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Greener synthesis of nanocrystalline ZSM-5

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GREENER SYNTHESIS OF NANOCRYSTALLINE ZSM-5

by

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CERTIFICATE OF APPROVAL

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MASTER'S THESIS

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This is to certify that the Master's thesis of

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has been approved by the Examining Committee for
the thesis requirement for the Master of Science degree
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To my parents who support me a lot and spent their time to see me in a higher level
To my brothers and sisters who have taught me how to be a successful person
To my wife for her support and patience
To my son and daughter
To my friends

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ABSTRACT

Nanocrystalline ZSM-5 zeolite, which is a well-known catalyst used in a variety of applications in industry, environment, and medicine, can be synthesized using different methods. However, a big challenge in synthesizing nanocrsytalline ZSM-5 is the use of an organic template such as TPAOH, which is very expensive. The template is required to facilitate the growth of the nanocrsytalline ZSM-5 during the synthesis. However, to use the nanocrsytalline ZSM-5, the template has to be removed by a calcination process to open the pores and reveal the active surface of the nanocrystalline ZSM-5. The calcination process requires a high temperature for a long time to remove the organic template. Consequently, synthesizing nanocrystalline ZSM-5 by using a templated method is considered to be time, energy, and materials inefficient. In addition, the production of CO_2 from the calcination process is a negative impact on the environment. Therefore, finding another method to synthesize nanocrystalline ZSM-5 without using an organic template would be beneficial. Here, nanocrystalline ZSM-5 was synthesized successfully in high yield and quality by using a seed-assisted method and without using the organic template. In addition, the effect of synthesis temperature, synthesis time, basic environment, amount of seeds, size of seeds, aging time, and use of calcined and uncalcined seeds are investigated in this study. The synthesized nanocrystalline ZSM-5 materials were characterized by using X-ray diffraction (XRD), gas adsorption isotherm (BET/BJH), and transmission electron microscopy (TEM).

PUBLIC ABSTRACT

Nanocrystalline ZSM-5 zeolite, which is a type of porous aluminosilicate material can be used in a variety of applications in industry, environment, and medicine. Nanocrystalline ZSM-5 can be prepared using different synthetic approaches. Almost all of these methods require a template, such that the nanocrystalline ZSM-5 materials are formed around the template and then the template is removed to introduce the porosity. The removal process can be done by heating the materials for a long time to decompose the template, but during this process carbon dioxide gas, which is considered harmful to the environment, is also formed. Consequently, using the template to form these nanocrystalline materials is considered time, energy, and money inefficient. Therefore, finding another way to synthesize these nanocrystalline materials without using the template would be beneficial. Here, nanocrystalline ZSM-5 materials were successfully formed by a new method without using the template. In this method, the yield and the quality of the materials are very high. In addition, the conditions that are used such as the time, the temperature, and the chemical materials used are changed in a way that helps to study the effect of these conditions on the formation of the desired materials. The obtained materials were characterized by using different instruments that help to identify the type and the properties of the materials.

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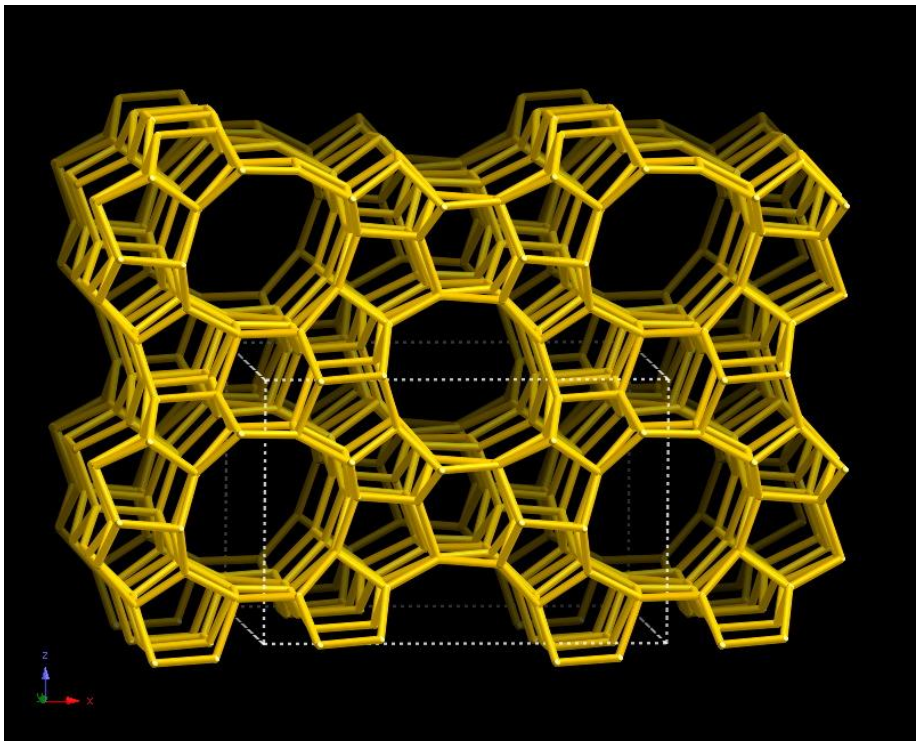
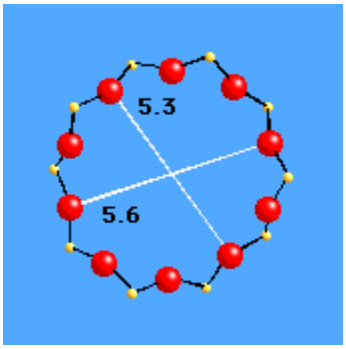
I. Introduction

Zeolite, which is a name of a chemical material, is derived from a Greek word that contains two parts, “zeo” which means “to boil”, and “lithos” which means “a stone”. Zeolites are crystalline aluminosilicate materials composed of silicon and aluminum that are arranged in a tetrahedral three-dimensional structure and are linked by oxygen atoms. In addition, the structure of the zeolite contains pores of molecular dimensions. Zeolites can be found in natural or synthetic forms. Several methods can be used to synthesize the zeolite commercially in different sizes and structures, including various crystalline structures. Currently, there are about 40 types of naturally occurring zeolites and about 200 synthetic versions. The chemical composition and structural framework of the materials determine the type and zeolite properties.[1,2]

One kind of zeolite is ZSM-5 (Zeolite Socony Mobil #5), which has MFI structure and a well-known zeolite framework. The structure of ZSM-5 is a three dimensional structure with two kinds of intersecting channels, straight channels and zigzag channels, that are formed by 10-ring pores with pore diameters of ~0.55 nm.[3] ZSM-5 zeolites are used in a variety of applications in industry, environment and medicine.[2,3] ZSM-5 is considered one of the most important catalysts used in environmental and industrial fields. ZSM-5 has been synthesized with different structures depending on its chemical composition (Al/Si) and both particle and pore size. The activity of the synthesized ZSM-5 zeolites depends on the active sites on the surface. In general, the surface of ZSM-5 zeolites has two type of active sites, Bronsted acid sites and Lewis acid sites. The Bronsted acid sites include the terminal silanol groups on the external surface and the bridging hydroxyl groups (Si-OH-Al), which are located at the channel intersections, while the



(A)



(B)

Figure 1. A view of MFI framework of ZSM-5 zeolite along [010] plane (A), and a pore profile of ZSM-5 zeolite with diameter in Angstroms (B).

Source: http://www.iza-online.org/

Lewis acid sites, which are electron acceptors, refer to extra-framework aluminum species. Because the activity of ZSM-5 zeolites involves the active surface sites, the performance of ZSM-5 will depend on the total accessible surface area of the structure and the diffusion path lengths.[4,5,6,7,8] In other words, increasing the total surface area of the ZSM-5 crystalline will increase its efficiency as a catalyst because the number of active sites on the surface will increase as well.

Decreasing the size of the particles increases the total surface area of ZSM-5 and the number of accessible active sites, and this leads to enhanced efficiency as catalysts. Therefore, several studies have decreased the size of the particles and created pores inside the structure in order to increase ZSM-5 zeolite catalytic efficiency.[9] Both microcrystalline (1 – 100 μm) and nanocrystalline (1-1000 nm) ZSM-5 zeolites have been successfully synthesized. However, many studies have focused on producing nanocrytalline ZSM-5 zeolite with particles size less than 100 nm and pore diameters of about 0.55 nm. [9,10,11] Nanocrystalline ZSM-5 exhibits novel properties with a high surface area, small pores, and adjustable surface with two types of active sites. These novel properties enhance the performance of the nanocrystalline zeolite ZSM-5 by increasing the total accessible surface area and shortening the diffusion path lengths.

