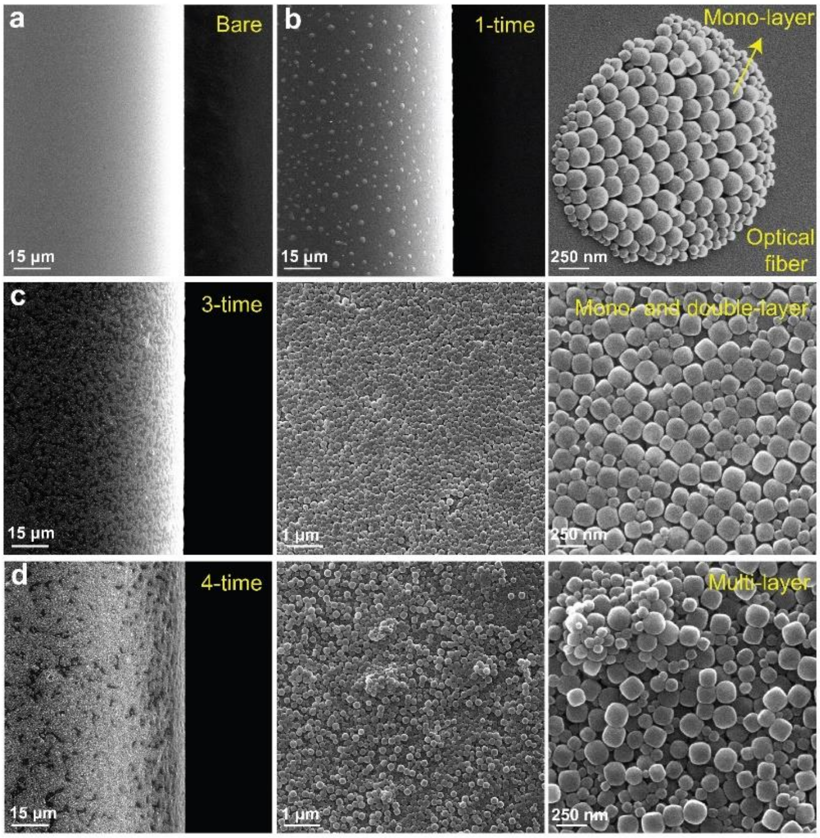

Figure 3. *Nano-sized zeolite A seed layer coatings on silica optical fibers. SEM images of* ***a)*** *bare silica optical fibers,* ***b)*** *one-time dip coated,* ***c)*** *three-time dip coated,* ***d)*** *four-time dip-coated samples with different magnifications*

3.2 Zeolite A Thin Film Formation Through Secondary Growth

The seed layers deposited on silica optical fibers (diameter of 250 µm) were grown by the secondary growth method (Figure 4) in freshly prepared growth suspension using the molar composition of $0.72\ Al_2O_3 : 5\ SiO_2 : 5.8\ (TMA)_2O : 0.12\ NaO_2 : 250\ H_2O$ (Mintova et al., 2001; Pradhan et al., 2000). The seeded silica fibers were diagonally placed in chromatography glass vials (Isolab), where they were completely immersed in the growth mixture. Then, hydrothermal treatments were carried out at 100 °C oven. Figures 4a and 4b show that when nearly continuous coverage of seed layers was not achieved (i.e., one-time and two-time seed layers), intergrowth of seed crystals could not be possible even though the reaction time increased to 7 hours (Figure 4a and 4b). Continuous growth of seed crystals prepared by one-time and two-time dip coating steps cannot be obtained due to the presence of ~ 15 µm spacing between island-like seed crystals. It was observed that as the reaction time increased to 7 hours to achieve epitaxial growth of island-like seed crystals, the thickness of the islands increased and separate phases appeared over the growth zone (Figure 4a and 4b, highlighted with red circles).

