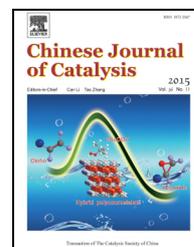


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Article

Synthesis and characterization of hierarchical nanoporous HY zeolites from acid-activated kaolin

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ABSTRACT

Hierarchical nanoporous HY zeolites were synthesized from acid-activated kaolin. The hierarchical factor (HF) was maximized by varying the aging and crystallization time. This was achieved by maximizing the external surface area without greatly reducing the micropore volume. The resulting products were characterized using X-ray diffraction (XRD), X-ray fluorescence, N₂ adsorption, and NH₃ temperature-programmed desorption. The nanoporous HY zeolite with the highest HF was obtained by aging for 48 h and a crystallization time of 24 h. The acidity and crystallinity varied depending on the operating parameters. Incorporation of an appropriate amount of NaCl was also vital in maximizing the HF, crystallinity, and acidity. The sample crystallinities were determined by comparing their XRD peak intensities with those of a conventional Y zeolite. The results show that optimizing this process could lead to a widely acceptable commercial route for HY zeolite production.

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1. Introduction

Faujasitic zeolites have gained immense popularity within the research community and commercially. This is because they have a uniform pore size, high specific surface area (SSA), and thermal stability [1]. They also have tunable pores and acidities, and are therefore useful in various petrochemical processes [2]. However, their average pore size is low, which limits their use in processes that involve bulky molecules. Such processes include organic waste treatment, and heavy crude oil and bio-oil upgrading. This is because of their mass transfer hurdle in bulky chemical reactions [3]. Several researchers have reported strategies for overcoming this transport limitation for bulky molecules. These include dealumination, desilication, synthesis of mesoporous zeolites and microporous zeolites, and use of structure-directing agents [4]. The use of commercially available dual-pore materials obtained from crystal-

line composite materials and crystalline physical mixtures has also been investigated [5,6].

However, these strategies do not give satisfactory results in terms of acidity, and structural, thermal, and hydrothermal stability [7]. Recently, one of the most potent strategies has been the synthesis of nanocrystalline materials with more than one porosity level, termed hierarchical nanoporous materials. These materials synergistically combine the properties of mesoporous and microporous zeolites [8,9]. Hierarchical nanoporous materials have high thermal and hydrothermal stability and pore channels with a bimodal pore system (micro- and mesopores) [7,10]. The connection of microporous and mesoporous channels in a highly ordered manner enables the microporous channels to reside in the matrix. This results in shorter diffusion paths for reactant molecules [11].

Several researchers have worked on the synthesis of these bimodal materials [7,12,13]. Tan et al. [7] investigated the syn-

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thesis of MY/kaolin composites with hierarchical mesoporous structure by overgrowth of mesoporous Y zeolites on kaolin. The synthesized MY/kaolin composites have short diffusion paths, high hydrothermal stability, and moderate acidities. However, they have low hierarchical factors (HFs), and the starting materials for the synthesis are expensive. It is therefore imperative to investigate the possibility of synthesizing hierarchical nanoporous zeolites from cheaper starting materials.

Kaolin clay mineral catalysts have been used in industrial application since the early 1930s. Significant progress in several industries such as the petrochemical industry, especially catalytic refining and bulk chemistry, became possible by using kaolinite as a precursor in active catalyst synthesis. This is because of the kaolin structure and pore size, which are suitable for the conversion of bulky molecules [14]. These factors explain the renewed interest in clay aluminosilicates for zeolite synthesis. However, kaolinites resist acid attack during activation because of their high octahedral alumina contents. Calcination at temperatures between 550 and 950 °C decreases this resistance by transforming the clay into metakaolin. However, this transformation deforms the crystalline structure of the clay. Liu et al. [15] investigated synthesis of NaY zeolites from coal-based kaolin. They reported that the optimum crystallization temperature is 107 °C; this gives a higher SSA and crystallinity.

In this work, we investigated the hydrothermal synthesis of hierarchical nanoporous HY zeolites from acid-activated metakaolin. The effects of aging, crystallization time, and NaCl incorporation on the crystallinity and HF of the synthesized HY zeolites were systematically investigated.

