RESEARCH PAPER

Kinetic and Thermodynamic Studies for Zeolites Synthesis

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ABSTRACT:

Zeolites are compounds which have many applications in chemistry and industry; therefore, studies of synthesis of zeolites are of great importance. In this work, kinetic and thermodynamic study of hydrothermal crystallization for zeolite synthesis process performed at different time intervals (17, 20, 23 and 26 h) and various temperatures (70, 90, 110 and 125 °C). By time intervals we got out the rate of the zeolite synthesis reaction in this research was first order. The synthesized zeolites were similar in their crystallinity according to the Zeolites synthesis at different of the time intervals. The thermodynamic parameters indicated that the change in Gibbs free energy was negative value. The degrees of crystallinity of the synthesized zeolites decreased with increasing the hydrothermal crystallization temperature. Moreover, the change of hydrothermal crystallization time and temperature caused synthesis of different types of zeolites. The synthesized zeolite samples characterized by Infra-Red (IR), X-ray diffraction (XRD), X-ray Fluorescence (XRF) and scanning electron microscopy (SEM). The variation of chemical compositions led to differences in morphologies and crystallinity of the synthesized zeolites.

KEY WORDS: Time and temperature, Zeolite, Synthesis, Ratio, Crystallization
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1. INTRODUCTION:

Zeolites are crystalline aluminosilicate inorganic polymers with a 3-dimensional, open framework consisting of oxygen-sharing $\text{TO}_4$ tetrahedral (see fig. 1), where T is Si or Al (Barbosa et al., 2000). Zeolites can be obtained naturally or by chemical synthesis (Min). Their framework structure contains interconnected voids, cavities, cages and channels. The internal surface area of these channels can reach as much as several hundred square meters per gram of zeolite, making zeolites extremely effective ion exchangers, adsorbent and catalyst. Another unique fact about zeolites is that they are one of the few minerals found in nature with a negative charge (Brändle and Sauer, 1998).

Also, Zeolites are hydrated aluminosilicates having microporous, regular structures that occur naturally (Mallada, 2016). The removal performance and the selectivity sequence of many mixed metal ions in aqueous solution were investigated by adsorption process on pure and chamfered-edge zeolite 4A, commercial grade zeolite 4A and the residual products recycled from CFA (Hui et al., 2005). Also, removal performance of a basic dye, methylene blue (MB), in aqueous solution was investigated by adsorption process on single-phase and high-crystalline zeolite A (Wang et al., 2009).

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The flexibility of the zeolite Si-O-Si bond explains the fact that more than 200 structures have been determined. Indeed, there is little energetic difference (10-12 kJ/mol) between these remarkable porous silicates and higher density phases such as quartz (Baerlocher and Meier, 2001). On the other hand, Hydrothermal process was employed by many researchers for synthesis of different types of zeolites (Carleen, 2010). The decrease in processing temperature is desirable for energy saving and low production cost so the present study designed to investigate the effect of crystallization time and temperature on the type and the properties of synthesized zeolites (Song, 2006).

2. MATERIALS AND METHODS

2.1. Chemicals

Analytical grade reagents and deionized water was used to prepare all solutions. Sodium Hydroxide (ALPHA CHEMIKA, Mumbai – 400 002), Hydrochloric Acid 37% (RFE, BP, Ph. Eur.), Sulphuric Acid 98% (GCC), Silica-precipitated acid washed (BDH chemicals Ltd Poole England), Silver Nitrate 99.8% (R.P.NORMAPURTMAR), Sodium Carbonate 99.5% (Riedel-deHaёn), Sodium Silicate (Riedel-deHaёn) and Sodium Aluminate (Riedel-deHaёn).

2.2. Procedure

The initial dry gel is amorphous, transforming to a crystalline layered phase during the first hour of heating and then progressing to a semi-crystalline phase after heating; formation of the crystalline trigonal product was complete (Sutrisno et al., 2018). All types of zeolites with different properties were hydrothermally synthesized as in the procedure reported in the literatures (Rahman et al., 2009, Abdullah and Shareef, 2015). To study kinetics and thermodynamics, so we satisfied the effect of hydrothermal crystallization time and temperature on the synthesized zeolites at the crystallization step was performed at four different time durations (aging): 17, 20, 23 and 26 h (hours) and four different temperatures: 70, 90, 110 and 125 °C (degree centigrade).

3. RESULTS AND DISCUSSION

3.1. Kinetic Study

In kinetic study of the zeolites synthesis same as in the reported procedure (the reactant basic materials were Sodium Hydroxide, Sodium Aluminate and Glass Silica) (Abdullah and Shareef, 2015) moreover, it took in crystallization step which was performed at 90 °C and for 17, 20, 23, and 26 h (see table 1) and the results have taken after production of the zeolites which it indicates went up the amount of silica as the basic component of the zeolites with increased the time. And there was raised the amount of Sodium oxide with the time, also the Alumina content went up gradually.