The adjustable surface of these nanomaterials gives rise to new properties that could lead to a variety of applications. For example, silanol groups on the external surface of nanocrystalline ZSM-5 zeolites can be used to modify hydrophobicity and reactivity of zeolites so they can be used in variety of applications. The functionalization of the external surface of ZSM-5 with long chain hydrocarbon compounds such as octylmethytrichlorosilane will enhance the hydrophobicity of the surface. Moreover, amine

groups (-NH_3), or sulfonic acid groups (-SO_3H) can be used to increase acid-catalyzed reactions of zeolite materials.[12]

Another possible adjustment to the surface area of these nanomaterials is to deactivate the active sites on the external surface area without changing the main structure of zeolite materials. For instance, the biomass conversion of the furan to olefin and aromatic happens on internal acidic active sites; however, the active sites on the external surface induce the formation of undesirable products (coke) by isomerization or alkylation reactions. These products will deposit on the particles and block the path to reach the internal active sites, and this will lead to a lower yield of the target product. For this reason and because the surface of nanocrystalline ZSM-5 is adjustable, the active sites on the external surface area can be deactivated by using leaching agents such as (HNO_3, HCl, H_3PO_4, 5-sulfosalicylic acid dehydrate, oxalic acid, and tartaric acid).[13] Moreover, the size and shape of the pore in these nanomaterials play an essential role in some of catalytic applications. For example, the conversion of glucose to aromatics by using nanocrystalline ZM-5 as a catalyst shows the highest yield when the pore size of the used nanocrsytalline ZSM-5 is between 5.2 and 5.9 Å.[14,15]

II. Applications

Nanocrystalline ZSM-5 zeolites have a variety of applications in different fields such as environment, industry, and medicine. Nanocrstalline ZSM-5 zeolites have great potential in catalysis, separations, adsorption, designing nanoscale devices, nanofilms, and membranes. Because nanocrsytalline ZSM-5 zeolites have a high surface area with different active sites, small pore sizes, and a short diffusion path, they can be used as catalysts. For example, catalytic cracking reactions in petrochemical industries use nanocrystalline ZSM-5 zeolites because they have acid sites (Bronstend acid sites) on the surface, which have catalytic activity toward cracking reactions.[16]

Furthermore, light olefins, which are considered a useful material in petrochemistry, can be produced simply by using methane with ZSM-5 as a catalyst instead of using a thermal cracking process.[11] Using nanocrystalline ZSM-5 to catalyze a selective catalytic reduction (SCR) of NO_x can reduce the emission of harmful pollutants such as nitrogen oxides.[12] Nanocrystalline ZSM-5 is used as a solid catalyst to convert different types of biomass to chemicals such as olefins and aromatics, which can be used as fuels.[13,14] Because nanocrystalline ZSM-5 zeolites have long-term stability under high temperature, resistance to harsh environments, and selectivity, designing membranes from nanocrystalline ZSM-5 materials is an efficient way to separate various liquid and gaseous mixtures. In addition, adding the nanocrystalline ZSM-5 to membrane separations increases the adsorptive and diffusive properties of the membranes.[17]

Furthermore, nanocrystalline ZSM-5 zeolites are used in optical devices and sensors because of their porous structure, catalytic activity, small particle size, and high surface area. In medical and biological fields, nanocrystalline ZSM-5 zeolites have a

variety of applications. For example, because nanocrsytalline ZSM-5 zeolites have no or very low toxicity, these nanomaterials can be used for skin cleaning, to absorb unpleasant odors, and to help speed the healing of the skin wounds. Moreover, the ability to modify the surface of nanocrystalline ZSM-5 with specific proteins or enzymes may lead to a wider variety of applications. For instance, the amine groups in proteins can be easily attached to the surface of nanocrystallian ZSM-5 to immobilize and increase the stability of the proteins. Nanocrystalline ZSM-5 can also be used for drug delivery and cancer cell targeting because of its porous structure, stability, low toxicity level, and modifiable surface. [2,11,18]

III. Synthesis of Nanocrystalline ZSM-5

In general, zeolites are formed in a closed system such as a Parr autoclave, where reactions lead to initial nucleation and crystal growth. Particle size can be controlled by varying the conditions of the nucleation step. In other words, to produce nanocrystalline zeolite, the synthesis conditions must be favorable to the nucleation process rather than crystal growth. There are three primary ways to synthesize nanocrystalline ZSM-5 zeolites: (1) using ultradense gels without bulk liquids; (2) using clear sols with only distinct gel particles; and(3) using a system which compresses both liquid and bulk solid together (hydrogel systems).[17] Several studies have been published describing different methods of synthesizing nanocrystalline ZSM-5 zeolites. Persson et al first synthesized nanocrystalline ZSM-5 using a clear sol system with a low temperature.[11] Because of the desire to produce very small particles and to make the reaction rate very fast, several methods have been developed. [12,19,20] In all these methods the synthesis of nanocrystalline ZSM-5 has been

accomplished by using an organic structure directing agent (OSDA) as a template such as tetrapropylammonium (TPA) template.[21]

Van Grieken et al synthesized nanocrystalline ZSM-5 with particle sizes between 15 – 60 nm and yields ca 50% by using a mixture of clear sodium with hydrothermal treatment at 170 °C. This can be done with low temperature of 70 – 90 °C and no sodium in the clear solution to produce a yield of 20-30 %.[11] Another method to produce nanocrystalline ZSM-5 with a particle size of about 15 nm is by modifying the clear solution used in Van Grieken's method.[19] In this method, the steps of the process are the same as in Van Grieken's method, but aluminum isopropyloxide is used as an aluminum source with some additional changes in reaction conditions. Confined-space synthesis is another way to synthesize nanocrystalline ZSM-5 zeolite. In this method, an inert matrix provides a steric hindered for crystal growth. Madsen and Jacobsen were the first team to prepare nanocrsytilline ZSM-5 zeolite by this method. The basic procedure is to do two impregnations: one by adding mesoporous carbon black to the clear solution that contains the tetrapropylammonium hydroxide (TPAOH) as a template, and the second one with tetraethylorthosilicate (TEOS). The next step is treat the matrix to an autoclave with enough water stream at 180°C to produce particle sizes between 30–40 nm. The calcination process is needed to remove both the structure-directing templates and carbon matrix.[17]

The challenge with using conventional methods is the use of the organic structure directing agent (OSDA) as a template to facilitate the growth of the nanocrystalline ZSM-5. These organic templates are expensive and have complex structures that have to be removed by calcination at a high temperature to get the pores and reveal the internal surface of nanocrystalline ZSM-5. This process consumes energy and produces gases that are

environmentally unfriendly such as CO_2. For these reasons, finding a method to synthesize nanocrystalline ZSM-5 without using the organic template will be strongly desired because it will be less costly and more friendly to the environment. Several studies have attempted to synthesize ZSM-5 and other zeolites types using template-free or seed-assisted methods. Grose and Flanigen reported the first synthesis of ZSM-5 by template-free and seed-assisted method in 1981 using high temperatures of 200 C and a long heating time of 68-72h.[22]

After that, many studies have been conducted to synthesize ZSM-5 and other zeolites without using the template. One of the proposed ways to synthesize zeolites without using the organic template is the seed assisted method. In these methods, seed crystals of the target zeolite are synthesized using the conventional method with an organic template, and then the synthesized seeds are added to a reactant gel that does not contain the organic template to get the desired zeolite. The added seed crystals increase the crystallization rate, and enhance the quality of the product zeolite by improving the crystallization.[23,24]

Although the seed-assisted methods have been used to synthesize different types of zeolites, the mechanism by which seed crystals stimulate the production of zeolites has not been fully understood. However, there are some hypotheses that have been established to explain the mechanism of seed-assisted methods. For instance, Xiao and coworkers have suggested that the seed-assisted synthesis for beta zeolite occurs through a core-shell growth mechanism.[25] Okubo *et al* have offered a more widely accepted hypothesis. They used the idea of the common composite building units between the seeds and the target zeolites to describe the growth of the product zeolites upon the seeds. In general, zeolites

have three-dimensional framework structures that consist of composite or secondary building units. These units of all zeolites types are summarized in the database collection of the Structure Commission of the International Zeolite Association (IZASC).[24]

According to Okubo *et al*, in the template-free or seed-assisted synthesis of zeolites, the added seeds and the reactant gel should have a common composite building unit between them to form the target zeolite. In other words, a desired zeolite should be added as seeds to a reactant gel that will give a zeolite type having the common composite building unit if the reactant gel is hydrothermally treated. In addition, the seed must have a common building unit with the product (Figure 2). For example, ZSM-5 zeolites have four composite building units (*mor, mel, mfi, and cas*), and ZSM-11 has three building units (*mor, mel, and mfi).* On the other hand, mordenite zeolites have one composite building unit (*mor*). Therefore, in case of synthesis of ZSM-5 using a seed-assisted method, the added seed should be either ZSM-5 or ZSM-11 crystals, and the reactant gel should give mordenite zeolites if it is heated without seeds because ZSM-5 and mordenite zeolites have the common composite building unit *mor*, and ZSM-11 has common building units(*mor, mel, mfi)* with ZSM-5. Therefore, ZSM-11 can be used as a seed to synthesize ZSM-5 crystals.[24,26]

Although there are several hypotheses to demonstrate the growth mechanism of product zeolites by seed-assisted syntheses, in general, the common idea that explains the role of the used seeds in the growth mechanism is that the seed crystals provide an active surface where the growth of new particles will occur.[24] It was found that the mechanism of the nucleation and growth process depends on the gel composition, and the framework of the seed and the target. The seeds have active sites on the external surface that will be used

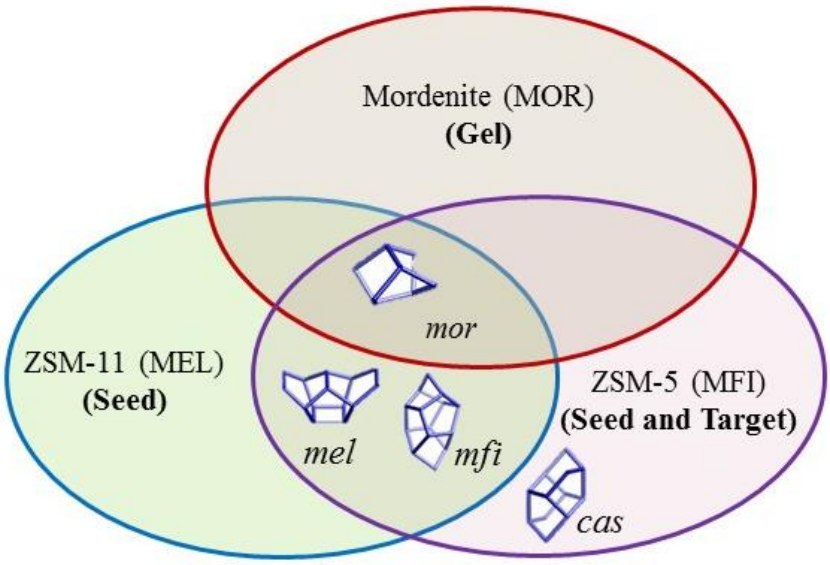


Figure 2. The common composite building units between three types of zeolites (ZSM-5, ZSM-11, and mordenite).

