

Green synthesis of hierarchical NaY zeolite for efficient Knoevenagel condensation

DONG Peng^{1,2}, ZHU Lin¹, LI Tiesen^{1,2}, CUI Qingyan¹, YUE Yuanyuan^{1,2,*}

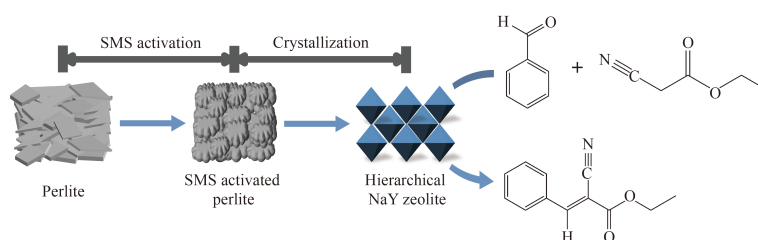
¹ College of Chemical Engineering, Fuzhou University, Fuzhou 350108, China;

² Qingyuan Innovation Laboratory, Quanzhou 362801, China

Abstract: Hierarchical aluminum-rich zeolites show promising potential in the Knoevenagel condensation; however, their synthesis is hindered by high preparation cost and energy consumption. To address these issues, a green synthetic route has been developed for preparing hierarchical

NaY zeolite using submolten salt (SMS) activated perlite as the sole source of silicon and aluminum. Comprehensive characterization shows that the NaY zeolite synthesized from SMS activated perlite exhibits high purity and crystallinity. This aluminum-rich NaY zeolite, with a framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of approximately 4.2, features intercrystalline mesopores, a large external surface and abundant basic sites. Investigation into the crystallization process of the hierarchical NaY zeolite indicates that during the initial stage, small crystals assemble and grow on the surface of SMS activated perlite. As crystallization proceeds, the zeolite crystals rapidly grow and aggregate around the activated sample, ultimately forming a crystal-packed morphology. In the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, the synthesized hierarchical NaY zeolite demonstrates higher benzaldehyde conversion compared to conventional counterparts.

Key words: NaY zeolite; hierarchical pore; perlite; green synthesis; Knoevenagel condensation



The Knoevenagel condensation constitutes a crucial role in synthetic chemistry, enabling the formation of C–C single bonds and the introduction of various functional groups into organic molecules^[1]. This versatility enables it indispensable for synthesizing complex organic compounds in the pharmaceutical and fine chemical industries^[2–4]. The Knoevenagel condensation is a typical base-catalyzed reaction, commonly employing soluble bases such as piperidine, pyridine and ethylenediamine as catalysts. However, the use of this type of catalysts poses several drawbacks, including difficulty in product separation, poor recyclability and environmental concerns^[5]. Recently, aluminum-rich zeolites (e.g., FAU and LTA zeolites) have demonstrated high catalytic activity and application potential in the Knoevenagel condensation. Their abundant basic sites, excellent stability at reaction temperature below 150 °C, and ease of separation make them being promising

alternatives to traditional liquid catalysts. Unfortunately, the inherent microporous structure (pore size below 1 nm) of conventional zeolite restricts the diffusion of reactant and product molecules, especially in the reactions involving bulky molecules, resulting in increased mass-transfer resistance, reduced catalytic efficiency, and even catalyst deactivation. Previous studies^[6–8] have indicated that hierarchical aluminum-rich zeolites not only offer abundant basic sites but also enhance the diffusion efficiency of reactants and products within their pore structure, thereby improving the catalytic activity. For example, Verboekend et al.^[9] demonstrated that the introduction of mesopores into FAU and LTA zeolites could enhance their catalytic efficiency by tenfold in the Knoevenagel condensation of benzaldehyde with malononitrile.

To date, the methods for preparing hierarchical zeolites can be classified into post-treatment and direct synthesis

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* Corresponding author. Tel: 18259129001, E-mail: yueyy@fzu.edu.cn.

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methods^[10]. Post-treatment technique involves primarily desilication and dealumination. In the case of aluminum-rich Y zeolite, the uniform distribution of framework aluminum atoms inhibits the effective desilication, thereby preventing the formation of mesoporous structure^[11]. The removal of aluminum species is a conventional method for creating hierarchical Y zeolite, however, it involves complex operational steps and demanding conditions. Direct synthesis method can be categorized into templating and template-free approaches, depending on whether a template agent is used. Significant progress has been made in synthesizing hierarchical NaY zeolite *via* templating method, which enables the pore structure tuning by adjusting template properties and synthesis conditions^[12]. Regrettably, the industrial application of this approach is limited by the high cost of templates and the environmental issues associated with their removal. In view of this, researchers have proposed the template-free approach for the preparation of hierarchical zeolites through. For example, Xiong et al.^[13] reported that the hierarchical Y zeolite with high crystallinity was fabricated by the *in situ* crystallization of a kaolinite microsphere and powder component mixture. Moreover, our previous works have successfully synthesized a series of hierarchical zeolites (e.g., hierarchical NaY, Beta and SAPO-11 zeolites) using submolten salt (SMS) activated natural aluminosilicate minerals as raw materials, without adding any mesoporous templates^[14–15]. This method relies on a self-assembly growth mechanism driven by the competitive coordination between crystallization and stabilization of oligomeric structural units formed during the depolymerization of aluminosilicate minerals. This can not only eliminate the need for organic templates, but also decrease the raw material cost associated with zeolite synthesis.

Even though hierarchical NaY zeolite was successfully synthesized from natural aluminosilicate minerals, this approach employed diatomite mineral as the main silicon source^[16]. This dependence brings about the following two issues. Firstly, the silicon species in diatomite necessitates activation *via* high-temperature calcination above 800 °C due to their low chemical reactivity, thereby resulting in significant energy consumption. Secondly, the diatomite contains some impurities, especially a stable quartz phase, which are difficult to transform during the synthesis of NaY zeolite. These residual impurities are consequently retained in the final product, ultimately reducing its purity. Therefore, searching for a natural aluminosilicate mineral with an appropriate SiO₂/Al₂O₃ molar ratio (SAR) and free of stable crystalline impurities is essential to circumvent the drawbacks of the conventional mineral system and further advance the green synthesis of zeolite.

