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Controlling Yield of NaY Zeolite Synthesis by Hydrothermal Method

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Abstract

NaY Zeolite was hydrothermally synthesized by seeding crystals into gel mixture without the presence of organic templates, structure-directing agent, and additives. An alternative condition for the production of NaY Zeolite was developed by modified the pH in gel formation. The effect of pH and crystallization time in yield NaY Zeolite crystal was investigated with reducing the pH value. The as-synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray Fluorescence (XRF), Brunauer-Emmett-Teller (BET), and Fourier-Transformation Infrared (FT-IR) spectroscopy and Raman spectroscopy. As results, we verify that NaY Zeolite obtained from hydrothermal condition, present a good degree of crystallinity and then can be suitable for using in adsorption and catalysis experiments.

Keywords: Catalyst; Characterization; Hydrothermal method; Molecular sieve; NaY Zeolite synthesis.

1. Introduction

Nowadays, zeolites as well as the other molecular sieves find several application units a diversity of areas. In particular, zeolites are hydrated, crystalline aluminosilicates constructed from TO_4 tetrahedra ($T=Al, Si$) where each apical oxygen atom is shared with an adjacent tetrahedron. Thus, the ratio of O/T is always equal to 2. Usually, zeolites are synthesized under hydrothermal condition in a period from a many hours to few days depending on the nature of zeolite, mixture composition and synthesis temperature [1-4].

Zeolite Y is a highly versatile molecular sieve from the faujasite family of zeolites whose 7.4 Å, three-dimensional pore structure and solid acidity make it useful as a catalyst, ion exchanger, adsorbent, and others. Zeolite Y is commonly prepared with high aluminum

content ($1.5 < nSi/nAl < 2.8$), but in most cases it is employed in a silicon-enriched form. Therefore, one major goal is to provide a direct synthesis of zeolite Y with a modification nSi/nAl- ratio, in adsorption of benzene in liquid phase (alkenes and aromatics) by zeolite Y, best nSi/nAl- ratio is 2.43, because cation site in zeolite Y interacted goodly by benzene molecule [5-7]. In zeolite Y, reduced in defect and selected nSi/nAl=2.43, cations located at different sites would be expected to affect adsorption properties in different ways [6-9]. In hydrothermal method, balancing the pH in gel mixture can reduce the amorphous phase in zeolite crystal [10-11].

In this work, the preparation of Y zeolite with nSi/nAl=2.43 was investigated under hydrothermal condition and successfully.

developed a pH synthesis for best mixing in gel formation. Also, the structure, crystallinity, surface area and Si/Al ratio of produced zeolites were characterized by XRD, FT-IR, SEM, BET and XRF.

2. Experimental

NaY Zeolite was synthesized according to the procedure was reported by using the gel composition in terms of oxides: 4.62 Na₂O; 10.0 SiO₂; Al₂O₃; 180 H₂O. The gel composition was: 10.67 Na₂O; 10.0 SiO₂; Al₂O₃; 180 H₂O. NaOH (4.07 g; Merck, 99%) was dissolved in 18.9 g of demineralized water. To the above solution, sodium aluminate (2.05 g; Carlo Erba, 54% Al₂O₃, 49.5% Na₂O and 0.5% H₂O) was added and the solution was stirred for 10 min. To the above gel, 23.84 g of sodium silicate (27.35% SiO₂, 8.3 Na₂O and 64.35% H₂O) solution was added and stirred for 20 min then this gel was transferred to a polypropylene bottle with 50 mL capacity and capped. The gel was kept at room temperature for 24hr.

The gel composition for the zeolite synthesis was: 4.3 Na₂O; 10.0 SiO₂; Al₂O₃; 180 H₂O. Four mixture were made four mixtures by NaOH (sample a=0.3, b=0.23, c=0.15 and d=0.1 g) to research the pH effect on gel formation. NaOH (sample a, b, c, d) was dissolved in 124.38 g of demineralized water. To this solution, 21.41 g of sodium aluminate was added and stirred until it dissolved. To this gel, 249.1 g sodium silicate solution was added and stirred vigorously for 30 min (1800 rpm with 2.5 inch diameter, 4 paddle radial mixers). Next, 27.5 g of seed gel was added slowly under rapid stirring. The final gel transferred to a polypropylene lined stainless steel autoclave (Fig. 1). The gel was kept at room temperature for 24h, and then heated at 100 °C for two times (7 and 7.5 hr) for all samples. Details are shown in Table 1. The product was washed with distilled water and dried at 383 K for 5 hr.

