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Original Research Paper

Synthesis, characterization and ion exchange isotherm of zeolite Y using Box–Behnken design

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ABSTRACT

Zeolites were synthesized from sodium metasilicate, aluminium oxide, sodium hydroxide and distilled water using hydrothermal method. Response Surface method called Box–Behnken was used to design the number of experiments considering three factors affecting the synthesis [(i) Crystallization time (A), (ii) crystallization temperature (B) and (iii) ageing time (C)]. The X-ray diffraction XRD pattern peak of zeolite Y are quite consistent with the reference samples and sample Y6had the highest percentage crystallinity of 75.03% at crystallization time of 7 h, temperature of 95 °C and an ageing time of 24 h. The scanning electron micrograph (SEM) for zeolite Y showed hexagonal crystal morphology. Sample Y6 has a surface area of 301.5 m^2/g, micropore area of 345.4 m^2/g and micropore volume of 0.1227 cm^3/g. The ion exchange isotherm for Ca^{2+}–Na^+–Y systems shows that although the entering cation was initially preferred, the incoming ion remains in solution not displacing the sodium ion in the zeolites which is in line with literature, while ion exchange isothermfor NH_4^+–Na^+–Y system shows unusual shape and the curves showed where the solution phase varies in composition with its equivalence in the zeolite phase.

1. Introduction

There are considerable progresses of functional nanoporous materials and related nanostructures [1–4]. Among them, zeolite families contribute greatly to practical applications. Zeolites are three-dimensional crystalline aluminosilicate minerals with well-defined structures [5]. The silicon and aluminium atoms are tetrahedrally coordinated with each other through shared oxygen atoms. The presence of aluminium in the framework results in a negative framework charge, which is balanced by positively charged ions such as Na^+, NH_4^+, Ca^{2+} [6].

Many research has been done on synthesis of zeolites from different sources ranging from pure chemical [7,8] to kaolin [9,10] and coal fly ash [11,12]. The major approach used by researchers is the hydrothermal method because it is similar to the natural process that aids the formation of natural zeolites. However, microwave method has been applied by some [8,13] because it requires shorter time and aids the formation of uniformly sized crystal as compared to the conventional heating method [13]. The most common synthetic zeolites are zeolites A, X, Y and ZSM-5.

Response surface method (RSM) is a gathering of factual and numerical methods helpful for demonstrating and investigation of issues, and the goal is to enhance this reaction which is influenced by a few variable when shifting them at the same time [14]. Box–Behnken design is a kind of reaction surface plan that does not contain an implanted factorial or partial factorial configuration and it requires a fewer number of runs. This response surface design does not have axial point (i.e. it is rotatable), it guarantees that all configuration focuses fall inside of a sheltered working zone and that all variables are not situated at their abnormal states in the meantime [15].

In this work, we report the synthesis of zeolite Y from pure chemicals. The effects of crystallization time, temperature and ageing time on the crystalline samples were studied analytically using Box–Behnken design. The ion exchange isotherm was analysed and synthesized samples properties such as surface area, crystal morphology and crystallinity were characterized using the XRD, SEM and BET surface analyser.

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2. Methodology

Chemicals used in this study were Sodium metasilicate (Fischer Scientific, 99%), Aluminium Oxide (Loba, 99%), Distilled water (Laboratory made).

2.1. Design of experiment

The data analysis was carried out with Design Expert® software version 7, applying response surface methodology with Box–Behnken design. The effect of three variables [hydrothermal treatment time (A), hydrothermal treatment temperature (B) and ageing time (C)] were studied. According to the Box–Behnken design, the total number of experiments is $N = 2k * (k - 1) + c_p$, where k is the number of factors and c_p is the number of central point [12]. In this work, twelve (12) experiments were carried out for the zeolites synthesized (see Table 1).

2.2. Synthesis of zeolite Y

Zeolite Y was synthesized from aluminosilicate gel mixture with molar composition $7.99Na_2O{:}1Al_2O_3{:}20.2SiO_2{:}323.41H_2O$.

1.198 g of alumina was added to 30 mL of distilled water and stirred for about 10 min. 19.915 g of sodium metasilicate was added to another 30 mL deionised water to form a homogenous solution in a beaker. The alumina and silicate mixtures were mixed together and stirred for about 20 min until the gel appeared somewhat smooth in the beaker.