To the best of our knowledge, the raw perlite is primarily composed of amorphous SiO₂, with a bulk SAR ranging between 8.5 and 10.0. This characteristic enables the use of perlite as the sole source of silicon and aluminum for the synthesis of NaY zeolite. However, the raw perlite has good chemical stability^[17]. When the untreated perlite was used as

the raw material, the resulting product is a composite of Y zeolite and perlite rather than a pure-phase Y zeolite^[18]. Based on our previous studies, this work applies the SMS activation method to depolymerize the perlite, and a hierarchical NaY zeolite is synthesized using this SMS activated perlite as the sole source of silicon and aluminum. The synthesis chemistry is systematically analyzed to determine the optimal conditions for preparing hierarchical NaY zeolite. Additionally, the physicochemical properties and crystallization process of the obtained zeolites are characterized and analyzed in detail. The catalytic performance of the synthesized hierarchical NaY zeolite is evaluated in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

1 Experimental

1.1 Materials

The raw perlite used in this work was purchased from Gongyi Bauhinia Longteng Co., Ltd. (China). Sodium hydroxide (≥96%) was bought from Shanghai Titan Reagent Co., Ltd. (China). Sodium aluminate (AR), sulfuric acid (≥98%) and ethanol (99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Silica sol (30% SiO₂) was purchased from Beijing Hongxing Technology Co., Ltd. (China). Commercial NaY zeolite was provided by Tianjin Nanhua Catalyst Co., Ltd. (China). Benzaldehyde (99.0%) and ethyl cyanoacetate (99.0%) were purchased from Shanghai Macklin Chemical Reagent Co., Ltd. (China). Deionized water was homemade in the laboratory.

1.2 Preparation of zeolites

SMS activation of the raw perlite. Typically, 30 g of sodium hydroxide were added into an open Teflon beaker containing 150 g of deionized water under vigorous agitation; subsequently, 25 g of the raw perlite were appended to the above sodium hydroxide solution. The resulting mixture was then placed in an oven exposed to air at a preset temperature of 280 °C for 2 h to yield an SMS activated perlite.

Synthesis of NaY zeolites. A structure-directing agent (SDA) with a molar composition of 16.2 Na₂O:1 Al₂O₃:15.0 SiO₂:295 H₂O was prepared by sequentially dissolving sodium hydroxide, sodium aluminate, and silica sol into deionized water under strong agitation for 2 h and aging the resulting mixture at room temperature for 28 h. Next, 10.0 g of SMS activated perlite were mixed with 32.3 g of deionized water at room temperature, and the obtained suspension was stirred for 15 min; a certain amount of the prepared SDA was then added to the suspension under continuous stirring; subsequently, 50% sulfuric acid solution was slowly added to adjust the pH value of the mixture, followed by stirring at 40 °C for 6 h;

finally, the resultant mixture was transferred to a Teflon-lined stainless-steel autoclave and crystallized at 100 °C under static condition and autogenous pressure. After crystallization, the obtained solid product was collected by filtration, washed with deionized water until pH value < 9, and dried overnight at 100 °C, yielding an as-synthesized sample designated as NaY-AP. For comparison, using silica sol and sodium aluminate as silicon and aluminum sources, a reference sample named NaY-CR was prepared under the same synthesis conditions used for synthesizing NaY-AP.

1.3 Characterizations

The X-ray diffraction (XRD) patterns of the zeolite samples were acquired on a Rigaku Ultimate IV diffractometer (Japan) using Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation at 40 kV and 40 mA and a scanning rate of 5(°)/min. The relative crystallinity (α) of the zeolite samples was determined according to ASTM D3906-19 standard, and calculated by Equation (1).

$$\alpha = \frac{I}{I_0} \times 100\% \quad (1)$$

where I and I_0 are the sums of the peak areas for the eight characteristic diffraction peaks ($2\theta = 15.7^\circ \pm 0.2^\circ$, $18.7^\circ \pm 0.2^\circ$, $20.4^\circ \pm 0.3^\circ$, $23.7^\circ \pm 0.4^\circ$, $27.1^\circ \pm 0.5^\circ$, $30.8^\circ \pm 0.5^\circ$, $31.5^\circ \pm 0.5^\circ$ and $34.2^\circ \pm 0.6^\circ$) of the test and standard samples, respectively. The commercial NaY zeolite was selected as the standard sample, with its relative crystallinity was defined as 100%.

The unit cell parameter (a) of the Y zeolite was calculated using pure silicon as the internal standard for angle calibration ($2\theta = 28.443^\circ$) in accordance to the ASTM D3942-19 standard, and the framework SAR_{XRD} value was obtained by Equation (2).

$$\text{Framework SAR}_{\text{XRD}} = \frac{2 \times (25.858 - a)}{a - 24.191} \quad (2)$$

The chemical composition of the solid samples was determined using an S4 Explorer X-ray fluorescence (XRF) spectrometer manufactured by Bruker Corporation (Germany). The morphology of the zeolites samples was observed by scanning electron microscopy (SEM) on a Helios G4 CX instrument (USA) at an accelerating voltage of 5 kV. The transmission electron microscopy (TEM) images of the samples were taken on a FEI Tecnai F20 instrument (USA). N₂ adsorption-desorption isotherms of the samples were measured using a Micromeritics ASAP

2046M instrument (USA). Prior to measurement, all the samples were pretreated under vacuum at 350 °C for 6 h. The BET specific surface area (S_{BET}) was calculated by the Brunauer-Emmett-Teller (BET) method in a relative pressure range of 0.05–0.25. The total pore volume (v_{total}) was estimated from the adsorption capacities at a relative pressure of 0.95. The micropore and external specific surface areas (S_{micro} and S_{exter}) and micropore volumes (v_{micro}) were estimated using the t -plot method. The mesopore size distribution was obtained by the Barrett-Joyner-Halenda model. The ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of the samples were measured on a Bruker Advance III 500 MHz instrument (Germany) and calibrated using tetramethylsilane (0.0) and saturated aluminum sulfate solution (0.0), respectively. The temperature programmed desorption of carbon dioxide (CO_2 -TPD) curves of the samples were recorded on a Tianjin Xianquan TP-5080-B apparatus (China).

1.4 Catalytic test

As shown in Figure 1, the catalytic performance of the NaY zeolites was evaluated using the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate as a model reaction. In a typical run, 20 mL of reaction mixture was prepared by mixing benzaldehyde (0.56 mol/L) and ethyl cyanoacetate (0.56 mol/L) in a molar ratio of 1:1 and using ethanol (85% of the total mixture) as solvent. The reaction was initiated by adding 3% of the catalyst and maintained at 70 °C under stirring. Upon completion, the product was collected, filtered, and analyzed by gas chromatography (GC) using a Shimadzu GC-2014 chromatograph equipped with flame ionization detector and RTX-1 capillary column. The chosen injection volume of this solution into the gas chromatograph was 0.5 μL with an injector temperature of 250 °C. The column was heated with 5 °C/min from 80 to 190 °C and kept for 3 min at 190 °C. Then, a heating ramp of 5 °C/min to 250 °C was applied followed by an isothermal step of 2 min at 250 °C. The conversion (x) of benzaldehyde was calculated using Equation (3) according to the GC curve.

$$x = \frac{C_{\text{benzaldehyde},0} - C_{\text{benzaldehyde},1}}{C_{\text{benzaldehyde},0}} \times 100\% \quad (3)$$

where $C_{\text{benzaldehyde},0}$ and $C_{\text{benzaldehyde},1}$ represent the concentration (mol/L) of benzaldehyde in the solution before and after the reaction, respectively.