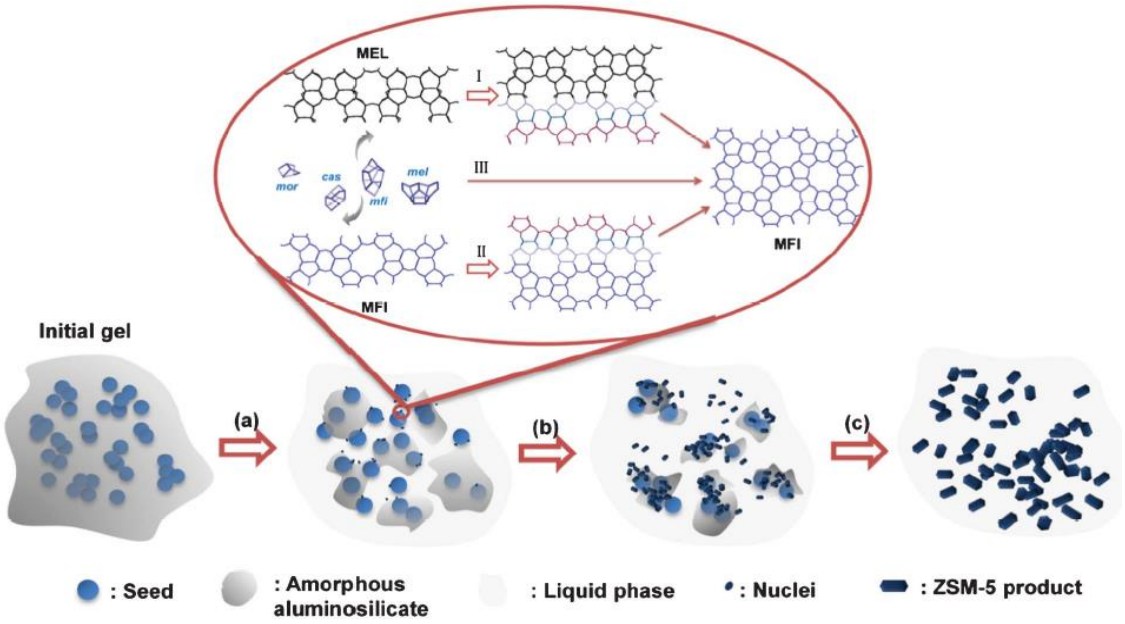


Figure 3. The mechanism in which new nanocrystalline ZSM-5 particles are formed by the seed-assisted method. Reproduced with the permission from Royal Society of Chemistry.[26]

as nucleation sites to form new nuclei. When the seeds are introduced to the mixture reaction, they will be dispersed, and an amorphous phase will be formed around the seeds (see Figure 3a). After that, the active sites on the external surface will be exposed by strongly basic conditions to help the formation of new nuclei (see Figure 3b). The formation of new nuclei and then new particles in this step will depend on the framework of the seed and the target. If the seed has common building units with the target, the external active sites on seed crystals will attract the common units from the liquid phase to be grown as new nuclei (see Figure 3 I and II). After formation of new nuclei on the surface of the seed crystals, these nuclei could stay and continue to grow to form new crystals or release to the liquid phase and serve as nucleation sites to produce new crystals (see Figure 3c). There is another possibility for the formation of the new crystals during the seed-assisted method which is a self-assembly process for the building units. This case occurs if there are no common composite building units available on the surface of the seed. During this process, the corresponding units will self-assemble to form the structure of the product (see Figure 3 III), but the growth rate in this case will be very low as there are no active sites to facilitate the nucleation and growth step.[22,23,25,27] According to the above explanation of the growth mechanism, the external surface, the gel composition, and the framework of the seed play a crucial role in the formation of the product. As the seed crystals have high external surface, more active sites will be available to be used during the nucleation process. This leads to large numbers of new nuclei that can be used to synthesize large numbers of new crystals with small size.

IV. Characterization of Nanocrytalline ZSM-5 Zeolites

Several techniques have been used to study nanocrytalline ZSM-5 zeolites, and each one of them has a certain purpose. In general, powder X-ray diffraction (p-XDR) is used for structure identification and nitrogen adsorption by BET is used to determine the surface area, the pore volume and the pore size. Inductively coupled plasma/optical emission spectroscopy (ICP/OES) is used to identify the elemental composition of zeolites. The size, the shape and the surface morphology of zeolite crystals can be measured by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Moreover, dynamic light scattering (DLS) can be used to determine the distribution of particle sizes. Silicon and aluminum sites on both external and internal surfaces can be identified using Fourier transform infrared spectroscopy and solid-state NMR spectroscopy. In this study, X-ray diffraction, BET, and Transmission Electron Microscopy were used to characterize the nanocrystalline ZSM- materials.

4.1 Powder X-ray Diffraction

X-ray diffraction is a technique used to study the structure of materials. In this technique, X-ray beams hit the structure and three main events occur: (1) the beam is scattered with the same energy (elastic scattering), (2) the scattered beam loses part of its energy (inelastic scattering), and (3) the X-ray beam is absorbed and an electron beam is emitted from the structure (X-ray photoelectron spectroscopy). X-ray diffraction uses elastic scattering to determine the structure of materials. Because atoms in crystals are arranged in periodic planes, these planes will diffract the X-ray beam. Once the X-ray beam hits the upper plane, it will be partially scattered. The part of the X-ray that is not reflected by the upper plan will pass to the next plane, and it will be partially scattered again. This

process will occur as long as the X-ray beam passes through the crystal. The reflected X-ray beams will have different path lengths depending on the distance between two consecutive planes. Depending on the net difference between planes which can be calculated as below, two types of interferences will occur.

$$AB + BC = 2d \sin(\theta)$$

Destructive interference will occur when the path length difference is not equal to an integer number of the X-ray wavelength, and the constructive interference occurs if the path length difference is equal to the integer number of the X-ray wavelength. The former will not show any peaks, while the latter will produce peaks in the X-ray pattern. Each structure has a distinct X-ray diffraction pattern, and the pattern serves as a fingerprint of a specific type of crystalline material.[3,28,29,30] In studies of nanocrystalline ZSM-5 zeolites, the X-ray diffraction patterns of synthesized materials can be compared to the standard nanocrystalline ZSM-5 zeolite pattern to determine if the produced materials have the same pattern of peaks or not.

Another advantage of X-ray diffraction is that it can be used to determine the crystallinity of materials. By using the XRD patterns of both target and standard materials, relative crystallinity (RC) can be estimated:[3,20]

$$RC = \frac{I}{I_{ref}} \times 100\%$$

Where I is the height or area of a specific peak of a target material, and I_{ref} is for standard sample of the same material. Knowing the crystallinity of materials, the quality of a product can be determined because materials with a certain amount of amorphous impurity will show lower peak intensities compared to a pure material. Figure 4 shows a standard XRD pattern with the specific area that can be used to calculate the relative crystallinity.

Furthermore, the crystal size in powder materials can be estimated from XRD patterns by using Scherrer's equation:[10]

$$\Upsilon = \frac{K \,.\, \lambda}{\beta . Cos\ \theta}$$

Where: Υ equals to the crystal size (nm).

K= crystal shape factor (K=1).

λ = wavelength of X-rays (1.5418A for Cu Ka radiation).

β = full width at half-maximum (FWHM)

θ = Bragg's angle

The full width at half-maximum (FWHM) of the peak can be measured using a high-resolution scan for a specific area in XRD pattern. From the above equation, as the crystal size decreases, the peaks in XRD pattern will be broadened. In other words, we expect to see narrow peaks in XRD patterns as the size of crystals increases.

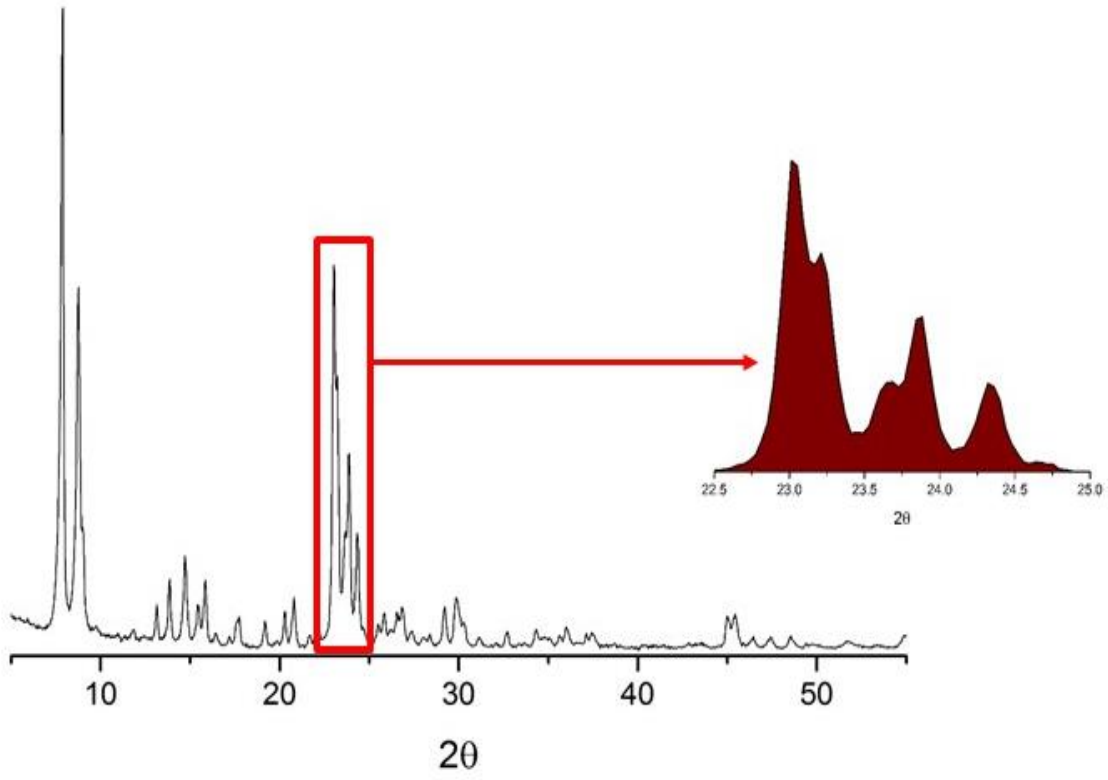


Figure 4. A standard XRD pattern with the main peaks between 2θ of 7° – 9° and 23° – 25°, and the inset shows the specific area that can be used to find the relative crystallinity of nanocrystalline ZSM-5.

