Zeolite NaY Synthesis by using Sodium Silicate and Colloidal Silica as Silica Source

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Abstract. Zeolite NaY (FAU) has been prepared through direct hydrothermal method by using Sodium Silicate and Colloidal Silica as the silica source. Aging time was carried out at 24 hours while hydrothermal temperature was performed at 90°C for 24 hours. Detailed comparisons and characterizations were performed by using several methods onto the synthesized zeolite NaY (FAU) by using powder X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Energy dispersive X-Ray spectroscopy (EDX). The results showed that the products obtained from the starting gel were highly dependent on the type of raw material used- silica source which affects the structure of the products.

1. Introduction
Zeolites are crystalline aluminosilicates with open-framework structures and have been widely used for various applications including separations, ion exchange and catalysis. Furthermore, the existence of uniformly distributed cavities and channels in molecular dimensions endows zeolites with unique molecular recognition, discriminations and organization properties [1]. One of it is molecular sieve zeolite from Faujasite (FAU) family with large three-dimensional pore structure and being perpendicular to each other of x-y-z (111) co-ordinations with pore openings at about 0.74nm [2–5]. In general, FAU zeolites are separated into two classes which are zeolite NaX and zeolite NaY which zeolite NaY has silicon to aluminium Si/Al molar ratio above 1.5 [2,6–8]. This value of Si/Al ratio is particularly important as it will determine the hydrothermal stabilities of the zeolite NaY. Previous investigations on influential parameters of zeolites synthesis revealed that the chemical composition of the reaction mixture was one of the most crucial factors in controlling the properties of the zeolites during the synthesis process [9]. Synthesis of zeolites will follow three main stages which are: (1) Mixing of chemicals in order to obtain aluminosilicate precursor solution, (2) Aging of the precursor solution and (3) Crystallization of the precursor solution which is conducted at higher temperature [10]. Normally, zeolites are prepared hydrothermally for a certain period of times ranging from within hours to a few days. As for zeolite NaY, it is prepared from precursor solution which mainly contains the mixture of the silica source and aluminium source to form concentrated aluminosilicate solutions which contain amorphous gel [4,8,11]. During the growth process under the alkaline state with suitable aging and crystallization time, this amorphous precursor solution serves as a reservoir for the crystals to grow hence to be deposited at the surface of the gel. Hence, the source of the precursor
solution is one of the important parameters that need to be investigated extensively in order to produce zeolite NaY with desired properties.

In the current study, two different of silica sources (Sodium Silicate and Colloidal Silica solution) were used separately in preparing the precursor solution for zeolite NaY synthesis. The effect of different silica sources on the formation of zeolite NaY was investigated. The synthesized samples were characterized by using different analytical techniques including X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) with Energy dispersive X-Ray spectroscopy (EDX).

The method applied during the synthesis is based on a method reported in previous studies [12–16].

2. Experimental

2.1. Materials

All chemicals were directly used as received without any further purifications. The reactants used were Sodium Hydroxide (NaOH), Sodium Aluminate (Fischer, 53 wt% Al₂O₃; 42.5 wt% Na₂O), Sodium Silicate (Fischer, Na₂O 51 wt%; SiO₂ 45.5 wt%), Colloidal Silica (Ludox, AS-40), commercial zeolite NaY powder (0.3 μm crystal size, Si/Al = 2.5, Tosoh) and deionized water (DI).

2.2. Synthesis of Zeolite NaY by Using Sodium Silicate and Colloidal Silica

Precursor solution with a molar composition of Al₂O₃: 12.8 SiO₂: 17 Na₂O: 975 H₂O was used for the hydrothermal synthesis of zeolite NaY in this study. During this procedure, identified amount of NaOH, Sodium Aluminate, and DI water were mixed. The resultant solution was heated at 70°C for 1h until a clear solution was obtained. After cooling down to room temperature, Sodium Silicate solution (as silica source) was added drop-wise and stirred until completely dissolved. After aging for 24 hours, the mixture was transferred to a Polypropylene (PP) bottle and then kept inside a heated oven at 90 °C for 24 hours. After cooled down, the solid product was vacuum filtered and washed with DI water repeatedly in order to remove any unreacted chemicals until pH 7-8. Similar procedure was repeated by using Colloidal Silica solution as the other silica source.