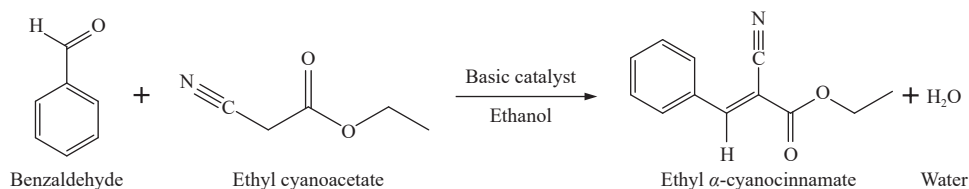


Fig. 1 Knoevenagel condensation reaction route of benzaldehyde with ethyl cyanoacetate

2 Results and discussion

2.1 Characteristics of raw zeolite

In this work, the raw perlite was selected as the silicon and aluminum sources to synthesize hierarchical NaY zeolite. As shown in Figure 2, the raw perlite is an amorphous aluminosilicate clay without any quartz phase, and it contains 14.47% Al_2O_3 and 75.24% SiO_2 (Table 1), confirming that it is a high-purity mineral. Importantly, the bulk SAR of the perlite is 8.8, which is comparable to that required in the synthesis of NaY zeolite. Additionally, the perlite inherently contains trace impurities such as Na_2O , K_2O and CaO .

2.2 Synthesis chemistry of NaY zeolites

In this work, SMS activated perlite was used for the first time as the sole source of silicon and aluminum to prepare NaY zeolite. To obtain the NaY zeolite with high-quality, key synthesis factors, including alkalinity ($n(\text{Na}_2\text{O})/n(\text{SiO}_2)$), SDA content, and crystallization time, were systematically investigated to identify the optimal synthesis conditions.

2.2.1 Effect of system alkalinity

Sodium ions play a crucial role during the synthesis of zeolite and are generally regarded as templates directing the zeolite crystallization^[19]. In the synthesis system of zeolite, increasing the alkalinity not only enhances the solubility of silicon and aluminum species in the liquid phase, but also reduces the polymerization degree of polysilicate ions, thereby accelerating the polymerization between polysilicate and aluminate ions. This can shorten the induction period and nucleation time for zeolite crystallization^[20].

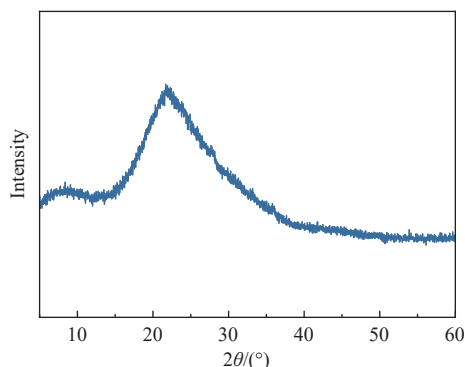


Fig. 2 XRD pattern of the raw perlite

Meanwhile, alkalinity influences physicochemical properties of the synthesized product, including acidity and crystal size^[21]. Therefore, it is essential to investigate the effect of alkalinity in the synthesis system on the preparation of NaY zeolite.

Figure 3 displays the XRD patterns of NaY zeolites synthesized under different $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ratios. It can be seen that when the $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ratio in the synthesis system ranges from 0.26 to 0.42, all the synthesized samples exhibit the diffraction peaks characteristic of FAU zeolite. Decrease of the $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ratio to 0.26 leads to the decrease of the diffraction intensity of the synthesized NaY zeolite, along with the appearance of a broad amorphous peak at $2\theta = 22^\circ$. This is due to the insufficient alkalinity, which is unable to fully depolymerize the silicon and aluminum species in SMS activated perlite. Moreover, the solubility of the formed aluminosilicate gel decreases in the low-alkalinity system, resulting in the increase of polymerization that hinders the transformation of the aluminosilicate gel into NaY zeolite^[22]. With the $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ratio increasing, the dissolution of the aluminosilicate gel is promoted while its polymerization is suppressed. This promotes the nucleation and crystallization of NaY zeolite. Nevertheless, further increase of the $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ratio induces to the formation of P zeolite, with the appearance of diffraction peaks at $2\theta = 12.6^\circ$ and 17.8° ^[23]. This indicates that excessively high alkalinity can cause the formation of the stable P zeolite phase, thereby hindering the synthesis of the metastable Y zeolite. Consequently, the optimal $n(\text{Na}_2\text{O})/n(\text{SiO}_2)$ ratio in this synthesis system is determined to be 0.34.

2.2.2 Effect of SDA content

The SDA is considered a key factor in preparing high-quality NaY zeolite, as it plays a structure-directing role in the synthesis of NaY zeolite^[24]. According to the results reported in literature^[25], it is difficult to synthesize the pure-phase NaY zeolite without SDA, and an insufficient amount of SDA results in low crystallinity. Therefore, it is necessary to investigate the effect of SDA amount on the synthesis of NaY zeolite.

As shown in Figure 4, amorphous phase is clearly visible in the synthesized sample without the using of SDA. When the SDA content ranges from 4% to 16%, all the synthesized samples display the diffraction peaks characteristic of Y zeolite, and the relative crystallinity of the synthesized NaY zeolites initially increased and then remains unchanged. It is worth noting that certain amount of P zeolite was generated at a low content of SDA, due to the insufficient nucleation sites for Y zeolite in the synthesis system under low content of SDA.

Table 1 Chemical composition of the raw perlite

Component	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	Fe_2O_3	BaO
Content w/%	4.54	0.25	14.47	75.24	0.30	3.65	0.86	0.53	0.16

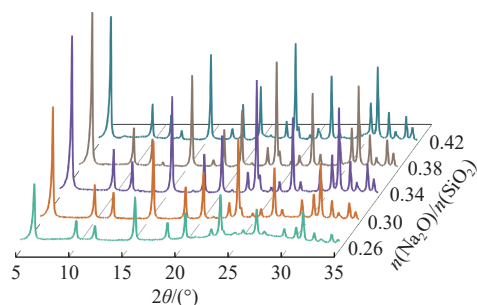


Fig. 3 XRD patterns of the resulting products at different $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratios

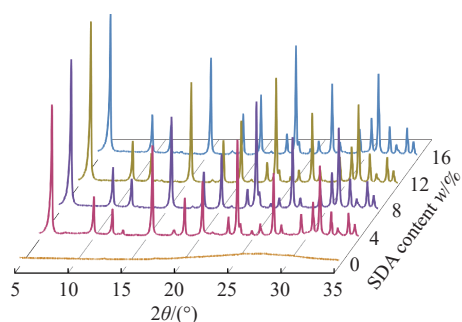


Fig. 4 XRD patterns of the resulting products at different amounts of SDA

Moreover, the number of nucleation sites required for the crystallization of NaY zeolite is fixed. Once the nucleation sites in the system become saturated, further addition of SDA no longer increases the crystallinity of NaY zeolite. To ensure optimal crystallinity of the synthesized sample and efficient utilization of the SDA, the optimal SDA content determined in this work is 8%.