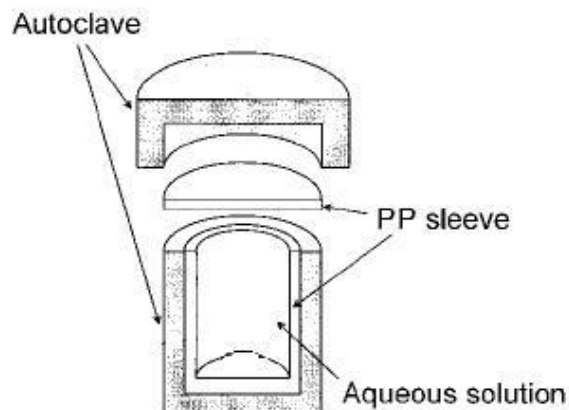


Fig. 1. Shape of autoclave reactor

Table 1. Synthesis condition for batches with reducing pH and increasing crystallization time

Batch	pH (NaOH)	Crystallization time	G F*
a	13.25	7 hr	Ok
b#1	12.84	7 hr	Ok
b#2	12.84	7 hr and 30 min	Ok
c	12.68	7 hr and 30 min	Ok
d	12.47	////	No

*G F = gel formation

Then ground into a powder form for powder XRD, FT-IR, XRF, BET, and SEM. Powder XRD (Philips X'pert diffractometer using CuK α radiation) was applied to determine the sample crystallinity. Also, FT-IR (Unicam Mattson 1000) was used to analyze sample structures.

XRF analyses were used to determine the chemical formula of the NaY Zeolite. A Philips PW 2404, XRF was used to analyze samples for Al₂O₃, SiO₂, Na₂O, and H₂O by X-ray. The particle size and its distributions were measured by scanning electron microscopy (SEM).

Nitrogen adsorption–desorption measurements were carried out at -196 °C on a micromeritics SORPTOMATIC 1990 Series and PASCAL 140 and 240 instruments to determine the Brunauer–Emmett–Teller (BET) surface area and to estimate the mesopore size distribution using the Barrett–Joyner–Halenda (BJH) calculation procedure. Before each

measurement, samples were evacuated overnight at 100 °C and <1 μm Hg. Higher temperatures were not used so that occluded template in the zeolite structure would not decompose or volatilize. The total pore volume, V_{total} , was taken from the desorption branch of the isotherm at $P_i/P_o=0.995$ assuming complete pore saturation. The volume of the micropores, V_{micro} , was determined by the t-plot method. The volume of the mesopores, V_{meso} , was estimated from the equation:

$$V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$$

3. Resulte and discussion

3.1. Powder X-ray diffraction and FT-IR spectroscopy

The effect of pH in gel formation and crystallization time was investigated.

The weight for NaOH was varied independently in order to determine the effect of the weight NaOH on crystallinity. In sample d, pH was low and unformed the feed gel in condition, thus suitable pH is higher 12.5. The

Fig. 2 presented the XRD patterns of batches a, b#1, b#2, c were taken over time and investigated the effect of pH and time on crystallization. Crystalline material emerges in batch b#1 near 7 hr of crystallization time at 100 °C, and its crystallinity increases with increasing crystallization time (batch b#2), and increases impurity in the product too.

The XRD pattern of batch c possess identical peak position and good crystallinity, low pH let better mixing in gel formation and reduce amorphous phase in the same crystallization time with higher pH (batch b#2).

The FT-IR spectra for washed samples from batches a, b#1, b#2, c is shown in Fig. 3. The position, height, and width of each peak are nearly identical for the four samples. The peak at 460 cm^{-1} is signed to the structure insensitive internal TO_4 (T=Si or Al) tetrahedral bending peak of zeolite Y. The peak at 565 cm^{-1} is attributed to the double ring external linkage peak assigned to zeolite Y in literature.