2. Experimental

2.1. Materials and catalyst preparation

Kaolin, NaOH, and H₂SO₄ (95%–98% pure) were obtained from R&M Chemicals Sdn. Bhd., Malaysia. The reagents were used without further purification.

The HY zeolite precursor was obtained by thermal activation at 850 °C for 2 h, followed by activation with H₂SO₄ (4 mol/L) at 90 °C for 3 h to produce amorphous aluminosilicate. After drying and calcination at 550 °C for 2 h, the precursor was added to an aqueous NaOH solution (14%) at a solute/solution ratio of 1:9. The solution was aged at room temperature for 24 to 72 h and then crystallized at 100 °C for 16–24 h. The resulting mixture was washed with distilled water and filtered, using a vacuum pump, until the pH was 9–10. The sample was dried at 110 °C overnight and then soaked with saturated NaCl solution to its equilibrium water content [16,17]. The sample was placed in a fume cupboard for removal of excess water and dried. The sample was transformed into the hydronium form in ammonium nitrate solution (0.2 mol/L) for 24 h. The resulting solution was filtered; the residue was dried at 110 °C overnight and then calcined at 550 °C for 2 h. The obtained samples are denoted by HY-*x*-*y*, where *x* represents the aging period (d), and *y* represents the crystallization time (h); for example, the

sample aged for 1 d and crystallized for 16 h is denoted by HY-1-16, and the sample without NaCl is denoted by HY-1-16_{ns}.

2.2. Characterization

The silica and alumina contents of the synthesized HY zeolites were determined using X-ray fluorescence. X-ray diffraction (XRD; Philip X'pert X-ray diffractometer) was performed using nickel-filtered Cu K_α radiation ($\lambda = 0.1544$ nm) in the 2θ range from 5.018° to 69.966°, with a step size of 0.026°. The (511), (440), (533), and (642) reflections were used to determine the average crystal size and relative crystallinities of the samples [18]. The crystallite sizes were calculated using PANalytical X'Pert HighScore Plus v.4.0 software [19]. We compared the crystallinities of the samples with that of a conventional Y zeolite to obtain the relative crystallinities (RC):

$$\text{RC (\%)} = \frac{\text{Sum of sample characteristic peak intensities}}{\text{Sum of reference characteristic peak intensities}} \times 100 \quad (1)$$

N₂ adsorption/desorption analysis was performed using a surface area and porosity analyzer (Micromeritics ASAP 2020) at -196 °C.

We used a Chemisorp 2720 instrument to perform NH₃ temperature-programmed desorption (NH₃-TPD) analysis. The instrument consisted of a TPx quartz sample tube microreactor installed in a vertical furnace. The desorption signal was detected using an online thermal conductivity detector (TCD). The sample (about 0.2 g) was placed in the microreactor and supported with quartz wool. Sample purging was performed using He flow (20 mL/min) at 550 °C for 2 h. The physisorbed NH₃ was then flushed out with the flow (20 mL/min) at 110 °C for 1 h. NH₃-TPD was performed from 70 to 500 °C in He flow (20 mL/min) at 10 °C/min, with continuous monitoring of desorbed NH₃ by the TCD.

2.3. Hierarchical factor

The HF is used to categorize the degree of structural order of a porous material; it estimates the degree to which the formation of fewer mesopores decreases micropore formation in a synthesized zeolite sample [20–23].

Zheng et al. [20] proposed a model for classification of hierarchical mesoporous zeolites based on conventional N₂ adsorption/desorption analysis. They defined HF using the ratio of the micropore volume to the mesopore volume ($V_{\text{micro}}/V_{\text{meso}}$) and relative mesopore SSA ($S_{\text{meso}}/S_{\text{BET}}$; S_{BET} is the Brunauer-Emmett-Teller surface area) of the weighed sample:

$$\text{HF} = \frac{V_{\text{micro}} \times S_{\text{meso}}}{V_{\text{meso}} \times S_{\text{BET}}} \quad (2)$$

3. Results and discussion

3.1. Characterization

Table 1 shows the silica and alumina compositions and Si/Al molar ratios of the HY zeolites produced from acid-activated metakaolin, and Fig. 1 shows the XRD patterns of the synthe-

Table 1

Silica and alumina contents of the samples.