2.2.3 Effect of crystallization time

To investigate the effect of crystallization time on the synthesis of NaY zeolite, the synthetic samples were obtained under conditions of aging temperature at 40 °C, crystallization temperature at 100 °C and a molar ratio of $3.0 \text{ Na}_2\text{O} : 1 \text{ Al}_2\text{O}_3 : 8.8 \text{ SiO}_2 : 228 \text{ H}_2\text{O}$. As shown in Figure 5, no diffraction peaks characteristic of FAU zeolite can be observed at the crystallization time of 4 h, confirming the difficulty in synthesis of NaY zeolite with an overly short crystallization time. When the crystallization time is extended to 8 h, weak characteristic diffraction peaks of FAU zeolite emerge in the XRD pattern. The intensity of the diffraction peaks gradually increases as the crystallization time and reaches a maximum at 24 h. However, further prolonging the crystallization time slightly lowers the intensity of diffraction peak, along with the appearance of diffraction peaks at $2\theta = 14.1^\circ$ and 24.6° assigned to SOD zeolite^[26]. This can be rationalized that overlong crystallization time leads to partial transformation of NaY zeolite into the more thermodynamically stable SOD zeolite.

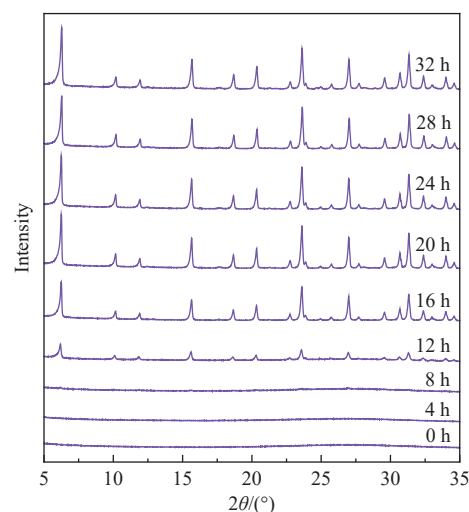


Fig. 5 XRD patterns of the resulting products at different crystallization times

2.3 Characteristics of NaY zeolites

In order to understand the properties of NaY zeolite synthesized from SMS activated perlite, the sample synthesized under optimal conditions was systematically characterized and compared with reference samples. As shown in Figure 6, both NaY-AP synthesized from SMS activated perlite and NaY-CR obtained from inorganic chemicals exhibit diffraction peaks characteristic of FAU zeolite. According to Equation (1), the relative crystallinity (91%) of NaY-AP is slightly lower than that of NaY-CR (94%), probably due to the enrichment of minor impurity elements from the SMS activated perlite into NaY-AP. Furthermore, the framework SAR_{XRD} of NaY-AP, NaY-CR and commercial NaY are calculated to be 4.19, 4.25 and 5.13, respectively based on Equation (2). These results indicate that under identical synthesis conditions, the framework SARs of the samples synthesized from SMS activated perlite and inorganic chemicals are comparable but lower than that of the commercial one. This is due to the relatively lower SAR in the synthesis system used for preparing NaY-AP and NaY-CR.

The morphologies of NaY-AP, NaY-CR and commercial NaY are given in Figure 7. NaY-AP exhibits well-defined octahedral crystals with the particle size of ca. 1.0 μm , along with agglomeration between crystals.

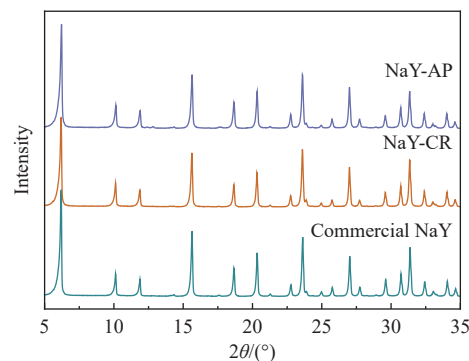


Fig. 6 XRD patterns of different NaY zeolites

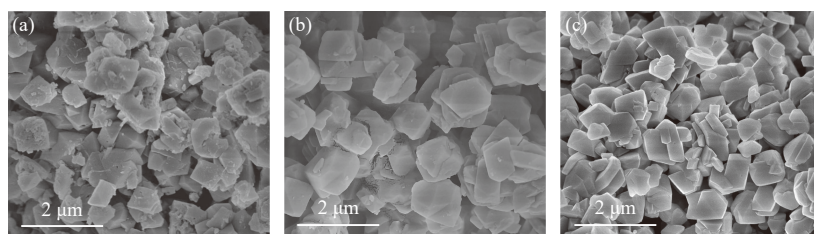


Fig. 7 SEM images of different NaY zeolites: NaY-AP (a), NaY-CR (b) and commercial NaY (c)

It can be seen that although both NaY-CR and commercial NaY also show typical octahedral morphology, their crystal size is increased to between 1.2 and 1.5 μm .

Furthermore, a well-defined morphology with a crystal size of ca. 1.0 μm and some intercrystalline mesopores between the crystals are also observed in the TEM images of NaY-AP (Figure 8(a)). Meanwhile, clear lattice fringes are visible, further confirming the high crystallinity of NaY-AP (Figure 8(b)).

As shown in Figure 9(a), the N_2 adsorption-desorption isotherms of NaY-CR and commercial NaY belong to type I, implying that both samples are microporous materials^[27]. In contrast, the isotherms of NaY-AP display the combined characteristics of type I and IV with an H4-type hysteresis loop. Notably, a significant increase in N_2 uptake is observed for NaY-AP in the range of relative pressure above 0.9, likely originated from the intercrystalline mesopores formed by the stacking of zeolite crystals^[28]. This is consistent with the observations of SEM and TEM images. The pore size distribution curve shown in Figure 9 (b) indicates that the mesopore size in NaY-AP is centered at ca. 20 nm.

Table 2 summarizes the textural parameters of different NaY zeolites. The S_{micro} and v_{micro} of NaY-AP are

comparable to those of NaY-CR, yet both are slightly lower than those of the commercial one, being in line with the XRD results. The S_{exter} of NaY-AP is 18 and 19 m^2/g higher than that of NaY-CR and the commercial one, respectively, while its v_{meso} is 2.5 times that of both reference samples because of the agglomeration of crystals in NaY-AP^[29].