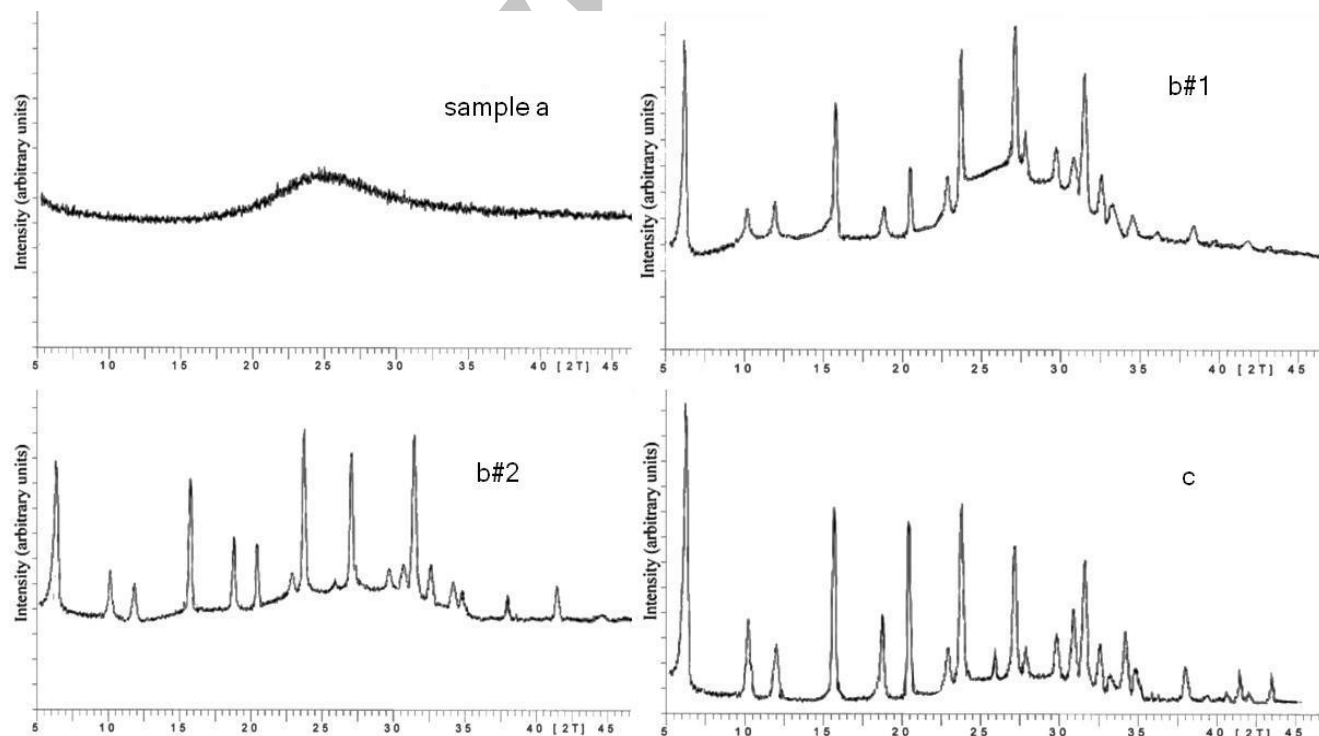


Fig. 2. XRD patterns of sample a, b#1, b#2, c

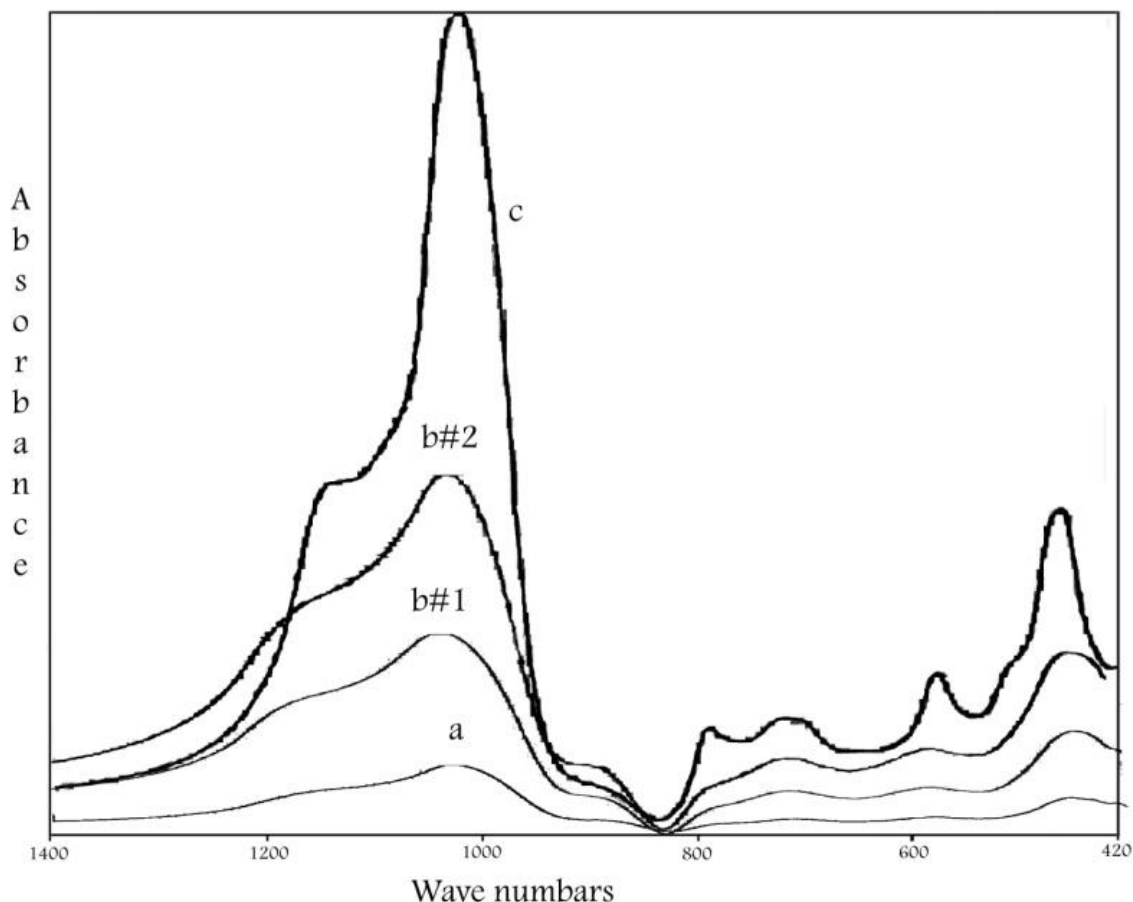


Fig. 3. FT-IR of as-synthesized NaY zeolite for four samples

The peaks at 685 and 775 cm^{-1} are assigned to external linkage symmetrical stretching and internal tetrahedral symmetrical stretching, respectively. The peaks at 1010 and 1080 cm^{-1} are assigned to internal tetrahedral asymmetrical stretching and external linkage asymmetrical stretching, respectively.

3.2. SEM and XRF for sample c

In Fig. 4, the SEM images reveal a uniform particle size of the sample with a regular shape. SEM results for sample c indicated a narrow distribution of particle size, with average crystal size of $<1 \mu\text{m}$.

The structural formulae of sample c were determined using XRF analyses on SiO_2 , Al_2O_3 , Na_2O and H_2O . This method was used to determine the Si/Al ratio to be 2.43. The resulting SiO_2 , Al_2O_3 , Na_2O and H_2O contents

and unit cell composition for zeolite Y from batch c are shown in Table 2.

Table 2. NaY Zeolite chemical content based on XRF analyses

Batch	Sample c
Al_2O_3 wt%	16.568
SiO_2 wt%	47.48
Na_2O wt%	10.098
H_2O wt%	25.854
Unit cell formula (mol)	$\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384} \cdot 180\text{H}_2\text{O}$
Si/Al	2.43

3.3. Brunauer–Emmett–Teller (BET)

The N_2 adsorption-desorption isotherm for as-synthesized sample c is shown in Fig. 5. The initial adsorption step at low relative pressure indicates complete filling of the micropores even though there has been no template removal attempted on the sample.