The overall gel was transferred into a 100 mL autoclavable Teflon bottle (sealed) and was aged for varying time (24–36 h) at room temperature. The aged mixture was transferred into an autoclave for hydrothermal treatment in an oven under autogenous pressure, maintained at distinguishable crystallization temperature and time using the Box–Behnken design matrix, until gel separated into solid and supernatant liquid showing a complete crystallization, and then cooled to room temperature.

The resulting solid product was separated by filtration, washed with distilled water until the filtrate pH was about 9. The solid products in various cases were transferred to the watch glass and dried in an oven at 100 °C overnight. The zeolite Y was weighed and placed in a plastic bottle.

2.3. Characterization and analysis

2.3.1. Characterization

X-ray diffraction patterns were measured by AXS Bruker advance-8 Diffractometer using CuKα ($\lambda = 0.1541$ nm) radiation at 40 kV and 40 mA. The diffraction patterns of the synthesized zeolites were obtained at a scan speed of 0.04° 2θ/88 sec. The areas, peak positions and widths were estimated using ORIGIN®8. The percentage crystallinity of synthesized zeolites were estimated by comparing seven (7) characteristic peak areas appearing at 2θ from 12° to 55° to that of the reference sample according to the following equation:

$$\%\ \text{crystallinity} = \sum P / \sum P_s \times 100\ [16] \tag{1}$$

Table 1
Levels of Independent Variable for Zeolite Y.

Levels	Low	Medium	High
Coding	−1	0	+1
Crystallization time (A) h	5	6	7
Crystallization temperature (B) °C	90	95	100
Ageing time (C) h	24	30	36

where P is the total areas of seven (7) characteristics peaks patterns of pure sample.
P_s is the total areas of seven (7) characteristics peaks of standard.

The crystal sizes were estimated from the XRD pattern using Scherrer's formula given as;

$$CS = k \times \lambda / \beta \times \cos\theta \tag{2}$$

where $K = 0.94$ is the shape factor for spherical crystal with cubic symmetry,
$\lambda = 0.1541$ nm is the wavelength of the diffraction,
β is the full width at half maximum (FWHM) in radians,
θ is value of $2\theta/2$ in radians.

The morphology of zeolite Y was obtained by Scanning Electron Microscopy (FEI Quanta 200 ESEM) imaging at 20 kV and magnifications of 500× and 2000×. Energy Dispersive Spectrometry (EDAX Genesis System) was used to derive compositional data on the zeolite.

The surface area, micropore area and volume of zeolite sample Y6 were determined by gas adsorption and desorption (Quantachrome Nova 5200). 0.15 g of sample Y6 were weighed and placed into the sample cell, heated to 573 K and held at that temperature for 3 h. The heating mantle was afterwards turned off and allowed to cool along with the samples at room temperature. This was done to outgas the samples. The degassed samples were dipped into liquid nitrogen and after adsorption has reached equilibrium, the sample cell was dipped into water bath at room temperature and the amount of nitrogen desorbed was measured.

2.3.2. Analysis

Ion exchange isotherm experiment was carried out on zeolite Y samples at 0.1 N constant normality and room temperature in a batch system. The acetate salts of ammonium and calcium were prepared by dissolving 7.708 g of CH_3COONH_4 and 7.91 g of $CH_3COO(Ca)_2$ in 1L of deionised water. 0.5 g of zeolite Y was measured in a centrifuge tube where 15 mL of ammonium and calcium acetate solution was added.

Zeolite Y in the centrifuge tubes was treated five times every 6 h and well shaken to find isotherm condition for each ion of exchange. Well shaken samples were allowed to settle and the clear supernatant solution were decanted and collected in well labelled sample bottles.

Concentrations of exchanging cations were determined using Bulk Scientific atomic absorption spectrophotometer (Accusys 211) for Ca^{2+} and ultraviolet (UV) spectrophotometer for NH_4^+. Equivalent fractions of cations in zeolite and in solution were evaluated. Ionexchange isotherms were plotted as equivalent fraction of exchanging ion in solution phase versus equivalent fraction of same ion in the zeolite phase for binary ion exchange system between NH_4^+–Na^+ and Ca^{2+}–Na^+.

3. Results and discussion

3.1. Characterization

The 7 characteristics XRD peak of zeolite Y at 2θ: 14.5°, 21.7°, 28.2°, 33.2°, 38.4°, 49.3°, 55.3° are quite consistent with the reference sample as reported by [17]. Zeolite P appeared at 2 theta: 12.5° and 17.6°. Zeolite Y and P contribute to the main crystalline phase with small amount of unreacted aluminium oxide.