Table 3 displays that apart from the main components (Na_2O , Al_2O_3 and SiO_2), the contents of other impurities in NaY-AP are higher than those in NaY-CR and the commercial one. This is mainly because, impurity elements in the perlite partially dissolve into the mother liquor during the synthesis of NaY-AP, while the undissolved impurities remain in the solid product. In addition, the bulk SARs of NaY-AP, NaY-CR and the commercial one are 4.36, 4.23 and 5.22, respectively.

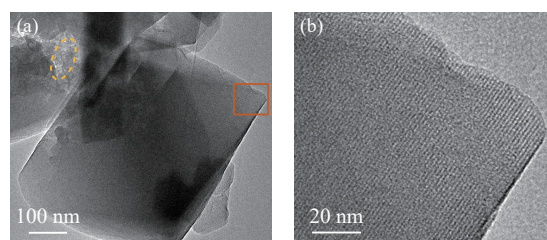


Fig. 8 TEM images of NaY-AP crystal (a) and its edge (b)

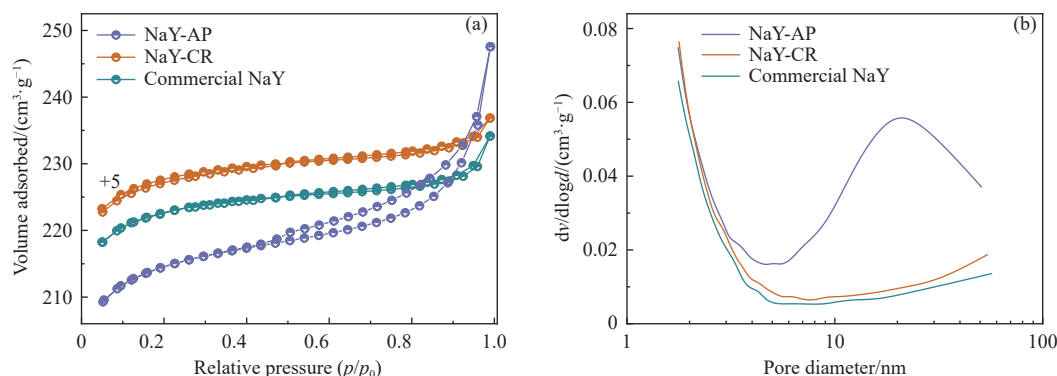
Fig. 9 N_2 adsorption-desorption isotherms (a) and pore diameter distribution curves (b) of different NaY zeolites

Table 2 Textural properties of different NaY zeolites

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{micro}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{exter}}/(\text{m}^2 \cdot \text{g}^{-1})$	$v_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{micro}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{meso}}^*/(\text{cm}^3 \cdot \text{g}^{-1})$
NaY-AP	653	597	56	0.37	0.32	0.05
NaY-CR	639	601	38	0.35	0.33	0.02
Commercial NaY	652	615	37	0.35	0.33	0.02

*: Mesopore volume $v_{\text{meso}} = v_{\text{total}} - v_{\text{micro}}$.

Table 3 Chemical compositions of different NaY zeolites

Sample	Component w/%							
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	BaO
NaY-AP	12.63	0.10	23.54	60.38	1.71	1.17	0.35	0.12
NaY-CR	14.03	0.08	24.48	60.96	0.16	0.18	0.11	–
Commercial NaY	12.79	0.09	21.30	65.42	0.19	0.14	0.07	–

The NMR characterization was employed to study the coordination environments of silicon and aluminum species in NaY-AP. Figure 10(a) shows that the ²⁹Si MAS NMR spectra of NaY-AP have five peaks at ca. –105, –100, –95, –90 and –85, assigned to the coordination of Si(0Al), Si(1Al), Si(2Al), Si(3Al) and Si(4Al), respectively^[30]. The framework SAR_{NMR} of NaY-AP is determined to be 4.14 according to Equation (4)^[31], consistent with XRD results. Figure 10(b) displays the ²⁷Al MAS NMR spectra of NaY-AP. Only a strong peak at 63, corresponding to tetracoordinated aluminum species in the zeolite framework^[30], is observed. This indicates that all aluminum species provided by SMS activated perlite are incorporated into the zeolite framework during the synthesis of NaY zeolite.

$$\text{Framework SAR}_{\text{NMR}} = \frac{2 \sum_{n=0}^4 I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^4 0.25n I_{\text{Si}(n\text{Al})}} \quad (4)$$

where I denotes the integrated intensity of a specific silicon resonance peak; n represents the number of AlO₄ units adjacent to SiO₄, taking values of 0, 1, 2, 3 and 4.

The basicity of NaY-AP, NaY-CR and commercial NaY

was investigated by CO₂-TPD technique. As shown in Figure 11, the CO₂-TPD profiles of these three zeolites display three desorption peaks at 135, 330 and 570 °C, ascribed to the interaction of CO₂ with weak, medium-strong, and strong basic sites, respectively. According to the results reported in literature^[32–34], the weak basic site of these zeolites primarily originates from alkaline hydroxyl groups on their surfaces, medium-strong basic site is associated with framework oxygen and alkali metal ion content, and strong basic site is mainly attributed to metal oxide clusters encapsulated within the cages of zeolite. The basic sites in these NaY zeolites were quantitatively estimated based on CO₂-TPD measurement, as summarized in Table 4. Among these three zeolites, the commercial NaY has the lowest total basic sites. This is because it has the highest SAR and lower alkali metal oxide. The number of weak and medium-strong basic sites in NaY-AP is essentially the same as those in NaY-CR, but the former possesses more strong base sites. This may be attributed to impurities (such as CaO, BaO, etc.) from SMS activated perlite remaining in the synthesized sample, resulting in the generation of a certain amount of metal oxide clusters in the supercages or SOD cages of NaY-AP.

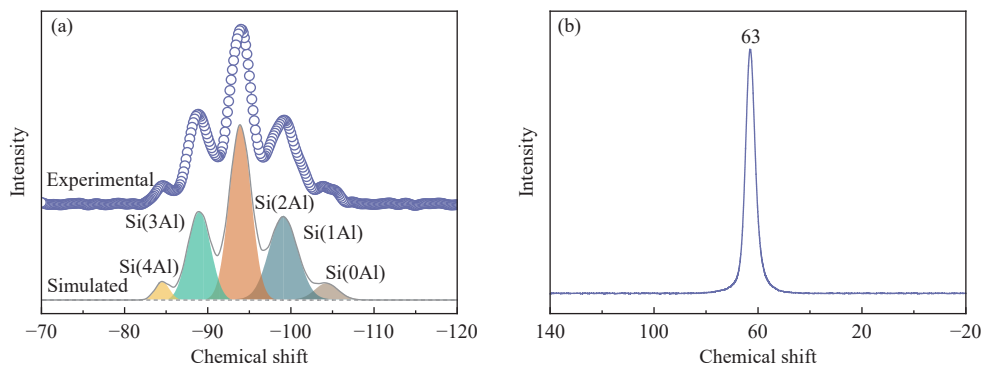
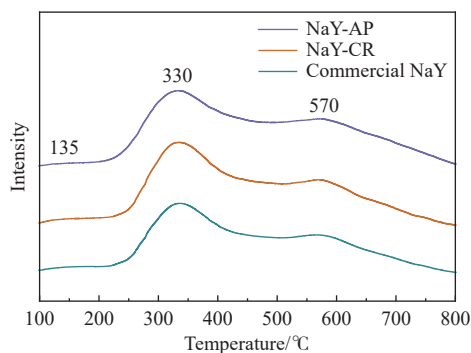
Fig. 10 ²⁹Si (a) and ²⁷Al (b) MAS NMR spectra of NaY-APFig. 11 CO₂-TPD profiles of different NaY zeolites