Besides that, commercial zeolite NaY powder (Tosoh) was also added as seeds into several samples of the precursor solution prior to heating in an oven at 90°C for 24 hours. On the other hand, several runs of the synthesis were conducted by varying the amount of NaOH used in the precursor solution with respect to its the molar ratio (Na₂O/Al₂O₃) under similar synthesis conditions (aging time for 24 hours at room temperature and heating in over at 90 °C for 24 hours) in order to study the effect of Na⁺ ions towards formation of zeolite NaY. Table 1 shows all the samples synthesized with different synthesis conditions in the current study.
Table 1. Samples synthesized at different conditions.

| No | Sample Name | Silica Source | Seeded | Na\(_2\)O/Al\(_2\)O\(_3\) |
|----|-------------|---------------|--------|--------------------------|
| 1  | S1          | Ludox-AS-40   | No     | 17                       |
| 2  | S2          | Ludox-AS-40   | Yes    | 17                       |
| 3  | S3          | Sodium Silicate | No     | 17                       |
| 4  | S4          | Sodium Silicate | Yes    | 17                       |
| 5  | S5          | Sodium Silicate | No     | 20                       |
| 6  | S6          | Sodium Silicate | No     | 25                       |

2.3. Characterizations of the Zeolites

The synthesized samples and commercial zeolite NaY (Tosoh) were characterized by several different techniques including X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) with Energy dispersive X-Ray spectroscopy (EDX). X-ray Diffraction (XRD) was conducted by using Cu-K\(_\alpha\) radiation with 40kV and 30mA in the measuring range of 2\(\theta\): 5-50° at a scanning rate of 4 min\(^{-1}\). XRD was used to analyze the crystallinity of the samples with respect to the reference sample (commercial NaY from Tosoh). The morphology of the samples was observed through FESEM at room temperature. The images of the samples are captured by the FESEM equipment from the electrons that are ejected over the surface of the samples at an acceleration voltage of 15kV. For Energy Dispersive X-ray Spectrometer (EDX) attached to the FESEM, it was used to conduct elemental analysis of the samples. The final Si/Al ratios for each sample were obtained by taking the average of at least 3 measurements at different spots.

3. Results and discussions

The XRD peaks for each sample synthesized were compared with the XRD of commercial zeolite NaY (Tosoh). It was reported that the main diffraction peaks should appear approximately at 2\(\theta\) of 6.31°, 10.31°, 12.10°, 15.92°, 20.71°, 24.06°, and 31.95° [9]. Figure 1 shows the XRD pattern for the synthesized sample and commercial zeolite NaY (Tosoh). When Colloidal Silica solution was used as the silica source, with NaY seeds (S2 sample) or without NaY seeds (sample S1), zeolite NaY was successfully formed as the XRD pattern agreed well with the XRD pattern of the commercial zeolite NaY (Tosoh). However, different results were observed whereby zeolite NaY was successfully formed only when NaY seeds (S4 sample) was added into the precursor solution as compared to sample S3 (without the addition of NaY seeds) which displayed amorphismy, indicating failure in forming zeolite NaY by using Sodium Silicate as the silica source. These results are in agreement with those reported by previous studies which used Sodium Silicate as its silica source that require NaY seeds in the starting gel [17,18]. Possibly, due to the availability of NaY seeds which acts as nuclei hence to assist in the crystallization process of NaY zeolite as compared to the samples without addition of seeds.
Figure 1. XRD patterns of synthesized samples and commercial NaY (Tosoh).

