

CHAPTER III

EXPERIMENTAL

3.1 Materials and methods

3.1.1 Materials

Silica gel was collected from desiccant packets in furniture boxes. Its silica purity analyzed by energy dispersive X-ray fluorescence (EDXRF, Horiba, XGT-5200) was 99%. It was dissolved in sodium hydroxide (NaOH) solution and used as a silica source. Zeolite NaA, NaX and NaY were synthesized according to the methods from the literature (Jantarit et al., 2020; Keawkumay et al., 2019; Khaosomboon et al., 2018).

3.1.2 Synthesis of zeolite A by using silica gel waste

Zeolite NaA was prepared through hydrothermal method with an overall gel composition of $3.165\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 1.926\text{SiO}_2 : 128\text{H}_2\text{O}$ (Khaosomboon et al., 2018).

NaOH (12.27 g) was dissolved in distilled water (90 mL) in a Teflon bottle under stirring. The solution was then split into two equal parts: one portion remained in the original beaker, while the other was transferred to a separate Teflon bottle.

In the Teflon bottle, silica gel waste (2.04 g) was introduced, and the mixture was stirred at 90 °C for 3 h. Meanwhile, in the beaker, anhydrous NaAlO_2 (6.36 g) was introduced and stirred at room temperature until a clear solution formed. The aluminate solution was then rapidly combined with the silicate solution, resulting in the formation of a thick gel. The container was sealed, and the mixture was stirred at room temperature for 30 min until homogeneous.

The overall gel was crystallized through the hydrothermal method at 80 °C for 2.5 h under static conditions. Once cooled, the sample was repeatedly washed with distilled. Finally, the samples were dried overnight at 90 °C.

3.1.3 Synthesis of zeolite X by using silica gel waste as silica source

Zeolite NaX was prepared through hydrothermal method with an overall gel composition of $\text{Na}_2\text{O} : 4\text{Al}_2\text{O}_3 : 16\text{SiO}_2 : 325\text{H}_2\text{O}$ (Jantarit et al., 2020).

The sodium silicate solution was prepared from silica gel waste. First, NaOH (4.83 g) was dissolved in distilled water (26.67 g) in a Teflon bottle under stirring. Then, silica gel waste (12.3 g) was added slowly, and the mixture was stirred at room temperature for 18 h.

A solution was prepared by dissolving NaOH (27.24 g) in distilled water (264 g) in a Teflon bottle and stirring until fully dissolved. Then, anhydrous NaAlO₂ (4.08 g) was added, and the mixture was stirred at room temperature for 1 h. After that, sodium silicate solution was added and stirred for another hour until homogeneous.

The overall gel was crystallized by hydrothermal at 90 °C for 18 h. After cooling, the samples were washed with distilled water until the filtrate's pH was below 7, using multiple centrifugation cycles at 4000 rpm for 5 min each. Finally, the samples were dried overnight at 90 °C

3.1.4 Synthesis of zeolite Y by using silica gel waste as silica source

Zeolite NaY was prepared through hydrothermal method with an overall gel composition of 4.62Na₂O: Al₂O₃: 10SiO₂: 180H₂O (Keawkumay et al., 2019).

The sodium silicate solution was prepared from silica gel waste by dissolving NaOH (11.5 g) in distilled water (59.8 g) in a Teflon bottle and stirring until a clear solution was obtained. Then, silica gel waste (28.7 g) was slowly added, and the mixture was stirred at room temperature for 24 h.

A seed gel was prepared by dissolving NaOH (1.02 g) in distilled water (5.1 g) in a Teflon bottle and stirring until a clear solution was obtained. Then, anhydrous NaAlO₂ (0.52 g) was added and stirred until homogeneous. After that, Na₂SiO₃ solution (5.66 g) was added, and the mixture was stirred for 10 min, capped, and aged at room temperature for 24 h.