Sample	Si (wt%)	Al (wt%)	$n(\text{Si})/n(\text{Al})$
HY-1-16	44.49	25.17	1.57
HY-1-16_ns	43.74	27.60	1.39
HY-2-16	45.46	25.84	1.55
HY-2-24	47.00	25.70	1.61
HY-3-16	42.69	26.99	1.39

sized catalysts with standard XRD peak positions. The results show a slight decrease in the Si/Al molar ratio as the aging time increases from 24 to 48 h, but a rapid decrease in increasing aging to 72 h. As the crystallization time increases from 16 to 24 h, the Si/Al molar ratio increases from 1.55 to 1.61. The XRD patterns of the samples show purely Y zeolite characteristic peaks (from (511), (440), (533), and (642)) without the presence of 4A, P, and MOR zeolite peaks. The results show that all the samples have the characteristic peaks of Y zeolites, but with lower intensity. The sample HY-3-16 has the lowest-intensity peaks.

The intensities of the characteristic peaks from the (511), (440), and (533) reflections are lower than those of the other peaks, and are nearly invisible in Fig. 1; more detail is shown in Fig. 2. This is because excess aging impedes crystallization. Table 2 lists the relative crystallinities and average crystal sizes of the catalysts, calculated using PANalytical X'Pert HighScore software from the reflection peaks (511), (440), (533), and (642). The optimum aging time is 2 d, and the optimum crystallization time is 16 h. This shows that excess aging and crystallization are detrimental to the HY zeolite crystallinity. The crystallinity of the sample without NaCl incorporation is lower than that of the sample with incorporated NaCl. The average crystal sizes of all the samples confirm that they are nanoporous.

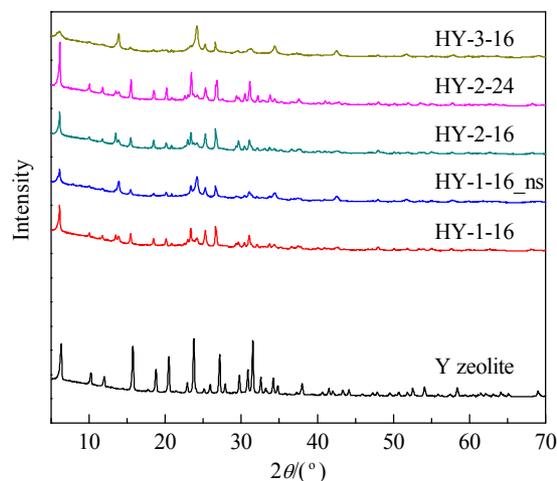
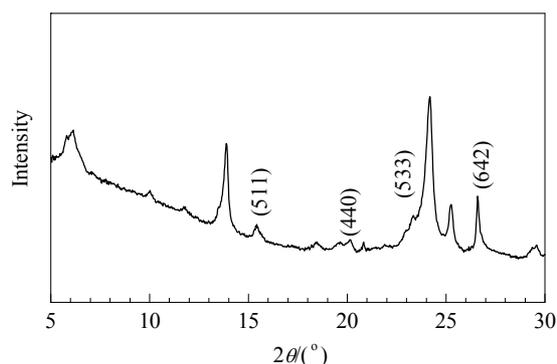
These results confirm that the synthesized HY zeolites have hierarchical nanoporosity.

Table 3 shows the results of the surface area and porosity analysis, performed using N_2 adsorption/desorption isotherms at a relative pressure (p/p_0) of 0.98. The BET model was used to obtain the SSAs and pore size distributions from the isotherms. The table also includes the computed HF values. Fig. 3 shows the N_2 adsorption/desorption isotherms of the HY zeolite samples. At $p/p_0 = 0.7$, the samples show substantial increases in adsorption, and the desorption curves show hysteresis loops.

Table 3

Textural parameters of synthesized HY zeolites.

Sample	S_{BET}^a (m^2/g)	S_{micro}^a (m^2/g)	S_{meso}^a (m^2/g)	V_{total}^a (cm^3/g)	V_{micro}^a (cm^3/g)	D_{meso}^b nm	HF	Acid site (mmol/g)
HY-1-16	248.73	222.54	26.19	0.18	0.10	4.87	0.147	1.43
HY-1-16_ns	181.67	147.86	38.80	0.19	0.07	4.12	0.108	0.94
HY-2-16	199.98	175.28	24.69	0.15	0.08	3.05	0.142	1.26
HY-2-24	316.50	287.62	28.88	0.19	0.13	2.42	0.214	2.06
HY-3-16	167.98	126.63	41.36	0.20	0.06	4.87	0.099	0.83

^a Calculated from the t -plot curve.^b BET method.**Fig. 1.** XRD patterns of synthesized HY zeolites.**Fig. 2.** XRD pattern of synthesized HY-3-16 zeolite.**Table 2**

Relative crystallinities and average crystal size of synthesized nanoporous HY zeolites, calculated from XRD data.

