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Original Research Paper

Synthesis of hierarchical nanoporous HY zeolites from activated kaolin, a central composite design optimization study

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ABSTRACT

In this article, we investigated the optimum formulation towards synthesis of hierarchical nanoporous HY zeolites from acid activate kaolin. A central composite design (CCD) helped to investigate the influence of aging (X_1), crystallization (X_2) and NaOH solution to kaolin ratio (X_3) on crystallinity ($C\%$), specific surface area (SSA) and hierarchical factor (HF). From the analysis of variance (ANOVA), we deduced that all the process variables show statistical significance towards obtaining high $C\%$ and SSA while only X_3 is statistically significant for optimal HF. The effectiveness of models was further evaluated using margin of error and tolerance interval. The Optimum formulation for this hierarchical nanoporous HY zeolite was obtained as 43.60, 64.23 and 6.97 for X_1, X_2, and X_3, respectively. The developed models show that X_3 is the most statistically significant variable because it has the highest coefficient and the lowest p-value in the entire model. These results give instrumental insight into the synthesis of hierarchical nonporous HY zeolite.

1. Introduction

Y zeolites have gained immense popularity within the research community and commercially due to their uniform pore size, high specific surface area and thermal stability [1–3]. Rational design of this Fajausite materials requires tailored pore architecture as well as controlled location, strength, and nature of acid sites [4]. Though there are well-established methods for tuning the strength and nature of acid sites, it is very difficult to control the location of active sites and pore architecture [4,5].

The utilization of Y zeolites is limited in processes that involve bulky molecules because they have relatively low pore size [6]. Such processes include organic waste treatment, heavy crude oil, and bio-oil upgrading because of the mass transfer limitation they pose to bulky chemical reaction. In view of this, immense effort has been dedicated to the synthesis of novel bimodal structured molecular sieve. These materials are termed “hierarchical porous” because they synergistically combine the outstanding properties of mesoporous and microporous zeolites [7–9]. Hierarchical nanoporous materials exhibit high thermal and hydrothermal stability and possess unique pore channel with bimodal pore system (micro- and mesopores) [10–12]. Connecting microporous channels to mesoporous ones in a highly ordered form results in the microporous channels residing in the matrix causing shorter diffusion path for the reactant molecules [12–14].

Many variables influence formation of these faujasitic materials [15,16]. This informs the need to employ multivariate experimental design to scrutinize the statistically significant independent variables [1]. In this case, response surface methodology (RSM) is a viable optimization tool. The methodology employs central composite design (CCD) as one of the design tools for model fitting through least square method [17]. To investigate the suitability of the proposed model equation, analysis of variance (ANOVA) is a vital tool [17]. ANOVA provides diagnostic checking test for the model by the use of Fisher’s statistical test (F-test). Response surface plots help to provide the location of optimal response and surfaces study. RSM also offers a robust evaluation of operation results and efficiency [17]. Several work has been done on Y zeolite synthesis [1,18,19], but few actually conducted optimization studies. Karami and Rohani [1] conducted optimization study for the synthesis of Y zeolite using soluble silicate and aluminum

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sulfate as silica and alumina source respectively in a two-level factorial design. However, the zeolite precursors are expensive. Chandrasekhar and Pramada [19] showed the prospect of producing Y zeolite from kaolin being a cheap source of both silica and alumina but the process variables are not systematically optimized.

In this work, an optimization study was conducted for the synthesis of hierarchical nanoporous HY zeolite from kaolin in a two-level full factorial design using CCD. The mathematical models were developed in terms of aging, crystallization and NaOH solution to kaolin ratio (NaS). This is to provide a quantitative evaluation of hierarchical factor (HF), crystallinity and specific surface area (SSA). The experimental design is made up of 20 run with the center point repeated 6 times. This is to ensure accurate measurement and satisfactory reproducibility towards producing pure hierarchical nanoporous HY zeolites.

2. Experimental

2.1. Materials

The kaolin (Si/Al = 1.06) used for this investigation is from R&M Chemicals Sdn. Bhd., Malaysia. The study used the reagents without further purification. R&M Chemicals Sdn. Bhd., Malaysia also supplied the NaOH and H_2SO_4 (95–98% pure).