4.2 Nitrogen Adsorption Isotherm by BET

When gas molecules hit a surface, they can be adsorbed on the surface either in a chemisorption or physisorption state. With BET the adsorption of nitrogen gas on the surface of ZSM-5 zeolites is physisorption, which is a van der waal interaction between the gas molecules (adsorbates) and the surface of ZSM-5. This method is based on Brunauer, Emment and Teller (BET) theory, which suggests that gas molecules will be adsorbed on the surface as a monolayer. By knowing the volume of the adsorbent and the area occupied by each molecule, which is usually a nitrogen gas molecule with a cross section of 0.162 nm, it is possible to determine the ZSM-5 surface area. Most studies of ZSM-5 have calculated the surface area before and after the calcination step, which removes the template, to obtain the internal and external surface area of ZSM-5 zeolite. Before the calcination step, the template is inside the structure; therefore, the internal surfaces are blocked by that template, and adsorption happens only on the external area. As a result, the calculated surface area is just for external surfaces. After removing the template by calcination, the measured surface area is the total surface area of both internal and external surfaces. The internal surface area can be found by subtracting the external surface area from the total surface area. The pore size and the pore volume can be determined by collecting the full isotherm (adsorption/desorption isotherm).[3,10,12,31,32,33]

4.3 Scanning and Transmission Electron Microscopy

Both scanning and transmission electron microscopy are useful for studying the surface of materials. They can provide information about the size, shape, and surface morphology of nanocrytalline ZSM-5 zeolites. In these techniques, an electron beam is created by an

electron gun and passed through a system that contains several magnetic lenses and apertures. These lenses and apertures work to correct and focus the path of electron beam toward the specimen. The images in these instruments are generated from either transmission or scattered beams. Because the electron wavelength is much smaller than the wavelength of the visible light, the generated images are high resolution even for a nanoscale specimen. In scanning electron microscopy (SEM), the electron beam (incident electrons) hits the surface of the specimen and electrons are emitted from the sample because of both elastic and inelastic scattering events on or near to the surface of the sample. For SEM images, secondary electrons, which are inelastic scattered electron beams from the surface, are collected to create an image of the surface.

In transmission electron microscopy (TEM), the electron beam passes through the sample, and then a specific detector to create a TEM image of the sample collects it. In case of nanocystalline ZSM-5 zeolite, the surface is nonconductive. So the sample must be coated to undergo the process in SEM and TEM. In SEM, the sample must be conductive to avoid a charge accumulation on the surface, which can distort the image. Therefore, a small amount of ZSM-5 is diluted, and a drop is placed onto the surface of SEM sample stud. After the sample dries, it is coated with a thin layer (several nanometers) of conductive material such as gold or platinum.[3,28, 29,] In TEM, a sample of ZSM-5 will be placed onto a thin metal grid coated with a thin carbon layer to be dried and then imaged by TEM without any coating.

V. Experimental Section

Materials

Seed synthesis: Tetrapropylammonium hydroxide (TPAOH, 40 wt % aqueous solution), Tetraethyl orthosilicate (TEOS), Sodium hydroxide (NaOH), and Aluminum isopropoxide.

Seed- assisted synthesis: Sodium aluminate, Silica sol (30 %), Sodium hydroxide (NaOH)

5.1 Synthesis of Nanocrystalline ZSM-5 Seeds

The synthesis of the nanocrystalline ZSM-5 seeds was done by following a method developed in our lab with making some modifications to the molar ratio to vary the particle size. [10] The synthesis procedure was as follow: a measured amount of aluminum isopropoxide was dissolved in distilled water with stirring, and then NaOH was added to the mixture followed by adding TPAOH and TEOS, respectively. The reaction mixture was left for 2 h at room temperature with a continuous stirring. After that, the mixture was transferred to an autoclave equipped with a Teflon liner following by a hydrothermal treatment at 165 °C for 120 h. After that, the particles were separated by the centrifugation and washed with distilled water twice and once with ethanol. The obtained particles were dried at 80 °C overnight to be used as seeds in the next synthesis part.

5.2 Seed-assisted Synthesis

To start the synthesis, a specific amount of the synthesized particles (70 ± 2 nm, 90 ± 4 nm, and 250 ± 5 nm) from the above method were measured to serve as seeds in this procedure. The seeds were added in 1.0 mL of ethanol to prepare a seed suspension. Then the seed suspension was sonicated for 2-3 h. In another vessel, an aluminosilicate gel with a chemical composition of $0.006SiO_2$:$0.0003Al_2O_3$:xNa_2O:$0.3H_2O$ (where x = 0.001, 0.0015, 0.0025 and 0.0035) was formed by dissolving a measured amount of sodium aluminate in distilled water following by adding the sodium hydroxide. Next, the silica sol was added to the mixture. The reaction mixture was stirred for 2 h at room temperature. Then, the seed suspension was added to the reaction mixture and transferred to an autoclave to be treated hydrothermally. Next, the synthesized nanocrystalline ZSM-5 particles were collected by centrifugation and washed with acidic ethanol (1.0 mL of HCl/ 1.0 L of Ethanol) one time, and twice with distilled water. Then, the collected particles were dried at 80 °C overnight (see Figure 5). The amount and size of the seeds, temperature, amount of NaOH, and time were varied to investigate their effect on the synthesis as listed in Table 1.

5.3 Instruments

The obtained materials were characterized by using a D-8 X-ray diffractometer with Cu Kα to collect the XRD pattern between 2θ angles of 5 to 55 with a 0.04 step size. Then, the XRD patterns were used to estimate the relative crystallinity (RC) of the samples by using the peaks between 2θ of 22.5 to 25°.

Surface area analysis was done by using BET method on a Nova 4200 Nitrogen adsorption instrument. To start the surface area measurement, approximately 100 mg of the obtained materials was dried over night at 120 $^{\circ}$C under vacuum by using the outgas station on the BET instrument. Then, surface analysis of 7-points BET isotherm was run to measure the surface area of the materials by using pure nitrogen gas as the adsorbate. For the seed samples, the external surface area before the calcination was used to calculate the particle size by using this equation; particle size = 3216/ external surface area.[19]

The TEM images were collected by using JEOL JEM-1230 Transmission Electron Microscopy. The samples were prepared by dissolving a small amount of the materials in ethanol following by sonicating for 20 min. A drop from the sample suspension was placed on a carbon grid coated with copper and left to dry at room temperature before doing the TEM analysis. Table 1 summarizes the synthesis experiments and the characterization results for the samples.

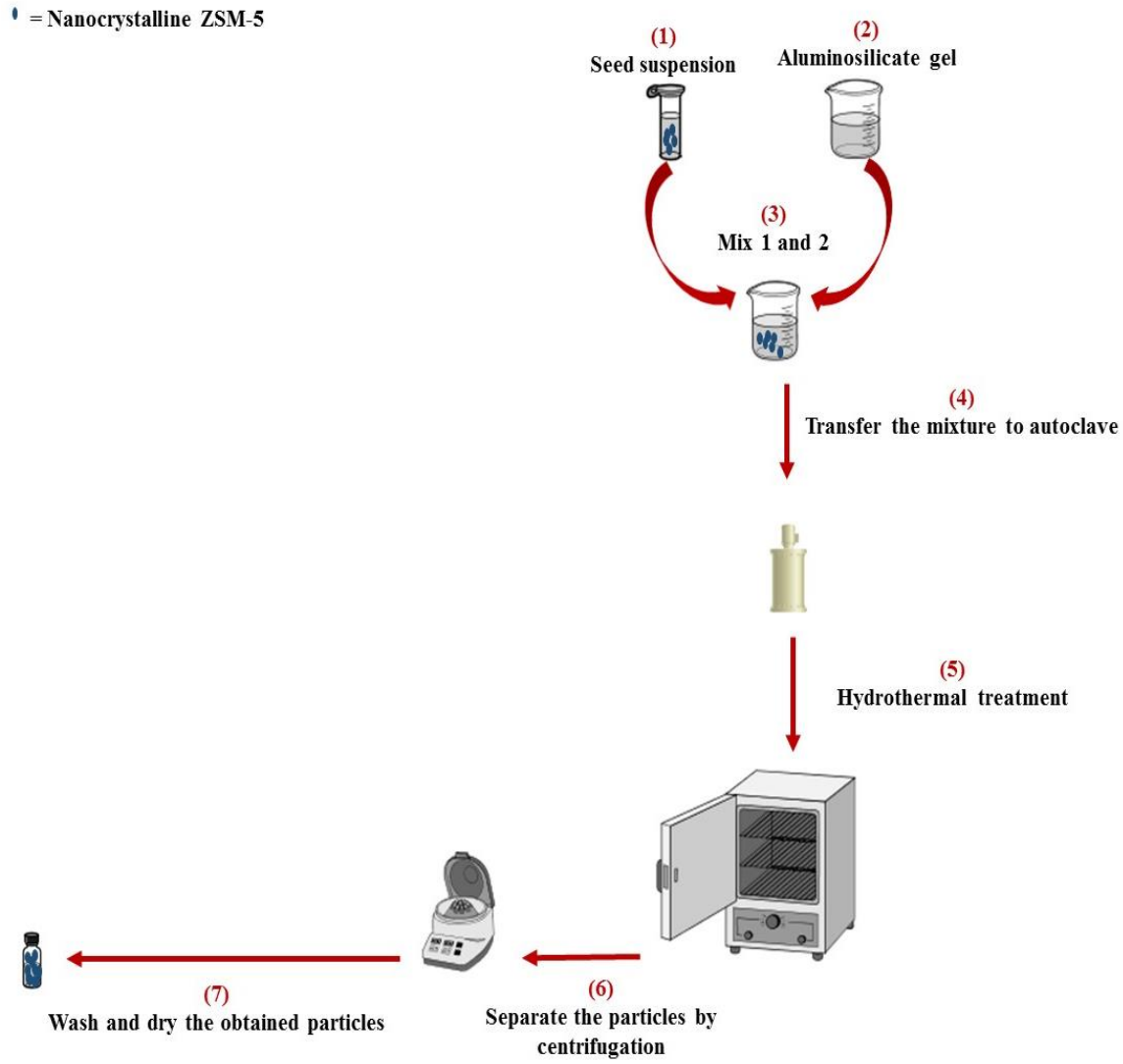


Figure 5. Schematic illustrates the steps of the seed-assisted synthesis of nanocrystalline ZSM-5