Sample	Total relative intensity	Relative crystallinity ^a	Average crystal size (nm)
Y zeolite	288.90	—	—
HY-1-16	181.24	62.73	74.72
HY-1-16_ns	143.75	49.76	70.29
HY-2-16	199.66	69.11	90.60
HY-2-24	147.08	50.91	82.58
HY-3-16	76.29	26.41	68.57

^a Computed using the relative intensity of the samples relative to the relative intensity of conventional Y zeolite.^b Computed using the peak area of the samples relative to the peak area of conventional Y zeolite.

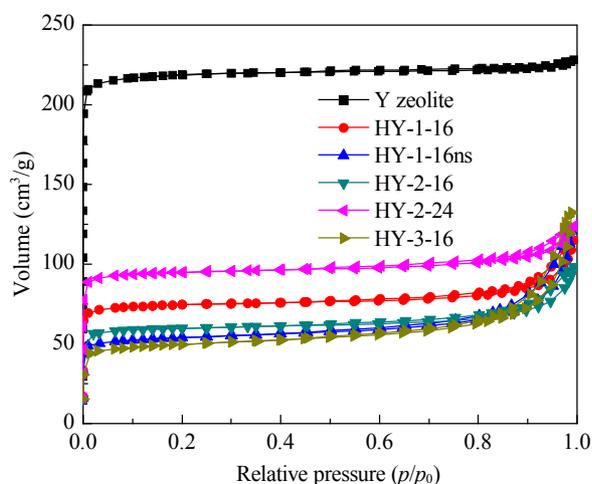


Fig. 3. N₂ adsorption/desorption isotherms of HY zeolite samples.

Fig. 4 shows the NH₃-TPD curves for the synthesized HY zeolite samples. These were used to determine the numbers and strengths of the acidic sites. The samples show a well-resolved symmetric peak at about 180 °C and a shoulder at about 300 °C. This shows that the HY zeolite samples have high numbers of mildly acidic sites. These sites can suppress catalyst deactivation in catalytic cracking, as reported by Konno et al. [24,25]. Mesoporosity can improve the properties of zeolites by preventing secondary reactions by decreasing the diffusion path length; this aids selectivity. Table 3 shows the total numbers of acidic sites, determined from the TPD peak areas of the samples. The results show that as aging increases from 1 to 3 d, the number of acidic sites decreases from 1.43 to 0.83 mmol/g after crystallization for 16 h. However, an increase in the crystallization time from 16 to 24 h increases the number of acidic sites from 1.26 to 2.06 mmol/g. Incorporation of NaCl also improves the acidity.

3.2. Effect of aging period, crystallization time, and NaCl incorporation on formation of HY zeolites

The effect of aging is important in zeolite synthesis. Tables 2

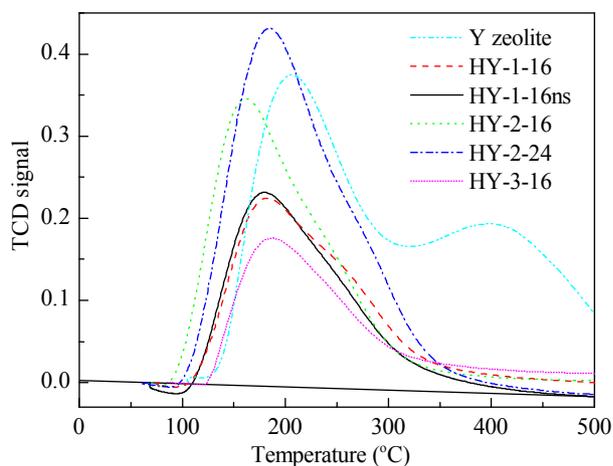


Fig. 4. NH₃-TPD curves for synthesized nanoporous HY zeolites.