Table 4 Basic properties of different NaY zeolites

Sample	Basicity from CO ₂ desorption/(mmol·g ^{–1})			
	weak	medium strong	strong	total
NaY-AP	0.05	0.79	1.07	1.91
NaY-CR	0.08	0.80	0.95	1.83
Commercial NaY	0.06	0.62	0.78	1.46

The above results demonstrate that a NaY zeolite with high crystallinity was successfully synthesized by employing SMS activated perlite as the sole silica and alumina sources. This NaY zeolite, featuring a framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of ca. 4.2, exhibits intercrystalline mesopores of around 20 nm in size, a substantial external surface, and a high density of basic sites.

2.4 Crystallization process of hierarchical NaY zeolite

To investigate the crystallization behavior of hierarchical NaY zeolite synthesized using SMS activated perlite as the sole source of silicon and aluminum, the relative crystallinities and morphologies of samples prepared at different crystallization times were obtained.

The crystallization growth curve of the NaY zeolite is shown in Figure 12. It can be observed that the crystallization process of the synthesized NaY zeolite consists of two stages: induction period and growth period. When the crystallization time is less than 8 h, the relative crystallinities of the resulting samples are quite low, corresponding to the induction period^[35].

During this period, large numbers of crystal nuclei are generated in the synthesis system, while they are difficult to be detected by conventional XRD measurement due to their small size. When the crystallization time reaches 8 h, the process enters the crystal growth period. In the early part of this stage, the high supersaturation of the gel leads to rapid crystal growth. When the crystallization time exceeds 24 h, the available silicon and aluminum species in the system are nearly depleted. Further prolonging the crystallization causes partial phase transformation of NaY zeolite, giving rise to the decrease of the relative crystallinity of the obtained sample.

Figure 13 shows SEM images of the prepared samples at different crystallization times. It can be seen that, at the end of low-temperature aging (i.e., the crystallization time of 0 h), the solid product consists of SMS activated perlite with flocculent morphology. At crystallization time of 8 h, small crystalline particles become visible on the surface of the flocculent agglomerates. Increase of the crystallization time to 12 h leads to the generation of a small number of crystals with the typical octahedral morphology. When the crystallization time is extended to 16 h, the resulting sample is composed of well-defined octahedral crystals that show clear agglomeration, indicating that most of the SMS activated perlite has been converted into NaY zeolite.

Together with the results presents in Figure 12, it can be inferred that zeolite nuclei initially form on the surface of the activated perlite during the early crystallization stage. As crystallization proceeds, the crystals grow rapidly around the flocculent activation product, ultimately yielding a hierarchical NaY zeolite with intercrystalline mesopores^[36].

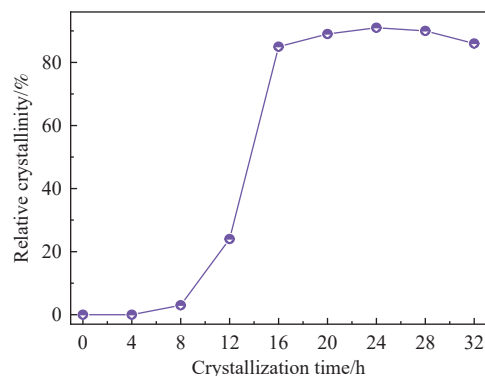


Fig. 12 Kinetic crystallization curve of the synthesized NaY zeolite from SMS activated perlite

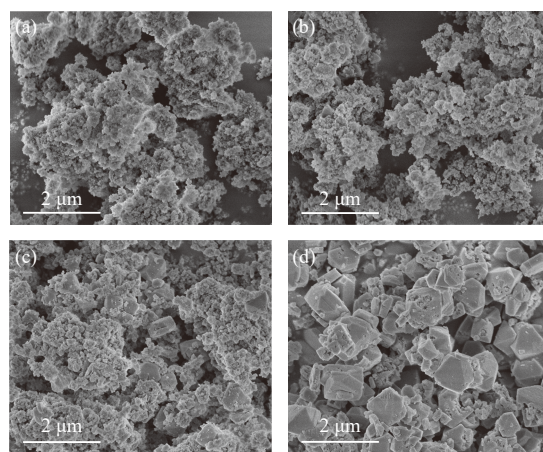


Fig. 13 SEM images of the synthesized samples at different crystallization times: 0 h (a), 8 h (b), 12 h (c) and 16 h (d)

2.5 Catalytic performance

To evaluate the catalytic performance of the synthesized hierarchical NaY zeolite, the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate was conducted at 70 °C using ethanol as the solvent. NaY-CR and commercial NaY were used as reference catalysts. Only ethyl α -cyanocinnamate and water are formed during the condensation reaction, with a constant selectivity of 100% for ethyl α -cyanocinnamate. As shown in Figure 14, the catalytic test results indicate that the conversion of benzaldehyde over all three catalysts increases significantly during the initial 2 h. Among them, the reaction rate of benzaldehyde is the fastest on NaY-AP and the slowest on the commercial NaY. Furthermore, the conversion of benzaldehyde essentially levels off until reaction time of 3 h, suggesting that the condensation reaction of benzaldehyde with ethyl cyanoacetate reaches equilibrium. Throughout the tested period (0–5 h), the catalytic efficiency of commercial NaY zeolite remains consistently the lowest, attributed to its lowest basic sites and the limitation of microporous structure. Even although the total basic sites (1.91 mmol/g) of NaY-AP is slightly higher than that of NaY-CR (1.83 mmol/g), the former exhibits a significantly higher equilibrium conversion (42%) of

benzaldehyde compared to the latter (28%). This obvious difference is related to their distinct pore structures.