Table 1 Summary of synthesis and characterization of nanocrystalline ZSM-5 by the seed-assisted method.

sample	Molar ratio	Size of seed (nm) [a]	% of seed	Temp. (°C)	Time (h)	Aging time (h)	Size of particle (nm) [b]	Crystallinity %	Surface area m^2/g	Type of impurity
S1-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	250	0.35	150	24	----	-----	----		Amorphous
S2-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	250	0.35	165	24	----	310	92	250	-----
S3-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	250	0.35	180	24	----	----	----	----	Keatite
S4-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	70	0.35	165	10	----	----	65	----	-----
S5-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	70	0.35	165	14	----	260	98	280	-----
S6-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	70	0.35	165	24	----	280	94	250	------
S7-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	70	0.35	165	48	----	----	----	----	Quartz
S8-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.001Na_2O$:$0.3H_2O$	70	0.35	165	24	----	----	----	----	Amorphous
S9-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0015Na_2O$:$0.3H_2O$	70	0.35	165	24	----	----	73	150	Amorphous
S10-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0035Na_2O$:$0.3H_2O$	70	0.35	165	24	----	----	----	----	Keatite
S11-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	70	0.20	165	24	----	----	80	190	Amorphous
S12-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	90	0.35	165	24	----	710	95	240	------
S13-ZSM-5	$0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$	250	0.35	165	24	24	----	----	----	Mordenite and Keatite

[a]: the particle size was calculated by the following equation: particle size (nm) = 3216/BET surface area of as-synthesized ZSM-5 samples.[10]

[b]: the particle size was calculated from the TEM images .

VI. Results and Discussion

During the seed-assisted synthesis process the synthesis temperature, synthesis time, basic environment, amount of the seeds, aging time, size of the seeds, and use the calcined and uncalcined seeds were changed in a way that allows studying the effect of these factors on synthesizing nanocrystalline ZSM-5 by using the seed-assisted method.

6.1 Effect of the Synthesis Temperature

In order to investigate the effect of the temperature on the seed-assisted synthesis process; three experiments (sample S1, S2, and S3-ZSM-5) were carried at different temperatures (150, 165, and 180 ℃) for 24h. The gel composition was $0.006SiO_2$:$0.0003Al_2O_3$:$0.0025Na_2O$:$0.3H_2O$ with 0.35% of the 250 nm seeds. The XRD patterns of the products show a strong effect of the synthesis temperature on the formation of ZSM-5 nanocrystals (see Figure 6). From the XRD patterns, it can be seen that at the low temperature 150 ° C, the formation of ZSM-5 crystals is not fully completed as amorphous materials show up in the XRD in the area between 2θ of 10°-20°. This indicates that at a low temperature, there is not enough energy to make the complete transformation of the precursor aluminosilicate to ZSM-5 crystals. Therefore, during the synthesis time of 24 h, only part of the aluminosilicate gel was transformed to ZSM-5 crystals while the remaining amount stayed as amorphous materials. Increasing the temperature was beneficial as the XRD of the sample with synthesis temperature of 165°C shows clear peaks for ZSM-5 nanocrystals with no impurities. The relative crystallinity of this sample is 92%, which represents a crystalline material. The surface area of these synthesized particles is 250 ± 10 m^2/g, which is typical for large ZSM-5 particles, and the yield of this sample was

very high (950 mg per 15 mL). Further increasing the synthesis temperature shows the formation of other zeolite forms in addition to ZSM-5. The XRD of the sample that was synthesized at 180 °C shows an additional peak at 25.8 °(indicated with an asterisk), which refers to a keatite zeolite phase that was formed along with ZSM-5. As a result, the synthesis temperature shows a strong influence on the formation of ZSM-5 zeolites by affecting both the nucleation and growth process.

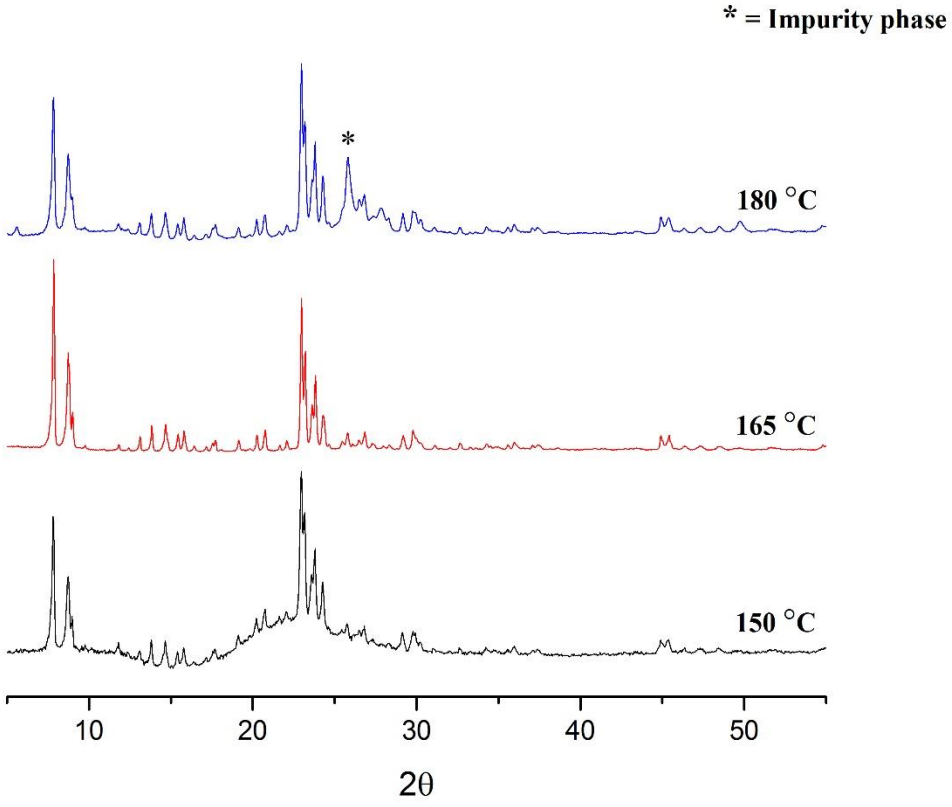


Figure 6. XRD of three samples (S1, S2, and S3-ZSM-5) that were synthesized at different temperatures (150, 165, and 180 °C) for 24h and by using 0.35% of the 250 nm seeds.

6.2 Effect of Synthesis Time

It was found that the synthesis time has a strong effect on the crystallization of the nanocrystalline ZSM-5 that are formed by templated synthesis methods.[12,19,20] In order to find the best time required to synthesize ZSM-5 by the seed-assisted method, the effect synthesis time was investigated by conducting four experiments (sample S4, S5, S6, and S7-ZSM-5) with different synthesis times (10, 14, 24, 48 h), respectively. The chemical composition of the initial gel, and the amount of seeds was the same as in the temperature effect studies. In this set of experiments, the ideal synthesis temperature of 165 °C that was found from the S1-S3 experiments was used with 0.35% of the 70 nm seeds. The collected XRD patterns of the products show that the crystallinity of the product was severely influenced by changing the synthesis time (see Figure 7). First, at a very short time of 10 h, the crystallinity of ZSM-5 is very low. The main peaks of ZSM-5 in the range of 2θ = 7-9 ° and 23-25 °appear in the XRD, but the relative crystallinity of this sample is 65%. This indicates that the crystallization process of the product was not completed and more time is needed. Increasing the synthesis time to 14 and 24 h shows a great positive impact on the crystallinity of ZSM-5 as the main peaks of ZSM-5 appear in the XRD, and the relative crystallinity is 98% and 94 % respectively. More characterization of these two sample were conducted such as BET and TEM measurements. The surface area of these two samples are 280 ± 10 m^2/g, and 250 ± 10 m^2/g respectively, and the yield was 850 mg and 900 mg per 15 mL of reaction mixture respectively. The TEM images show a particle size of 260 ± 40 nm for the ZSM-5 that was synthesized at 14 h, and 280 ± 50 nm at 24 h (see Figure 8). It is clear that increasing the synthesis time forms large particles, as the growth rate will increase with increasing the time during the hydrothermal treatment.

Further increasing in the synthesis time at 48 h facilitated the formation of other materials along with ZSM-5 nanocrystals. The two additional peaks in the XRD of the sample that was synthesized at 48 h relate to quartz materials that are considered as impurities. From the above study, increasing the synthesis time has both advantages and disadvantages. Long synthesis time is required to form fully crystalline materials, but excessive synthesis time will promote the formation of other undesired materials along with nanocrystalline ZSM-5.