Table (1): XRF pattern for zeolites synthesized at 90 °C.

| Zeolites | Na2O | Al2O3 | SiO2 | P2O5 | SO3 | CaO | MnO | Fe2O3 | Time/h |
|---------|------|-------|------|------|-----|-----|-----|-------|--------|
| 1       | 0.167| 14.622| 21.876| 0.725| 0.119| 7.473| 0.031| 0.127 | 17     |
| 2       | 0.191| 15.247| 23.253| 0.673| 0.127| 7.415| 0.03  | 0.112 | 20     |
| 3       | 0.208| 15.504| 23.323| 0.713| 0.152| 7.429| 0.028| 0.13  | 23     |
| 4       | 0.2  | 15.799| 24.321| 0.688| 0.11 | 7.408| 0.029| 0.124 | 26     |

The basic compounds and ratios of zeolite compositions are ratios of silica to alumina and sodium oxide to silica (M. Chigondo and Nharingo, 2013). Generally the effect of hydrothermal crystallization time on the ratios of SiO2/Al2O3 let to raise the silica to alumina ratio by increasing time of the crystallization step in the final step, after fluctuation in the curve before the last value. On the other hand, the ratio of Na2O/SiO2 was went down at the end of the
crystallization times, however, in start the curve raised (fig. 2 and fig. 3).

3.1.1. Rate of Hydrothermal Crystallization

The graphical method was used to determine order of zeolite synthesis reaction (Upadhyay, 2007), so the variation in concentration of the main components of synthesized zeolites with crystallization time were followed the zero, first and zero order for the kinetic model of rate of reaction (Liu and Shen, 2008) for Aluminium oxide, Silicate and Sodium oxide respectively (fig. 4, 5 and 6).

Thus, the overall rate of zeolite preparation reaction would be in the form below and it had first reaction order:

\[ \text{Rate} = k \ [\text{SiO}_2] \]  \hspace{1cm} (1)

Where \text{Rate} is the rate of zeolite synthesis, \( k \) is the rate constant and the brackets are referring to component concentration. By this way, we can say that the zeolite synthesis depend only on silica content.

3.1.2. Infra-Red (IR) Analysis

Peaks are observed in IR spectra (see fig. 7) of the synthesized zeolite samples at different times identify success in their preparation. IR spectra for the three zeolites Z2, Z3, and Z4 which are prepared at crystallization times of 20, 23 and 26 h respectively have approximately the same peak positions with different in the intensities which may be due to the different concentration of the same compound content. While there was different behavior of Z1 (prepared at crystallization time of 17h) may be attributed to short crystallization time. Whereas, all of the prepared zeolites showed nearly the same peak position in the range 800 cm\(^{-1}\) to 400 cm\(^{-1}\) for ring of the zeolite structures (Mainganye and Dakalo, 2012).
3.1.3. X-ray Diffraction (XRD) Analysis
The XRD spectra for the synthesized zeolites at different hydrothermal crystallization times were (see fig. 8) showed the crystalline region of the spectra. The variation in the number and the position of the characteristic peaks of zeolites synthesized at different time intervals caused produce different zeolites types (Choi et al., 2006). While they were similar in their crystallinity but they weren’t the same, according to literature, a highly crystalline zeolite sample must have a quite flat baseline (Muller et al., 1998). The X-ray powder diffraction instrument characterization for the prepared samples were as follows: zeolite Z1 which was prepared at crystallization time of 17 h was identified as zeolite type Na-LSX (Parise and Y.J., 1998), zeolite Z2 which was prepared at crystallization time of 20 h was identified as zeolite type Faujasite Y (Lim and Seo, 2006), zeolite Z3 which was prepared at crystallization time of 23 h was identified as zeolite X-1.25 (Lobo R. F. and M., 1998), and finally zeolite Z4 prepared at crystallization time of 26 was identified as zeolite NaY-dehydrated type (Corbin and C.P., 1997).

3.1.4. Scanning Electron Microscopy (SEM) Analysis
The SEM images were (as shown in Fig. 9) synthesized zeolites at different hydrothermal crystallization times and the images magnified to 100 μm. Figure 9a refers to the structure of Z1, prepared at time interval of 17 h, which consist of a large number of fine crystals with different sizes indicating good crystallinity. Figure 9b reveals a uniform particle size and regular shape of the sample prepared at crystallization time of 20 h. Figure 9c belongs to sample Z3 which was synthesized at 23 h crystallization time interval. It indicates the presence of larger crystals with well-defined shapes. Large crystals with different shapes and sizes were shown in figure 14d which represents the spectra of Z4, zeolite prepared at longest crystallization time (26 h). SEM spectra of the synthesized samples show that the crystal size increases with increasing the crystallization time and the samples crystal size were in the following order: Z2 < Z1 < Z3 < Z4.