The crystal structure of the synthesized zeolite NaY was reported to be in octahedral shape [11,19–21]. The FESEM images of the synthesized samples are shown in Figure 2. For the samples synthesized using Colloidal Silica and Sodium Silicate as silica source with the addition of NaY seeds (Tosoh), the FESEM images showed fine octahedral shape with particle sizes around 500-800nm. Meanwhile, for zeolite NaY samples synthesized with Sodium Silicate used as its silica source without the addition of NaY seed (Tosoh), only amorphous phase could be observed. For EDX results, all samples synthesized from Colloidal Silica and Sodium Silicate with the addition of NaY seed (TOSOH) displayed Si/Al molar ratio of more than 1.5 which represents zeolite NaY, which is in agreement with the value reported in the previous studies [2,6–8].
It was showed that even without the addition of NaY (Tosoh) seeds zeolite NaY were successfully synthesized by using Colloidal Silica as its silica source. This could be results from the availability of Na\(^+\) ions which are solely from NaOH that are more easily to dissociate into ions as compared to Na\(^-\) ions from Sodium Silicate which are only slightly soluble in water. High availability of Na\(^+\) ions in the colloidal solutions helps to stabilize the highly open FAU structures [22]. Furthermore, a higher amount of Na\(^+\) ions also resulted in the increase of alkalinity of the colloidal solution which permit higher solubility of aluminosilicate in order to form crystalline NaY zeolite which interrelated to the crystallization rate of the zeolite itself [2,19,23]. Apart from that, due to lower solubility of Sodium Silicate in water, less amount silicalite anions could be released into the surrounding solution in order to react with aluminate anions hence to produce aluminosilicate solids. These aluminosilicate solids which are rich in Al\(^3+\) and hydrated Na\(^+\) cations are crucial in the formation of zeolite NaY (FAU) during crystallization process [22]. An EDX analysis was performed on the solid products synthesized from Colloidal Silica and Sodium Silicate used as the silica source together with or without zeolite NaY seeds (Tosoh). Higher amount of Na element was found in the samples synthesized by using Colloidal Silica as compared the one synthesized by using Sodium Silicate used as the Silica source. This shows the importance of Na\(^+\) ions in the precursor solution during the aging process which allow on the stabilization of the highly open zeolite structures and to form zeolite NaY [22]. This also indicates that the zeolite NaY is strongly dependent on Na\(^+\) ions concentration in the synthesis mixture [11].

Table 2 showed the EDX results of the samples.

| No | Sample Name | Silica Source     | Seeded | EDX Na (wt%) | Phase          |
|----|-------------|-------------------|--------|--------------|----------------|
| 1  | S1          | Ludox AS-40       | No     | 12.36        | Zeolite NaY    |
| 2  | S2          | Ludox AS-40       | No     | 11.87        | Zeolite NaY    |
| 3  | S3          | Sodium Silicate   | No     | 9.15         | Amorphous      |
| 4  | S4          | Sodium Silicate   | Yes    | 11.72        | Zeolite NaY    |
Figure 3 shows XRD micrographs of the samples synthesized with different Na$_2$O/Al$_2$O$_3$ molar ratio in the precursor solution. It was observed that as the amount of Na$_2$O/Al$_2$O$_3$ molar ratio was not varied, no definite diffraction peaks were observed from the XRD indicating the sample was still in an amorphous phase. However, as the amount of Na$_2$O/Al$_2$O$_3$ molar ratio was increased, phase transformation started to occur from amorphous to a crystal phase. Nonetheless, an increase in Na$_2$O/Al$_2$O$_3$ molar ratio assists in the crystallization rates of the samples as well as resulted in the formation of other impurities i.e. NaP (GIS) instead of NaY (FAU) zeolite in the synthesized samples. This could be seen from the’ spacing (2θ) as well as miller indices at (301) co-ordinations which indicates the existence of zeolite NaP (GIS) zeolite in the synthesized samples i.e. sample S6[24]. This could also be the results of too high sodium concentration in the synthesis solution which favors the condensation reactions on the surface of particles hence contributes to their growth and irregular shapes as well [19]. This result is in agreement with previous studies indicating zeolite NaP (GIS) which is in more stable phase is the most competing phases with zeolite NaY (FAU) [6,25–27]. Figure 4 showed the FESEM images for each of the samples synthesized at different Na$_2$O/Al$_2$O$_3$ molar ratio whereby Zeolite NaP (GIS) could be identified by its spherical/ globular shape which is different from zeolite NaY (FAU) which is in octahedral shape [7,19,21].
4. Conclusions
By using Colloidal Silica as the silica source without NaY seed (Tosoh) in the precursor solution, zeolite NaY was successfully obtained with octahedral crystal structure as confirmed by XRD patterns and FESEM micrographs after aging time 24 hours followed by heating at 90°C for 24 hours. Higher amount Na⁺ ions are readily available when Colloidal Silica was used in the precursor solution in order to form aluminosilicates which are crucial in the formation of zeolite NaY (FAU). This was confirmed by the studies on variations of Na₂O/Al₂O₃ ratio which indicates the effects of readily available Na⁺ ions in the precursor solution which helps to stabilize the highly open zeolite NaY (FAU) structures. Thus, it could be seen by having Colloidal Silica as an alternative to Sodium Silicate as the silica source in the synthesis solution is effective in synthesizing NaY (FAU) zeolite with the octahedral shape.

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6. References
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