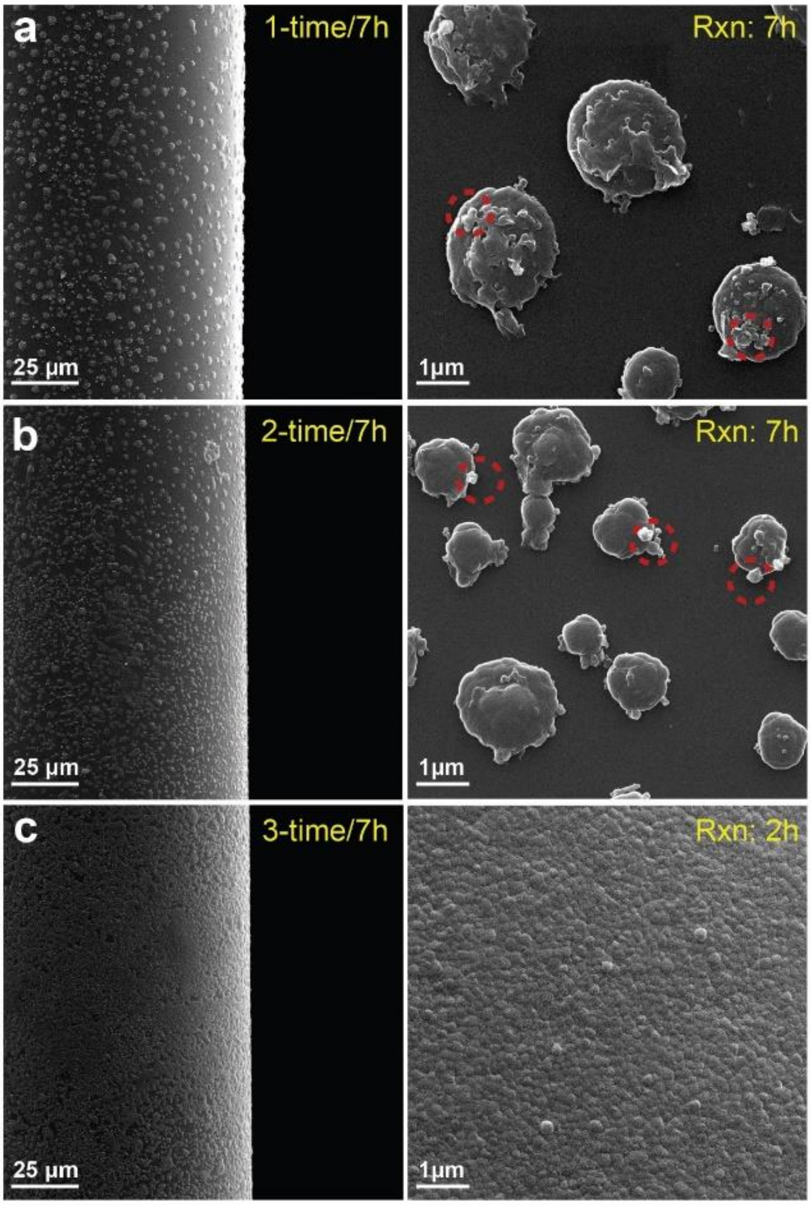

Figure 4. *SEM images of zeolite A thin films formed on silica optical fibers through secondary growth of seed crystals dip-coated **a**) one-time, **b**) two-time, and **c**) three-time. The separate zeolite A phase that appeared over the growth zone is highlighted with red circles*

To obtain nearly continuous zeolite A thin films, the spacing between seed crystals must be in the range where intergrowth of the crystals can occur. As shown above, three-time dip coating of the seed layer was found to be optimum to obtain mono- or double-layer zeolite A crystals on silica fibers. Besides, the spacing between the seed crystals was in the range where intergrowth of seed crystals can occur (Figure 4c).

To alter and control zeolite A thin film thicknesses, different hydrothermal reaction times of 2 h, 3 h, 4 h, 6 h, and 7 h were carried out for optical fibers seeded with a three-time dip coating step (Figure 5). For the optical fibers seeded with three-time dip coating step, intergrowth of the homogenous mono-layer seed crystals can be achieved even after 2 h secondary growth reaction time (Figure 4c). However, it was found that 2 h reaction time was insufficient to achieve continuous growth when there was spacing between the seed crystals (spacing > ~ 1 µm) (Figure 5a). Nearly continuous zeolite A thin films were obtained via intergrowth of seed crystals by applying 3 h secondary growth reaction time (Figure 5b). When the reaction time increased to 4 h, a separate zeolite A phase appeared as can be seen in Figure 5c (highlighted with red circles). Further increase of the reaction time to 6 h resulted in thicker growth with a substantial amount of unattached cubic zeolite A crystals on the surface of the film (Figure 5d, highlighted with red circles).