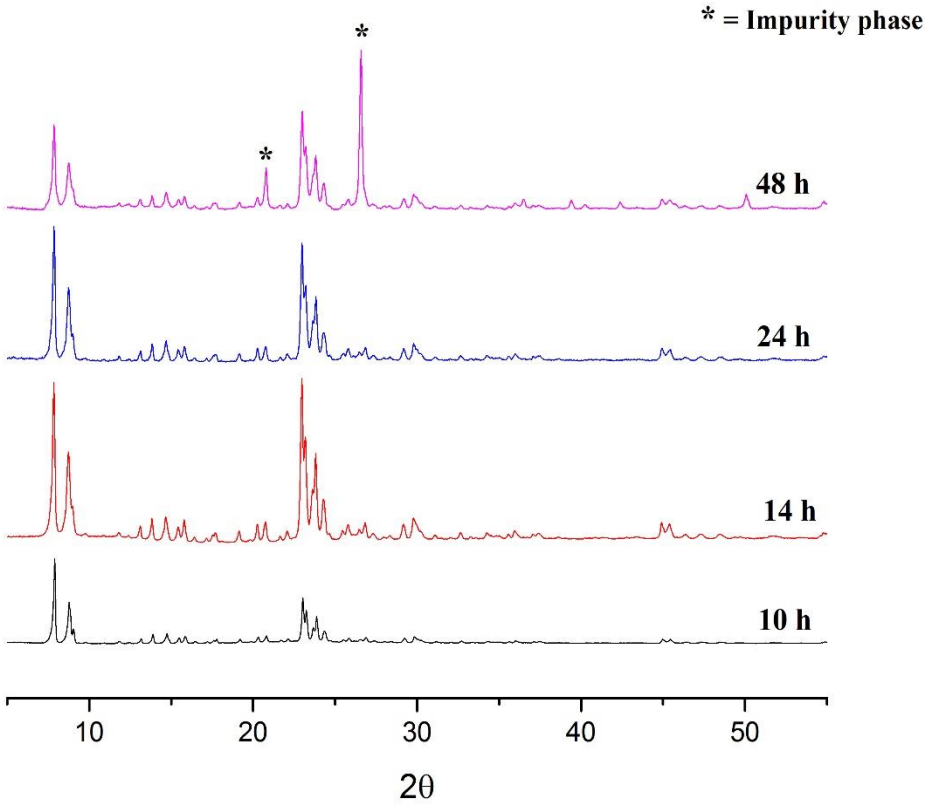


Figure 7. XRD of four samples (S4, S5, S6, and S7-ZSM-5) that were synthesized by using different synthesis time (10, 14, 24, and 48 h) at 165 °C and by using 0.35% of the 70 nm seeds.

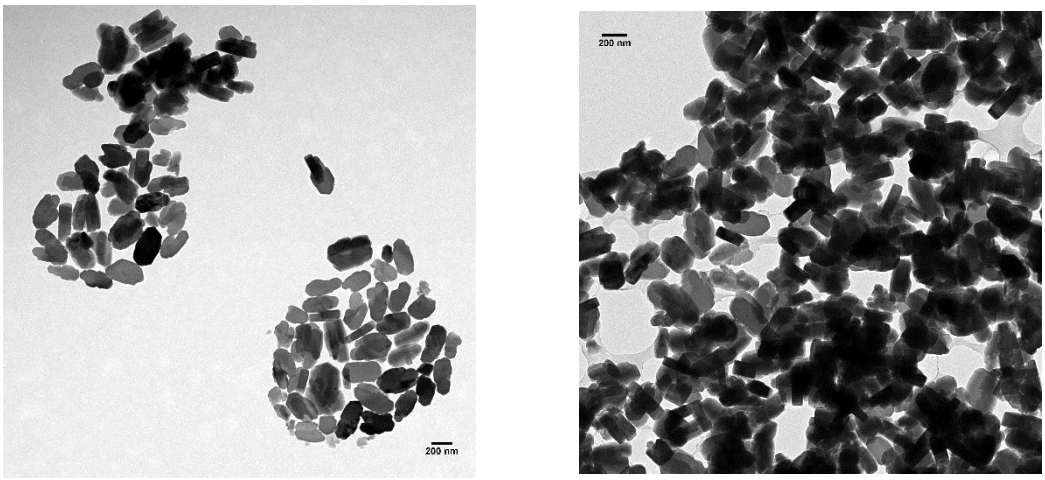


Figure 8. TEM images of the sample S5-ZSM-5 (280m^2/g) that was synthesized at 14 h (left image), and the sample S6-ZSM-5 (250 m^2/g) that was synthesized at 24 (right image) with a scale bar of 200 nm.

6.3 Effect of the Basic Environment

It was proposed that a basic environment is needed if a seed-assisted method is used to synthesize zeolite crystals.[24,26] When the seed particles are introduced to a gel mixture, the external surface of the seed particles will be gel-wrapped. Therefore, the basic environment will partially dissolve the gel-wrapped surface and expose the surface of the seed particles to be used as nucleation sites. In another study, it was found that the Na^+ cation has a strong effect in the formation of zeolite crystals in the absence of both organic templates and seeds.[34] Therefore, to study the effect of the basic environment in the seed-assisted synthesis of nanocrystalline ZSM-5, four experiments were run by using different amounts of NaOH (sample S6, S8, S9, and S10-ZSM-5). The synthesis temperature and time were kept at 165°C for 24 h, and the amount of the seeds was 0.35% with an average size of 70 nm. The study was conducted in term of Na_2O/SiO_2 ratio. The NaOH is the source of Na_2O in the mixture, so increasing the amount of NaOH will increase Na_2O/SiO_2

ratio. The collected XRD patterns of the four are represented in Figure 9. The results show that with a very low amount of NaOH (Na_2O/SiO_2 = 0.16) the crystallinity of ZSM-5 is very poor, and this is clear from the presence of amorphous materials in the area between 2θ of 10 ° – 20 °. Increasing the amount of NaOH (Na_2O/SiO_2 = 0.25) enhances the crystallinity to 73 %, but the amorphous materials are still present with the ZSM-5 crystals. In addition to the low surface area of that sample which is 150 ± 6 m^2/g, the TEM image of the sample shows the presence of amorphous materials clearly (see Figure 10A). The fully crystalline ZSM-5 materials were obtained at Na_2O/SiO_2 = 0.4 with relative crystallinity of 94 % and surface area of 250 ± 10 m^2/g. On the other hand, using a very high amount of NaOH (Na_2O/SiO_2 = 0.6) shows a negative impact by the formation of a keatite zeolite phase. Consequently, a strongly basic environment is required to improve the formation and the crystallinity of nanocrystalline ZSM-5 by enhancing the nucleation process on the surface of the seed crystals. However, using a very large amount of NaOH will result in a very strongly basic environment that facilitates not only the formation of ZSM-5 crystals but also other zeolite phase crystals.

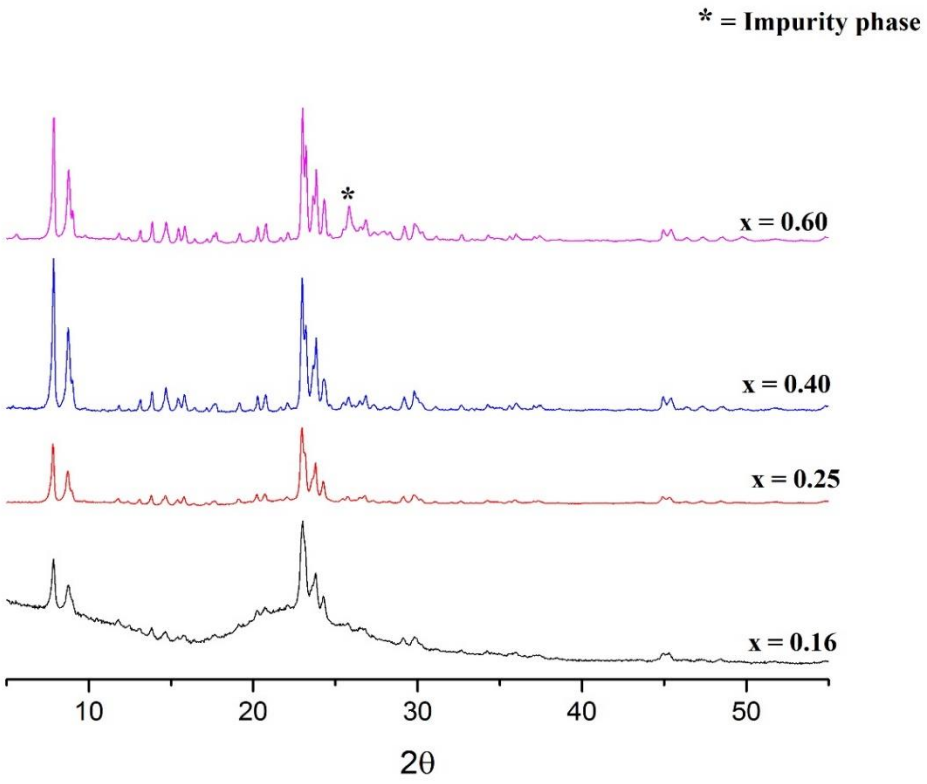


Figure 9. XRD of four samples (S8, S9, S6, and S10-ZSM-5) that were synthesized by using different amount of NaOH at 165 C for 24h and by using 0.35% of the 70 nm seeds, and x = Na_2O/SiO_2 molar ratio

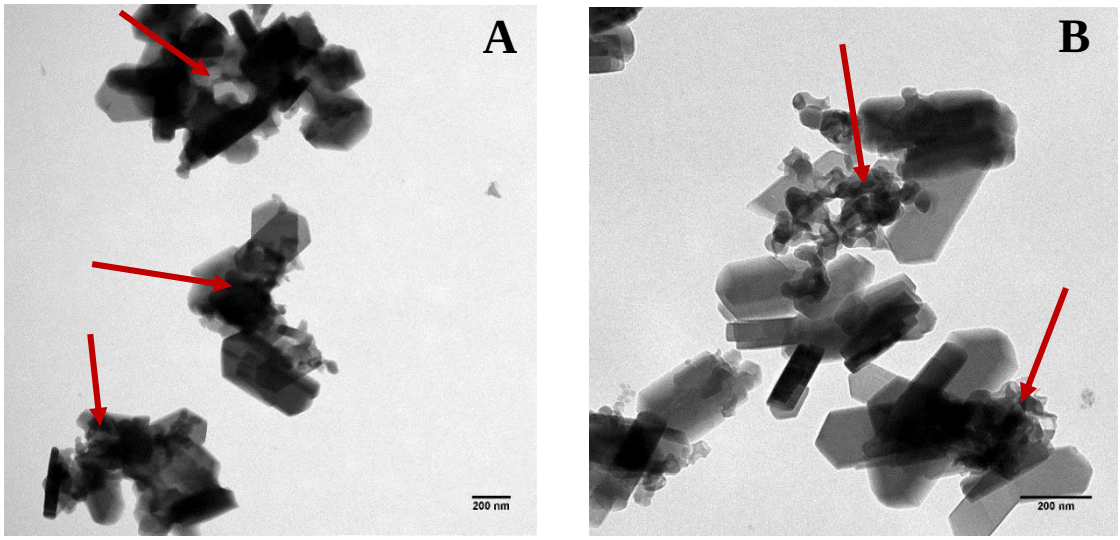


Figure 10. TEM images that show nanocrystalline ZSM-5 with amorphous materials (indicated by the arrow) for the sample S9-ZSM-5 that was synthesized with N_2O/SiO_2= 0.25 (A), and the sample S11-ZSM-5 that was synthesized by using 0.2% of the seeds (B).