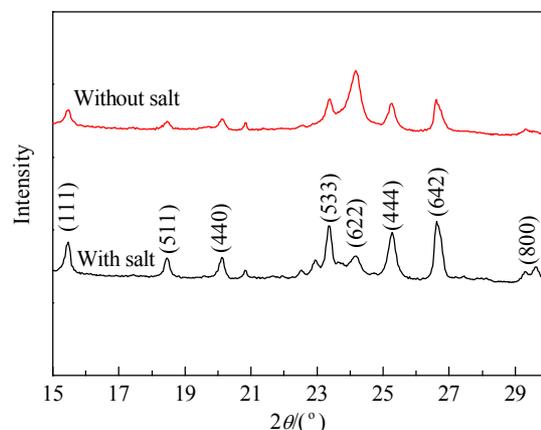


Fig. 5. XRD patterns for samples with and without NaCl, aged for 1 d and crystallized for 16 h.

and 3 show the effects of aging on the crystallinity, SSA, HF, and acidity. The most appropriate aging time is 1 d, because this gives the highest SSA for all samples hydrothermally crystallized for 16 h. Further increases in the aging period are detrimental to HY zeolite synthesis, because they lead to reductions in the HF, SSA, crystallinity, micropore volume, and number of acidic sites in the samples.

The effect of crystallization is also important in HY zeolite synthesis. Table 2 shows that crystallization for 16 h gives the highest relative crystallinity. An increase in the crystallization time from 16 to 24 h for the sample aged for 2 d greatly reduces the pore size and crystal size, but increases the number of acidic sites, SSA, total pore volume, micropore volume, and HF, as shown in Table 3.

The purpose of NaCl incorporation is to enhance the crystallinity and hydrothermal stability and maintain the initial porous structure. However, excess NaCl causes the mesopore walls of mesoporous materials to collapse [16,17]. Fig. 5 shows the XRD patterns for nanoporous HY zeolites with and without NaCl incorporation. The XRD reflection peaks from (511), (440), (533), and (642) for the samples with NaCl are more highly resolved than those for the sample without NaCl. The non-faujasitic peak from (622), which is more pronounced in the XRD pattern of the non-salted sample, may account for its lower crystallinity. This indicates that the NaCl incorporation method proposed by Chandrasekhar and Pramada [16], which was used in this work, is appropriate. NaCl incorporation not only enhances the relative crystallinity, SSA, pore size, and HF, but also increases the number of acidic sites in the sample.

4. Conclusions

Hierarchical nanoporous HY zeolites with maximum HF values were synthesized. This was accomplished by varying the aging and crystallization time. Crystallite sizes of about 68–91 nm and Si/Al ratios ranging from 1.39 to 1.61 were obtained. The aging time was varied from 1 to 3 d; the optimum aging period was 1 d. The sample aged for 2 d was crystallized for 16 or 24 h. Sample HY-2-24 had the lowest relative crystallinity but highest number of acidic sites, Si/Al ratio, surface area, and

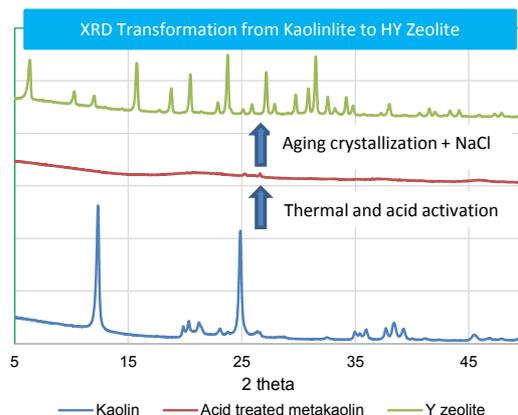
Graphical Abstract

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Synthesis and characterization of hierarchical nanoporous HY zeolites from acid-activated kaolin

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We investigated the effects of aging and crystallization time, and NaCl incorporation on the formation of hierarchical nanoporous HY zeolites. These three factors influenced the acidity, crystallinity, hierarchical factor, and surface area.



HF. NaCl incorporation after crystallization also enhanced the HF, number of acidic sites, and relative crystallinity, and preserved the mesoporous structure. A highly crystalline, mildly acidic, hierarchical nanoporous HY zeolite with a high surface area was therefore obtained by varying the aging and crystallization time.

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