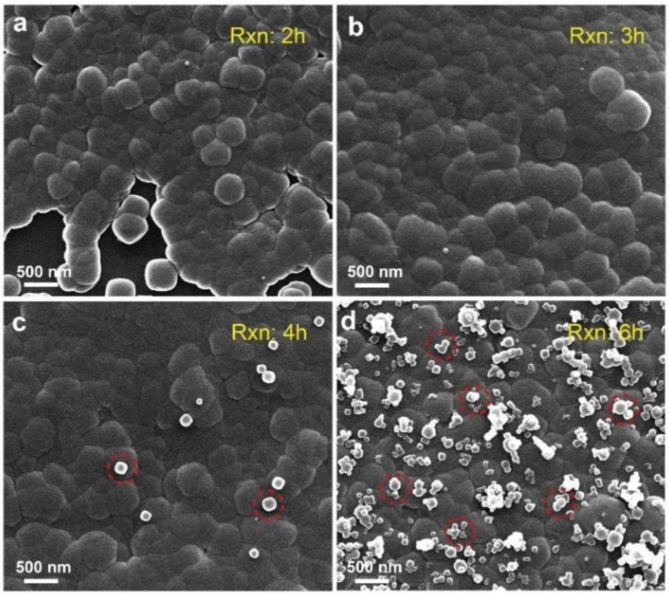

Figure 5. *Top view SEM images of zeolite A thin films grown on optical fibers via the secondary growth method with **a**) 2 h, **b**) 3 h, **c**) 4 h, and **d**) 6 h secondary growth reaction times. The silica optical fibers were seeded with three-time dip coating step*

The initial transparent color of the secondary growth suspension in the glass vial was still transparent after 2 h secondary growth reaction time and light milky after 3 h reaction time. However, the white precipitation of the crystals started after 4 h reaction time with milky suspension at the top. Distinct segregation was observed after 5 h reaction time, that is, a significant amount of white precipitation (i.e., crystalline zeolite A) was observed at the bottom of the glass vial and a clear suspension appeared at the top. This phenomenon can be clearly observed from the presence of a considerable amount of unattached cubic zeolite A crystals on the surface of the film after 6 h of reaction time (Figure 5d, highlighted with red circles).

To further analyze thin film thicknesses altered upon increasing the secondary growth reaction time, optical fibers were cut with a razor blade after growth. The fibers with thin film were placed on cross-section SEM stub and analyses were carried out. The film thicknesses averaged out from at least six different spots. The film thicknesses of 255.3 nm ± 10.1 nm, 283.2 nm ± 18.6 nm, 649.6 ± 28.1 nm, and 632.1 nm ± 72.5 nm (average ± standard deviation) were obtained for 2 h, 3 h, 4 h, and 6 h secondary growth reaction times, respectively (Figure 6).

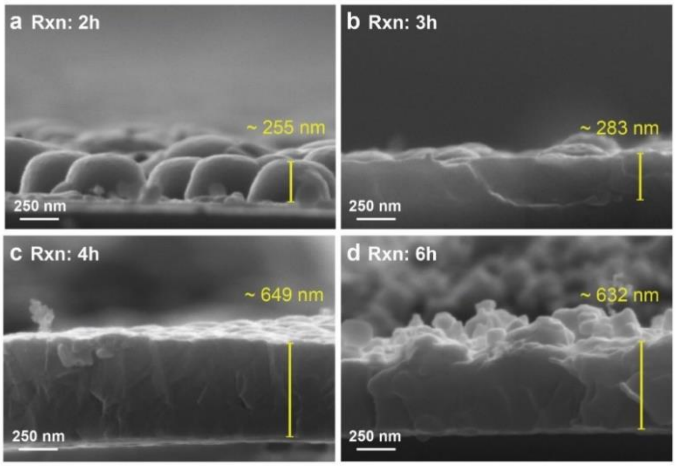

Figure 6. *Cross-sectional SEM images of zeolite A thin films formed on optical fibers via secondary growth method with **a**) 2 h, **b**) 3 h, **c**) 4 h, and **d**) 6 h secondary growth reaction times. The silica optical fibers were seeded with three-time dip coating step*