2.2. Methods

The synthesis HY zeolites precursor was by thermal activation at 850 °C for 2 h and subsequent activation with 6 M H_2SO_4 at 90 °C for 2 h to produce amorphous aluminosilicate. The precursor was added to an aqueous NaOH solution (14%) at different NaOH/Solid ratio (ml/g). The solution was aged at room temperature for 4.4–43.6 h and subsequently crystallized at 100 °C for 8.8–87.2 h. This was followed by washing and filtering with distilled water using vacuum pump until pH of 4.1–13.9. Further, drying took place at 110 °C overnight and subsequently soaked in a solution saturated with NaCl to its equilibrium water content [19]. The essence of NaCl imbibement is to enhance the crystallinity and hydrothermal stability and maintain the initial porous structure [19,20]. However, excess salt collapse the mesopore wall of mesoporous materials [19,21]. Further, the samples were placed in a fume cupboard to remove excess water and dried. The samples were transformed into hydronium form in 0.2 M ammonium nitrate solution for 24 h. The filtering and drying of the resulting solution took place at 110 °C overnight and then calcination followed at 550 °C for 2 h. The resulting materials were designated HY36-72-6 for sample aged for 36 h, crystallized for 72 h using NaOH solution/solid ratio of 6.

2.3. Characterization

XRF analysis gives the silicon and aluminum composition of the synthesized HY zeolites. X-ray diffractometer (Philip Expert X-ray Diffractometer) helps to carry out the XRD analysis using nickel-filtered Cu Kα radiation (λ = 1.544 Å) ranging from 5.018 to 69.966° (2θ) with a step size of 0.026° for all the samples. The peak reflections at (511), (440), (533), and (642) helped to determine the relative crystallinity of the samples [22].

$$Relative\ Crystallinity\ (\%) = \frac{Sum\ of\ sample\ characteristic\ peak\ area}{Sum\ of\ the\ reference\ characteristic\ peak\ area} \times 100 \qquad (1)$$

The crystallite size of the aforementioned peaks was computed with the aid of PANalytical X'Pert HighScore software [23]. Further, we compared the crystallinity of the samples with that of conventional Y zeolite to obtain the values of relative crystallinity.

Perkin Elmer Spectrum RX FT-IR was used for the infrared spectroscopy (IR) to confirm Y zeolite fingerprint. Surface area and porosity analyzer (Micrometrics ASAP 2020) gave the nitrogen adsorption-desorption analysis using analysis bath temperature of 77.350 K.

The morphology of the synthesized HY zeolites was visualized by Scanning electron microscopy (SEM, FEI Quanta 400 FE-SEM) using 20 kV as the accelerating voltage. The HY zeolites samples were coated with gold, prior to the examination, to enhance the electrical conductivity.

2.4. Hierarchy factor

Hierarchy factor is a viable tool to categorize the degree of structural order of porous materials. This tells how less mesopore formation penalize the micropore formation of the synthesized zeolite sample [20,24–26].

Zheng et al. [26] proposed a model as a tool for classification of hierarchy mesoporous zeolites as derived from the conventional N_2 adsorption analysis. From the ratio of micropore volume to mesopore volume (V_{micro}/V_{meso}) and relative mesopore specific surface area (S_{meso}/S_{BET}) of the weighed sample, they defined hierarchy factor (HF) as follows:

$$HF = \frac{V_{micro} * S_{meso}}{V_{meso} * S_{BET}} \qquad (2)$$

where V_{micro} is the micropore volume; V_{meso} is the mesopore volume; S_{meso} is the specific surface area of the mesopore and S_{BET} is the BET surface area. The V_{micro}, V_{meso} and S_{meso} are obtained by using *t*-plot. The value of HF increases as V_{micro} and S_{meso} increases, whereas, it decreases with increase in V_{meso}.

2.5. Experimental design and data analysis

A two-level blocked full factorial design by CCD was conducted in which three process parameters was used. The parameters are aging, crystallization and NaOH solution to kaolin ratio were expressed as dimensionless (X_1, X_2, and X_3 respectively). The coded values are −1, 0, 1 for low, center and high level respectively. The process parameter levels selection was centered on the results of our earlier works [20].

Minitab® 16.2.2 was used for the regression and statistical analysis of the experimental data. The total number of runs is 20 which entails 8 cube point, 4 center points in a cube, 6 axial points, and 2 center points in axial. The distance between the center point and the axial point is α for low/high level while the remaining factors maintained their center values. That is, the axial points are situated at (0, 0, ±α), (0, ±α, 0) and (±α, 0, 0). Generally, α is a function of a number of factors, k and is given as $(2^k)^{0.25}$. Nevertheless, Minitab® 16.2.2 provides the user an option of choosing the value of α. The value of α used in this work is 1.633. The number of runs replicated at the center point served as materials for experimental error determination. The responses chosen for RSM study are crystallinity, SSA, and HF that were designated as Y_1, Y_2, and Y_3 respectively.

Table 1
Levels of HY zeolites Independent variables for the CCD.

Variable	Symbol	Coded variable levels		
		−1	0	1
Aging time (h)	X_1	12	24	36
Crystallization time (h)	X_2	24	48	72
NaOH to sample ratio (ml/g)	X_3	6	9	12

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