According to previous reported results^[37–39], the micropore size of NaY zeolite is ca. 0.74 nm, while the kinetic diameters of benzaldehyde, ethyl cyanoacetate, and ethyl α -cyanocinnamate are approximately 0.58, 0.62 and 0.70 nm, respectively. Although benzaldehyde and ethyl cyanoacetate can enter the micropore channels of NaY zeolite catalysts, ethyl α -cyanocinnamate has a kinetic diameter close to their micropore size, leading to diffusion limitation within their microporous channels. Specifically, the sole microporous structure of NaY-CR restricts the diffusion of the formed bulky product. As the product accumulates within the channels in NaY-CR, its basic sites are gradually covered, reducing the number of active sites and consequently decreasing the catalytic efficiency of NaY-CR. In contrast, the abundant external specific surface area and mesoporous structure of NaY-AP can not only promote the diffusion of bulky molecule and enhance the diffusion efficiency of reactants and product, but also facilitate the exposure of more basic sites. This allows reactants to fully contact the active sites inside NaY-AP, thereby promoting the conversion of benzaldehyde.

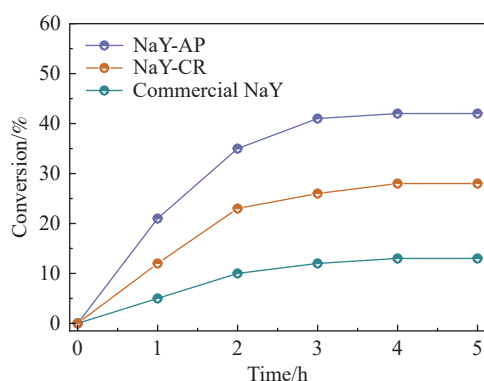


Fig. 14 Benzaldehyde conversion over different NaY zeolites as a function of reaction time

3 Conclusions

In summary, the green synthesis of hierarchical NaY zeolite has been achieved using SMS activated perlite as the sole source of silicon and aluminum. A series of characterizations were performed on the NaY zeolite synthesized under optimal conditions ($n(\text{Na}_2\text{O})/n(\text{SiO}_2) = 0.34$, SDA content of 8%, and crystallization time of 24 h). The results indicate that the resulting sample is an aluminum-rich NaY zeolite (framework SAR of ca. 4.2) with high purity and crystallinity, and features intercrystalline mesopores centered at ca. 20 nm. Compared with NaY zeolite synthesized from inorganic chemicals and the commercial one, it exhibits larger mesopore volume and more abundant basic sites. Investigation of the crystallization process reveals that silicon and aluminum species from SMS activated perlite assemble and form

small crystals on its surface during the initial stage. These crystals subsequently grow and aggregate around the activated perlite, creating intercrystalline mesopores. In the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate, the synthesized hierarchical NaY zeolite shows higher benzaldehyde conversion than the reference catalysts, due to its hierarchical pore structure and abundant basic sites. Overall, this work provides a green catalyst with application potential for the Knoevenagel condensation while achieving high-value utilization of natural perlite.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] YU J F, LUO Z Q, SUN X Y. Carbon dots as new effective catalysts for Knoevenagel condensation reaction and synthesis of cyclic carbonates under solvent-free conditions[J]. ChemistrySelect, 2024, 9(4): e202304217.
- [2] LI N, LIU X, ZHANG Y, et al. Research progress of homogeneous and heterogeneous catalysts in CO_2 cycloaddition reactions[J]. J Fuel Chem Technol, 2024, 52(1): 105–130.
- [3] XIAO W, DONG P, WANG C, et al. Facile synthesis of hierarchical NaX zeolite from natural kaolinite for efficient Knoevenagel condensation[J]. Chin J Chem Eng, 2024, 65: 75–84.
- [4] JOHAR S, JOHAN M R, KHALIGH N G. How important is the metal-free catalytic Knoevenagel reaction in medicinal chemistry? An updated review[J]. Curr Med Chem, 2024, 31(27): 4286–4311.
- [5] ZAPELINI I W, CARDOSO D. Amine-grafted Na-LTA zeolite precursors as basic catalysts for Knoevenagel condensation[J]. Microporous Mesoporous Mater, 2021, 324: 111270.
- [6] WANG X M, WEN C L, FAN Y. Synthesis of hierarchical SAPO-11-based catalysts with Al-based metal-organic framework derivative as mesopore to improve n-decane branched isomerization[J]. Pet Sci, 2022, 19(6): 3171–3181.
- [7] AL A, DARTONO R J, SNEDDON S, et al. Nanostructured zeolites: The introduction of intracrystalline mesoporosity in basic faujasite-type catalysts[J]. ACS Appl Nano Mater, 2018, 1(1): 310–318.
- [8] WANG Y Q, FAN C Y, LI H Y, et al. Facile One-pot synthesis of ZSM-5 aggregates with inter-and intra-crystalline mesopores for methanol to gasoline conversion[J]. Trans Tianjin Univ, 2019, 25(1): 9–22.
- [9] VERBOEKEND D, KELLER T C, MITCHELL S, et al. Hierarchical FAU- and LTA-type zeolites by post-synthetic design: A new generation of highly efficient base catalysts[J]. Adv Funct Mater, 2013, 23(15): 1923–1934.
- [10] CHEN L-H, SUN M-H, WANG Z, et al. Hierarchically structured zeolites: From design to application[J]. Chem