As can be seen from cross-section images, the boundaries of the cubic seed crystals were still observable for 2 h reaction time (Figure 6a) while complete intergrowth of the seed crystals. Besides, the thin films were attached to optical fibers with reaction times of 3 hours and 4 hours, ensuring a strong adhesion (Figures 6b and 6c). Besides, the surfaces of the films grown by 3 h and 4 h secondary growth reaction times were smoother compared to those grown by 6 h reaction time as observed in top view SEM images as well (Figure 5). The average film thicknesses indicate that film growth is saturated after 4h reaction time. As the reaction time increased, growth was achieved not only in the lateral direction (i.e., intergrowth) but also in the vertical direction, thus increasing the thickness of the films and the roughness of the thin film surface as well.

4. CONCLUSION

The feasibility of forming zeolite A thin films on silica fibers was investigated. Mono-layer or double-layer zeolite A thin films were formed on silica fibers to use them in potential gas sensor applications. First, hydrothermal synthesis of nano-sized zeolite A crystals (average crystal size: 247.3 nm) was performed. Then, seed layer coating on silica fibers was optimized. One-time or two-time dip coating steps were not sufficient to obtain full coverage of silica fibers while four-time or five-time dip coatings resulted in multi-layer seed formation neither of which are desired for potential gas sensor applications. Accordingly, three-time dip coating of the seed layer was found to be optimum to obtain mono- or double-layer zeolite A crystals on silica fibers (thicknesses of the mono-layer seed layers ~ 200 nm). Then, seed layers deposited on silica fibers (diameter of 250 µm) were grown by the secondary growth method. To obtain nearly continuous zeolite A thin films, the spacing between seed crystals must be in the range where intergrowth of the crystals can occur (i.e., less than 1 µm). When nearly continuous coverage of seed layers was not achieved (i.e., one-time and two-time seed layers), intergrowth of seed crystals cannot be achieved even though the reaction time increased to 7 h due to the presence of ~ 15 µm spacing between island-like seed crystals. It was observed that as the reaction time increased to 7 h to achieve epitaxial growth of island-like seed crystals, the thickness of the islands increased and separate crystal phases appeared on the growth zone. To alter and control zeolite A thin film thicknesses, different secondary growth reaction times of 2 h, 3 h, 4 h, 6 h, and 7 h were carried out for optical fibers seeded with three-time dip coating step. Intergrowth of mono-layer seed crystals can be achieved even after 2 h secondary growth reaction time. As the reaction time increased to 4 h, a separate zeolite A phase appeared on the surface of the film. When the reaction time was increased to 6 h, a substantial amount of unattached cubic zeolite A crystals were observed on the surface of the films. The film thicknesses of 255.3 nm ± 10.1 nm, 283.2 nm ± 18.6 nm, 649.6 ± 28.1 nm, and 632.1 nm ± 72.5 nm (average ± standard deviation) were obtained for 2 h, 3 h, 4 h, and 6 h secondary growth reaction times, respectively. Smoother surfaces were obtained for the films grown by 3 h and 4 h secondary growth reaction times compared to those grown by 6 h reaction time. Nearly continuous and firmly attached zeolite A thin films were obtained via intergrowth of seed crystals by applying 3 h secondary growth reaction time for the optical fibers seeded with three-time dip coating step. The nanoporous zeolite A films formed on optical fiber can be used as potential gas sensors. These sensors function by detecting changes in optical reflection caused by the differential adsorption of gases.

ACKNOWLEDGEMENT

The current study is supported by TÜBİTAK with the research project numbers of 118F115 and 120F147.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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