6.4 Effect of Seed Amount

In order to achieve optimal crystallization of nanocrystalline ZSM-5, the effect of the seed amount was investigated by conducting two different experiments (sample S11 and S6-ZSM-5) using different amounts of seeds (0.2 % and 0.35 %). The initial gel composition was prepared with the appreciate amount of NaOH found from the above study. The temperature and time synthesis were kept at 165 °C for 24 h. From the XRD patterns (see Figure 11), calculated relative crystallinities, and TEM images, we can observe that using a small amount of seeds 0.2% will give ZSM-5 nanocrystals with some amorphous materials, and this is demonstrated by the low relative crystallinity of 80 %, low surface area of 190 ± 8 m^2/g, and by the TEM image that shows a clear presence of amorphous materials with ZSM-5 nanocrystals (see Figure 10B). On the other hand, using the appropriate amount of seeds 0.35 % shows a great enhancement of the ZSM-5 crystallinity (relative crystallinity of 94 % and surface area of 250 ± 10 m^2/g). In addition, the TEM image shows fully crystalline ZSM-5 nanocrystals (see Figure.13A). As a result, the amount of the seeds has a strong affect on the crystallinity of the ZSM-5. Using an appropriate amount of seeds tends to be beneficial by increasing the crystallinity, but the low amount will be resulting in nanocrystalline ZSM-5 with a low crystallinity.

6.5 Effect of Aging Time

Because it was found that aging the reaction mixture for a period of time before the hydrothermal treatment tends to be useful by enhancing the nucleation process in the template-free synthesis,[34] the effect of aging time in the seed-assisted method of nanocrystalline ZSM-5 was explored in this study. Two experiments (sample S13 and S2-ZSM-5) were conducted: one with aging the reaction mixture for 24 hours before the hydrothermal treatment, and another without aging. The initial gel was prepared according to the ideal amounts and conditions found from the above studies. The XRD of these two samples are represented in Figure 12. The typical peaks of nanocrystalline ZSM-5 appear in the XRD pattern when the sample was synthesized without aging the mixture. However, the XRD of the sample synthesized with aging the mixture for 24 h shows additional peaks along with the main peaks of nanocrystalline ZSM-5. The additional peaks refer to mordenite and keatite zeolite phases, which are considered as impurities. Therefore, aging the mixture for a period of time is not beneficial to be used with the typical conditions found from the above studies of the seed-assisted method to synthesize nanocrystalline ZSM-5.

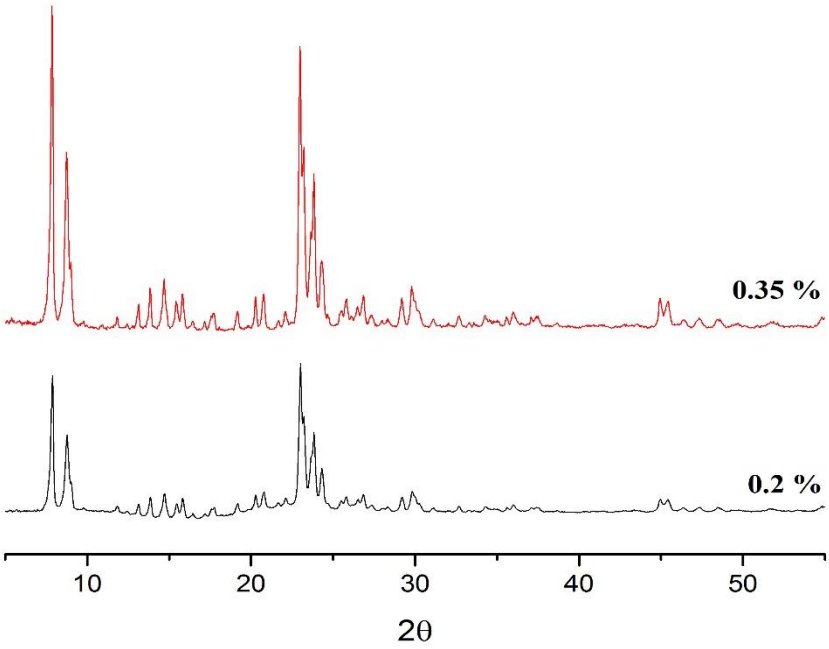


Figure 11. XRD of two samples (S11, and S6-ZSM-5) that were synthesized by using different amount of seeds (seed wt% listed)

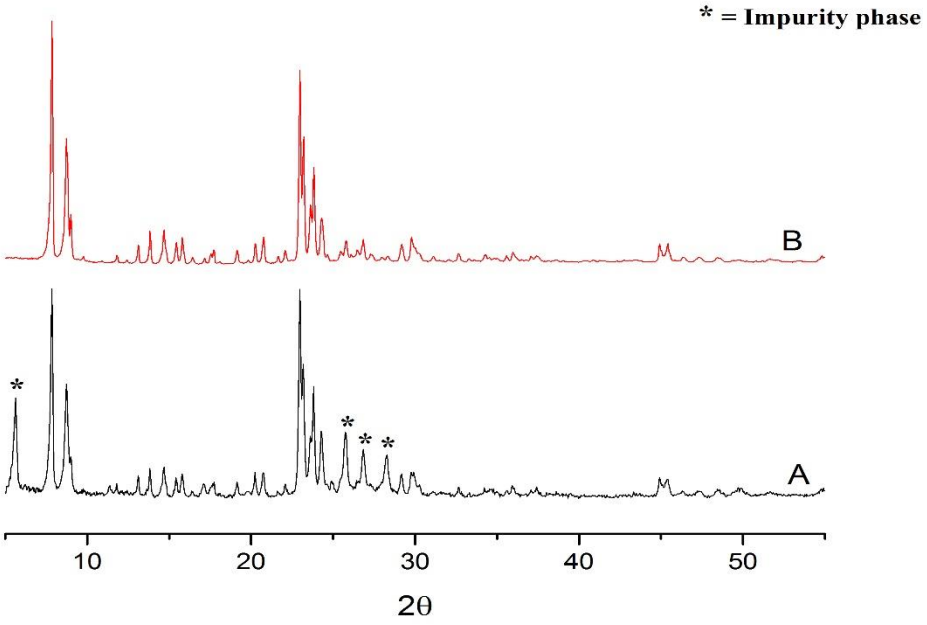


Figure 12. XRD of the two samples (S13, and S2-ZSM-5) that were synthesize with aging time of 24 h (A), and without aging (B).

6.6 Effect of Seed Particle Size

Three different seed crystal particle sizes were used to study the relationship between the size of the seeds and the size of the product. The average size of the seeds are 70 ± 2 nm, 90 ± 4 nm, and 250 ± 5 nm (sample S6, S12, and S2-ZSM-5 respectively). The typical gel composition and conditions were kept as in the previous study. The collected XRD patterns of the three samples show the main peaks of nanocrystalline ZSM-5 without any impurities (see Figure 14). The relative crystallinity is 94 %, 95%, and 92% respectively. The size of the synthesized particles was larger than the size of the seeds. The TEM images show that the 70 nm seeds resulted in particles with an average size of 280 ± 50 nm, the 90 nm seeds resulted in particles with an average size of 710 ± 70 nm, and the 250 nm seeds resulted in particles with an average size of 310 ± 50 nm (see Figure 13). The surface area of these three samples is 250 ± 10 m^2/g, 240 ± 10 m^2/g and 250 ± 10 m^2/g respectively (see Table 1). By looking at the TEM images of the seeds, we can make an observation about why the small seeds give particles with sizes bigger than that of the large seed crystals. The TEM images of both the 70 nm and 90 nm seed crystals show that these particles are forming large complex aggregates that are formed by very small particles (see Figure 13. A and B left images). On the other hand, the TEM image of the 250 nm seeds shows monodispersed isolated particles without any aggregations. These particles are relatively large enough to be stable (see Figure 13.C left image).

Therefore, the nucleation and growth process in the seed-assisted synthesis were strongly affected by the way in which the seeds are present in the mixture. In the first sample with 70 nm seeds, the TEM image of the seeds shows some discrete small particles with some large aggregates. Therefore, the nucleation and the growth of new ZSM-5

particles during the seed-assisted synthesis were promoted by both isolated and aggregated particles. However, the TEM image of 90 nm seeds shows relatively big complex aggregates with size more than 200 nm. These complex aggregates contain small particles, and the growth of new particles in the seed-assisted synthesis occurs on the surface of these aggregates. In contrast, the TEM image of 250 nm seeds shows discrete isolated particles, and the growth of new particles occur directly on the external surface of the seed particles.

From the above explanation, we can observe that there are two types of growth systems in the seed-assisted synthesis: one by using large complex aggregates of seeds, and another by using isolated seed particles. In the former one, the growth will occur on the surface of the seed particles, which are close to each other in an aggregated system, and this will lead to form a very large particles. This is what happens with using the 90 nm seeds. Because of the large aggregates in these seeds, the synthesized ZSM-5 particles are very big (710 ± 70 nm) (see Figure 13.B). As the system has low aggregated complexes with some isolated seeds, the size of the product will be relatively small as the 70 nm seeds with less aggregated particles forms particles with 280 ± 50 nm (see Figure 13.A). The good control over the size of the product shows with using the 250 nm seeds. Because these seeds are fully isolated and no aggregates are present, the growth is controlled by discrete, isolated particles rather than aggregated complexes, and this gives a good control over the size of the product (310 ± 50 nm) (see Figure 13.C). As a result, having fully isolated monodispersed particles will allow for a great control over the particle size of the product. Having a system with discrete and small particles will facilitate the nucleation and the growth of the new particles with size relatively close to the size of the seeds.