- Rev, 2020, 120(20): 11194–11294.
- [11] GROEN J. On the introduction of intracrystalline mesoporosity in zeolites upon desilication in alkaline medium[J]. *Microporous Mesoporous Mater*, 2004, 69(1/2): 29–34.
- [12] HARTMANN M, THOMMES M, SCHWIEGER W. Hierarchically-ordered zeolites: A critical assessment[J]. *Adv Mater Interfaces*, 2021, 8(4): 2001841.
- [13] XIONG X, PAN Z, DU X, et al. Preparation of Y zeolite with high crystallinity by mixing kaolin microspheres and powder[J]. *Pet Process Petrochem*, 2023, 54(1): 52–57.
- [14] YUE Y Y, ZHU H B, WANG T H, et al. Green fabrication of hierarchical zeolites from natural minerals[J]. *Natl Sci Rev*, 2020, 7(11): 1632–1634.
- [15] WANG C, CHI Z Q, LIU S, et al. Mesopore-free synthesis of hierarchical SAPO-11 from kaolin for hydroisomerization of n-alkanes[J]. *Pet Sci*, 2025, 22(3): 1370–1379.
- [16] YANG J B, LIU H Y, DIAO H J, et al. A quasi-solid-phase approach to activate natural minerals for zeolite synthesis[J]. *ACS Sustainable Chem Eng*, 2017, 5(4): 3233–3242.
- [17] LV P Z, LIU C Z, RAO Z H. Review on clay mineral-based form-stable phase change materials: Preparation, characterization and applications[J]. *Renewable Sustainable Energy Rev*, 2017, 68: 707–726.
- [18] WANG W N, KONG S S, ZHOU X X, et al. Perlite templated Y zeolite assembly and its potential as an efficient catalytic cracking catalyst[J]. *Microporous Mesoporous Mater*, 2017, 243: 130–134.
- [19] HE D W, YUAN D H, SONG Z J, et al. Eco-friendly synthesis of high silica zeolite Y with choline as green and innocent structure-directing agent[J]. *Chin J Catal*, 2019, 40(1): 52–59.
- [20] MENG B, REN S Y, LI Z, et al. A facile organic-free synthesis of high silica zeolite Y with small crystal in the presence of Co^{2+} [J]. *Microporous Mesoporous Mater*, 2021, 323: 111248.
- [21] MENDOZA C, ECHAVARRÍA A. A systematic study on the synthesis of nanosized Y zeolite without using organic structure-directing agents: Control of Si/Al ratio[J]. *J Porous Mater*, 2022, 29(3): 907–919.
- [22] KANG N Y, SONG B S, LEE C W, et al. The effect of Na_2SO_4 salt on the synthesis of ZSM-5 by template free crystallization method[J]. *Microporous Mesoporous Mater*, 2009, 118(1-3): 361–372.
- [23] VAIČIUKYNIENĖ D, JAKEVIČIUS L, KANTAUTAS A, et al. Conversion of silica by-product into zeolites by thermo-sonochemical treatment[J]. *Ultrason Sonochem*, 2021, 72: 105426.
- [24] LIU P, XIA T, NIE S F, et al. Strategy for the synthesis of zeolite Y by artificial-fish-reef breeding negative crystals[J]. *Inorg Chem Front*, 2022, 9: 2182–2193.
- [25] POLAK F, CICHOCKI A. Mechanism of Formation of X and Y Zeolites[M]. Poland: American Chemical Society, 1973: 209–216.
- [26] DARINCHULUUN T, PENG H, VAUGHAN J, et al. Anion effect on zeolite X synthesis and its phase transformation[J]. *Miner Eng*, 2025, 228: 109343.
- [27] FU T, HONG X, TIAN Y, et al. Preparation of Ag^+ modified NaY zeolite and its adsorption and denitrogenation properties[J]. *J Fuel Chem Technol*, 2024, 52(3): 384–394.
- [28] ZHOU J, LUO Y, ZONG B. Formation mechanism of porous zeolite Y composite[J]. *Pet Process Petrochem*, 2012, 43(1): 26–31.
- [29] QU Y L, DONG P, YANG L, et al. Synthesis of NaY zeolite from a submolten depolymerized perlite: Alkalinity effect and crystallization kinetics[J]. *Chin J Chem Eng*, 2024, 70: 130–138.
- [30] LIU P, LI Z, LIU X Y, et al. Steaming driven chemical interactions of ZnCl_x with Y zeolite framework, its regulation to dealumination/silicon-healing as well as enhanced availability of Brønsted acidity[J]. *ACS Catal*, 2020, 10(16): 9197–9214.
- [31] FYFE C A, FENG Y, GRONDEY H, et al. One- and two-dimensional high-resolution solid-state NMR studies of zeolite lattice structures[J]. *Chem Rev*, 1991, 91(7): 1525–1543.
- [32] BARTHOMEUF D. Framework induced basicity in zeolites[J]. *Microporous Mesoporous Mater*, 2003, 66(1): 1–14.
- [33] VERZIU M, COJOCARU B, et al. Sunflower and rapeseed oil transesterification to biodiesel over different nanocrystalline MgO catalysts[J]. *Green Chem*, 2008, 10(4): 373–381.
- [34] ZHANG P B, CHEN X, LENG Y, et al. Biodiesel production from palm oil and methanol via zeolite derived catalyst as a phase boundary catalyst: An optimization study by using response surface methodology[J]. *Fuel*, 2020, 272: 117680.
- [35] ZHENG S, HUANG S, HAN Y, et al. Kinetic process on the in-situ crystallization of NaY zeolite from sepiolite[J]. *Acta Pet Sin (Pet Process Sect)*, 2011, 27(4): 657–661.
- [36] PARSAPUR R K, SELVAM P. Rational design, synthesis, characterization and catalytic properties of high-quality low-silica hierarchical FAU- and LTA- type zeolites[J]. *Sci Rep*, 2018, 8(1): 16291.
- [37] CUNDY C S, COX P A. The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time[J]. *Chem Rev*, 2003, 103(3): 663–702.
- [38] LIU C, CAO C Y, LIU J, et al. One methyl group makes a major difference: Shape-selective catalysis by zeolite nanoreactors in liquid-phase condensation reactions[J]. *J Mater Chem A*, 2017, 5(33): 17464–17469.
- [39] LUO Q, SONG X, JI M, et al. Molecular size- and shape-selective Knoevenagel condensation over microporous $\text{Cu}_3(\text{BTC})_2$ immobilized amino-functionalized basic ionic liquid catalyst[J]. *Appl Catal A: Gen*, 2014, 478: 81–90.

等级孔 NaY 分子筛的绿色合成及其催化 Knoevenagel 缩合反应

董 鹏^{1,2}, 朱 琳¹, 李铁森^{1,2}, 崔勍焱¹, 岳源源^{1,2,*}

(1. 福州大学 化工学院, 福建 福州 350108; 2. 清源创新实验室, 福建 泉州 362801)

摘 要: 等级孔富铝分子筛在 Knoevenagel 缩合反应中展现出良好的应用潜力, 但其制备面临着高成本及高能耗的问题。基于此, 开发了一条以亚熔盐活化的珍珠岩为全部硅铝源制备等级孔 NaY 分子筛的绿色合成路线。合成样品的表征结果表明, 基于亚熔盐活化的珍珠岩合成的 NaY 分子筛具有高的纯度及结晶度, 其硅铝比约 4.2 的富铝 Y 型分子筛, 具有晶间介孔结构以及较商业样品更高的介孔孔容和更丰富的碱性位点。对该分子筛晶化过程的研究表明, 在分子筛晶化初期, 珍珠岩亚熔盐活化产物提供的硅铝物种在其表面组装生长出小晶体颗粒; 随着晶化反应的进行, 分子筛晶体颗粒在活化产物周围迅速生长、聚集形成具有晶粒堆积形貌的分子筛材料。上述制备的等级孔 NaY 分子筛在用于苯甲醛与氰乙酸乙酯的 Knoevenagel 缩合反应时, 表现出较参比催化剂更高的苯甲醛转化率。

关键词: NaY 分子筛; 等级孔; 珍珠岩; 绿色合成; Knoevenagel 缩合反应

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作者简介:



董鹏(1994), 博士, 博士后, 研究方向为高性能分子筛的制备、VOCs 吸附与催化燃烧, dongpeng@qyil.ac.cn。



岳源源(1988), 博士, 教授, 从事石油化工和环境保护催化材料及催化剂的研究, yueyy@fzu.edu.cn。