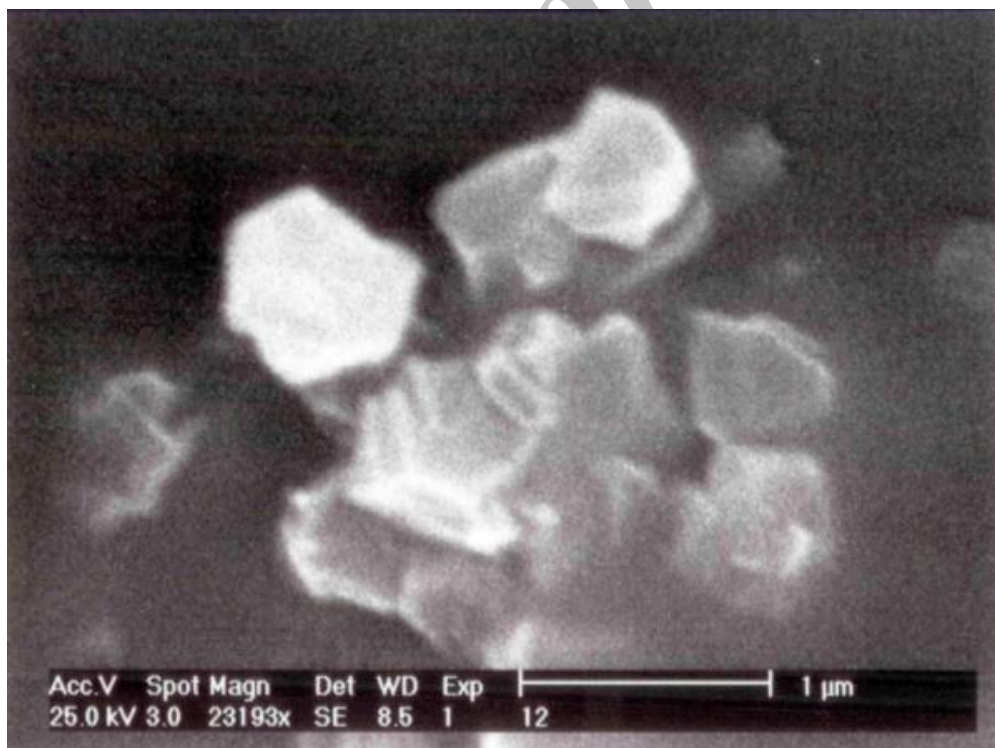
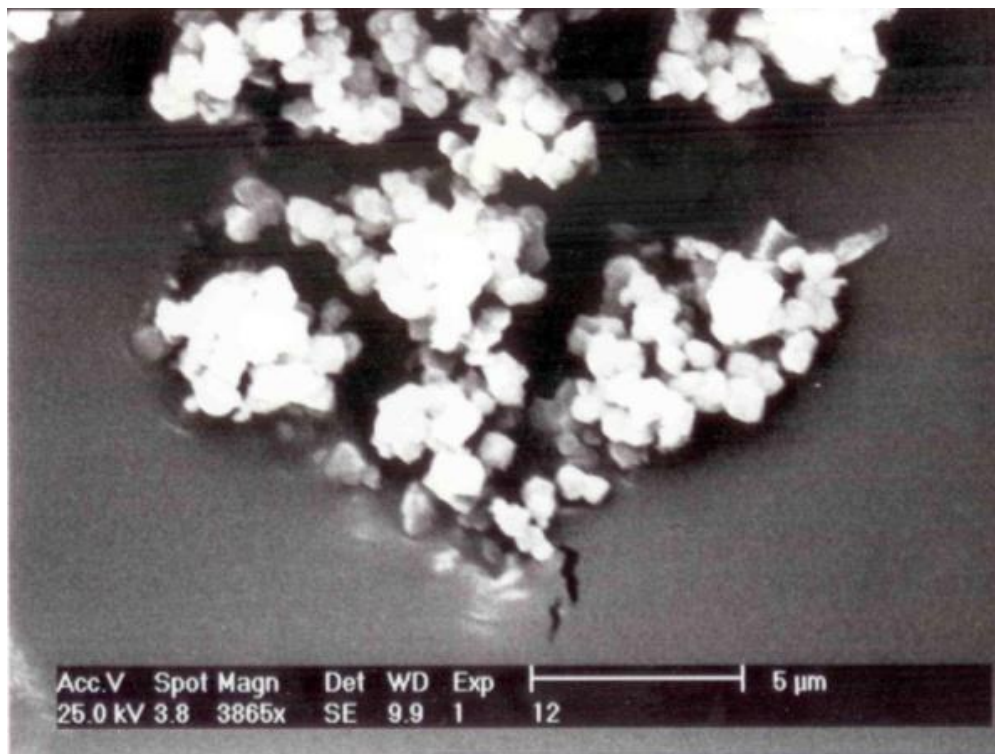