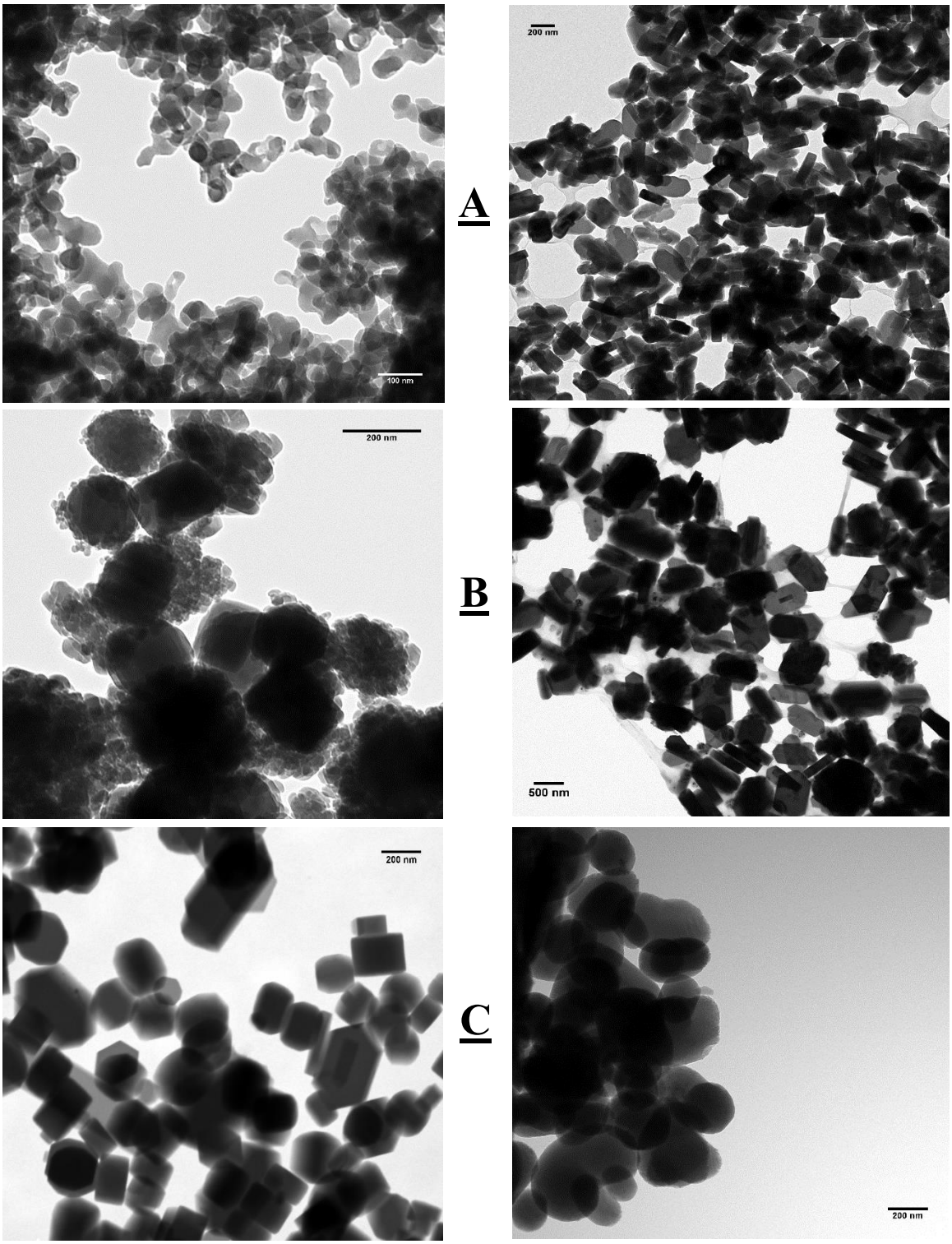


Figure 13. TEM images of the seeds (left images), and the synthesized nanocrystalline ZSM-5 by using the seeds on the left (right images). In group (A), the 70 nm seeds (left), and the sample S6-ZSM-5 (250 m^2/g) (right). In group (B), the 90 nm seeds (left), and the sample S12-ZSM-5 (240 m^2/g) (right). In group (C), the 250 nm seeds (left), and the sample S2-ZSM-5 (250 m^2/g) (right).

6.7 Effect of Using Calcined and Uncalcined Seeds

Because in the seed-assisted method we are using seeds that are synthesized by using the organic template, and because of the need to use a synthesis method without any organic templets involved in it, the effect of calcined seeds; seeds without organic templates, and uncalcined seeds; seeds with organic templates, was investigated in this study. One additional experiment was conducted with the same gel composition and conditions as in sample S6-ZSM-5 with the use of calcined 70 nm seeds. The XRD of this sample shows the main peaks of nanocrystalline ZSM-5 without any impurities (see Figure 14). The relative crystallinity of the product is 95% with surface area 270 ± 10 m^2/g, and high yield of 980 mg per 15 mL. This indicates that by using the seed-assisted method with the ideal conditions that were found in this study, the calcined seeds could be used instead of the uncalcined to synthesize pure nanocrystalline ZSM-5 zeolites with a high yield and quality.

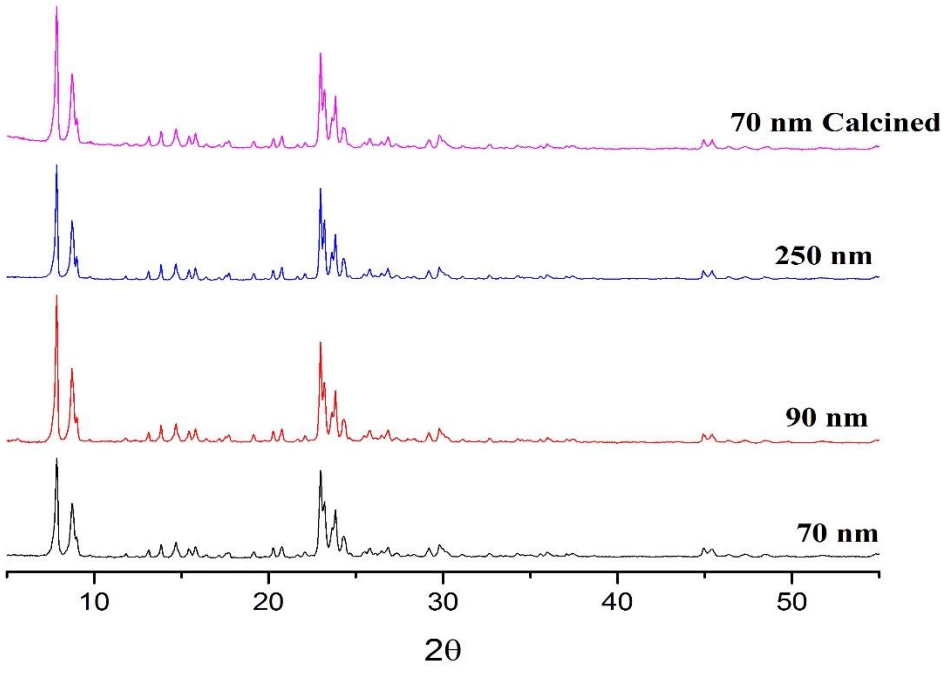


Figure 14. XRD of synthesized nanocrystalline ZSM-5 by using seeds with different sizes 70 nm, 90 nm, and 250 nm (sample S6, S12, and S2-ZSM-5 respectively), and by using the 70 nm calcined seeds.

VII. Conclusion and Future Work

7.1 Conclusion

Nanocrystalline ZSM-5 zeolites can be synthesized by using the seed assisted method with the following molar ratio $0.006SiO_2:0.0003Al_2O_3:0.0025Na_2O:0.3H_2O$. The temperature and the time of synthesis show a strong affect on the crystallinity of the synthesized nanocrystalline ZSM-5. The ideal temperature for the synthesis to obtain fully crystalline ZSM-5 nanoparticles is 165 $^{\circ}$C. The time of the synthesis between 14-24h is ideal in synthesizing nanocrsytalline ZSM-5 with high crystallinity and yield. The basic environment is necessary during the synthesis process to facilitate the nucleation step. However, using a very high strong basic environment will result in the formation of impurities along with ZSM-5 particles. Controlling the size of the synthesized particles by using different sizes of the seeds is another observation that is found in this study. Using seeds that have monodispersed, isolated particles in the synthesis system will help control the size of the synthesized nanocrystalline ZSM-5. However, the seeds that have large complex aggregates will form very large particles compared to the size of the seeds. Moreover, the amount of the seeds in the mixture plays a crucial role in controlling the crystallinity and the yield of the product. Having an appreciate amount of the seeds (0.35%) will provide enough nucleation and growth sites that form crystalline ZSM-5 particles. Using calcined seeds without any organic template in their structures to synthesize nanocrsytalline ZSM-5 in this study tends to be beneficial as there is no need for the calcination step to remove the template. Therefore, the calcined seeds can be used in this method to synthesize nanocrystalline ZSM-5 particles with a high crystallinity and yield.

7.2 Future Work

The future work of this project could be in two directions. One direction is controlling the size of the products, and another is further developing these materials for applications. In terms of controlling the size of the products, trying to have better control over the size of the products by controlling the size and the aggregation system of the seeds is the next goal in this project. From this study, we observed that the system in which the seeds are present in the mixture has a strong effect on the size of the product. This is can be explained by the presence of isolated, monodispersed particles or aggregated particles. Therefore, having a seed system with small-sized monodispersed particles would be beneficial in obtaining nanocrystalline ZSM-5 with a particle size that is close to the particle size of the seeds. Using the synthesized nanocrystalline ZSM-5 by the seed-assisted method in catalytic applications is the second direction of the future work. Therefore, the synthesized nanocrystalline ZSM-5 could be used as a solid catalyst in a biomass conversion process to study the catalytic efficiency of these materials.

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