3.2. Effect of Crystallization Temperature
To study the effect of crystallization temperature on the properties of the synthesized zeolites satisfied at 70, 90, 110 and 125 °C in crystallization step. Table 2 shows the chemical composition of zeolite samples prepared at different crystallization temperature. The compositions were observed in silica and alumina fluctuated with the temperatures variations.

| Zeolite | Na₂O | Al₂O₃ | SiO₂ | P₂O₅ | SO₃ | CaO | MnO | Fe₂O₃ | T/°C |
|--------|------|------|------|------|----|-----|-----|-------|------|
| 1      | 0.08 | 25.73| 19.39| 0.69 | 0.12| 7.72| 0.05| 1.51  | 70   |
| 2      | 0.18 | 14.81| 23.52| 0.62 | 0.07| 7.36| 0.02| 0.10  | 90   |
| 3      | 0.19 | 15.03| 22.93| 0.66 | 0.15| 7.34| 0.03| 0.08  | 110  |
| 4      | 0.14 | 18.45| 19.77| 0.73 | 0.11| 7.59| 0.04| 1.17  | 125  |
3.2.1. Thermodynamic Parameters

According to the equations (2, 3 and 4) (LEVINE, 1995) and table (3) at specific temperature we determined the thermodynamic parameters which is the indicate all (ΔG) change in Gibbs free energy is negative value therefore the zeolite molecules produced spontaneously, on the other hand, the values of entropy decreased from first to the final that was said us that the best value were second and third values (see table 3).

\[ \Delta G = RT \sum n_i \ln x_i \quad (2) \]
\[ \Delta G = \Delta H - T \Delta S \quad (3) \]
For mixture \( \Delta H = 0 \) (Peter Atkins, 2006) then,
\[ \Delta G = -T \Delta S \quad (4) \]

Where \( R \) is gas constant, \( T \) is temperature in kelvin degree, \( n_i \) is the number of moles of \( i \) compound, \( x_i \) is the mole fraction of \( i \) compound, \( \Delta S \) is the degree of randomness and \( \Delta H \) is the enthalpy of the zeolite mixture solution.

Table (3): Thermodynamic parameters of the zeolites.

| \( T(K) \) | \( \Delta G(KJ) \) | \( \Delta S(J.K^{-1}) \) | \( \Delta H(J.K^{-1}) \) |
|-----------|-----------------|-----------------|-----------------|
| 343       | -2.42425        | 7.067776        | 0               |
| 363       | -2.13102        | 5.870584        | 0               |
| 383       | -2.26167        | 5.905136        | 0               |
| 398       | -2.52931        | 6.355062        | 0               |

3.2.2. Infra-Red (IR) Analysis

The IR spectra of zeolite samples showed that the zeolites were correctly synthesized at crystallization temperatures of 70, 90, 110 and 125 0C (as shown in fig. 10). The good similarity between IR patterns of the synthesized zeolite products indicates that no significant effect of crystallization temperature on their structures(Shirazi et al., 2008).

3.2.3. X-Ray Diffraction Pattern (XRD)

To gain information about the effect of crystallization temperature on crystallinity of the synthesized samples used XRD pattern spectra, the experiments were done at 70, 90, 110 and 125 0C, for 23 h (see fig. 11 and 12). The results of XRD spectra (fig. 12) showed that the change in the temperature caused change in the type of zeolite sample which was identified at 70 0C of crystallization step it was zeolite Y (F., 2005) and at 90 0C of crystallization step it was zeolite X-1.25(Lobo R. F. and M., 1998) but at 110 0C of crystallization step it was Zeolite NaECR32 (dehydrated)(Chao and J.L., 1992) and at 125 0C of crystallization step it was zeolite AFX(S.T. Wilson and Kirchner, 1999, C. Baerlocher and Olson, 2007).

3.2.4. Scanning Electron Microscopy (SEM) Analysis

The morphology of four different zeolites synthesized at 70, 90, 110 and 125 0C crystallization temperature and for 23 h. Figure 13a showed that the sample prepared at 70 0C has large crystal particles with present very small amorphous region while figure 13b showed that the sample prepared at 90 0C has large amount of small crystal aggregation. However, the sample prepared at 110 0C (figure 13c) crystals with different crystal shapes aggregation forming smooth surface. Finally the sample prepared at
125 °C showed large crystals with different surface shapes.

Figure (13): SEM micrographs of Zeolites synthesized at a) 70°C; b) 90°C; c) 110°C; d) 125°C.

4. CONCLUSIONS

Zeolites are basic compounds in many applications especially using as catalyst. So, we felt that kinetic and thermodynamic studies in synthesis of zeolites are great. The kinetic study of zeolite synthesis at 17, 20, 23, and 26 h of hydrothermal crystallization time revealed overall the rate of hydrothermal crystallization process is first order reaction, Rate = k [SiO₂]. While, different types of zeolites with different morphologies were synthesized due to change in hydrothermal crystallization time and temperature. The temperature changing caused increasing in sodium oxide content of the synthesized zeolites. While it was caused irregular change in silica and alumina contents in the samples. Thermodynamic parameters show that the zeolites produced spontaneously. The degrees of crystallinity of the synthesized zeolites decreased with increasing the hydrothermal crystallization temperature. The crystallization time for Zeolite synthesis have higher effect than crystallization temperature.

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