Fig. 4. SEM images of NaY Zeolite synthesized in batch c

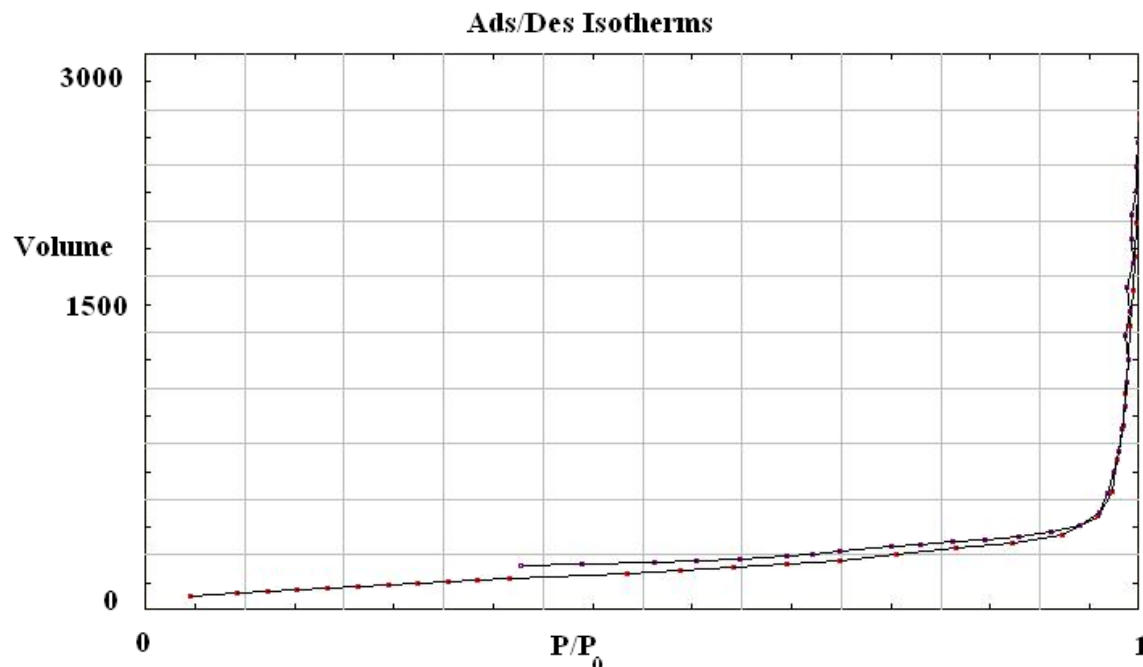


Fig. 5. N₂ adsorption-desorption isotherm for as-synthesized batch c NaY Zeolite.

The as-synthesized NaY Zeolite from batch c exhibited a BET surface area as high as 464 m²/g. The micropore and mesopore volume were 0.08 cm³/g and 0.17 cm³/g which were calculated by the t-plot method.

4. Conclusion

The results showed that the crystallization time reduced with reducing the pH in gel formation. The Variation of pH value in the synthesis mixture gives excellent control over the final product crystallinity and reduced amorphous phase. The crystallinity of NaY zeolite in batch c obtained is highest which was obtained from XRD and FT-IR tests.

The structural formulates and Si/Al ratio, 2.43, found using the XRF analysis. The NaY Zeolite synthesized has a uniform distribution of particle size that SEM image shows. The as synthesized NaY zeolite shows the high N₂ adsorption, the BET surface area and

micropore volume are 464 m²/g and 0.08 cm³/g, respectively.

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