A feedstock gel was prepared from NaOH (0.035 g) dissolved in distilled water (32.74 g) in a plastic beaker, followed by adding anhydrous NaAlO₂ (3.27 g). The mixture was stirred until homogeneous. Then, Na₂SiO₃ solution (35.61 g) was added and stirred vigorously for 10 min.

The feedstock gel was then added into the seed gel, stirred for 10 min, sealed, and aged for 24 h at room temperature. The overall gel was crystallized using the hydrothermal method at 90 °C for 24 h. After cooling, the white precipitate was washed

repeatedly with distilled water until the filtrate's pH was below 9, using multiple centrifugation cycles at 4000 rpm for 5 min. Finally, the product was dried overnight at 90 °C.

3.2 Spectroscopic measurement

The elemental compositions of the products were determined using a wavelength-dispersive X-ray fluorescence spectrometer. The X-ray source was an Rh X-ray tube with a collimator size of 150 μm . A sample holder with an optical path diameter of 37 mm was used for measurement. The X-ray generator was operated at 50 kV and 60 mA.

The identity of the zeolite products was confirmed using X-ray diffraction (XRD) on a Bruker D8 ADVANCE with a monochromatic Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$), operated at 40 kV and 40 mA. The samples were analyzed over a 2θ range of 5–50° with a scan speed of 0.2 s/step and an increment of 0.02 °/step.

The morphology of the zeolites was characterized using scanning electron microscopy (SEM-EDX, JEOL JSM-6400) with an accelerating voltage of 20 kV, a vacuum pressure of 10^{-4} Pa, and a tungsten filament. The synthesized samples were spread on carbon tape and coated with gold or carbon. The particle size of the zeolite was analyzed from SEM images using ImageJ software along the X-axis (horizontal), Y-axis (vertical), and Z-axis (depth), with at least three measurements per sample.

The zeolites' functional groups were analyzed using Fourier transform infrared spectroscopy (FTIR) on a Bruker Vertex 70 + RamII FTIR spectrometer in attenuated total reflectance (ATR) mode. The measurements were performed with a resolution of 4 cm^{-1} .

The N₂ adsorption–desorption analysis was performed on a Micromeritics ASAP 2010 analyzer over a relative pressure range of 0.01 to 0.99. Prior to measurement, the zeolite samples were degassed under vacuum at 300 °C for 8 h. Surface areas were determined using the Brunauer-Emmett-Teller (BET) method, while external surface areas, micropore areas, and micropore volumes were calculated using the t-plot method.

CO₂ temperature-programmed desorption (CO₂-TPD) was conducted using a BEL-CAT B chemisorption analyzer to determine the basicity of each adsorbent. Each sample (0.050 g) was placed in a quartz U-tube reactor, pretreated at 500 °C for 3 h under a helium flow of 50 mL/min, and then cooled to 70 °C while maintaining the helium flow. The system was then exposed to 10% CO₂ diluted in helium at a total flow rate of 50 mL/min for 30 min to allow adsorption.

Next, the sample was heated to 100 °C, and purged for 1 h to remove physisorbed CO₂. Finally, the temperature was ramped at a rate of 10 °C/min from 100 °C to 800 °C. The amount of CO₂ absorbed (in mmol of CO₂) was determined online using a thermal conductivity detector (TCD) by comparing the peak area with a calibration curve obtained from a known amount of CO₂ in the injection loop.

The basicity in mmol CO₂ g_{adsorbent}⁻¹ was calculated by

$$\text{Basicity (mmol CO}_2\text{ g}^{-1}) = \frac{\text{CO}_2\text{ adsorbed of sample (mmol)}}{\text{sample weight (g)}}$$

CO₂ adsorption experiments was performed with a method from the literature (Keawkumay et al., 2024). Samples were degassed under vacuum at 300 °C for 3 h to remove adsorbed molecules. Adsorption measurements were conducted at 25 °C over a pressure range of 0–100 kPa using a Quantachrome Autosorb IQ3. Adsorption isotherms were obtained by plotting the amount of CO₂ adsorbed against pressure. The CO₂ adsorption capacity (mmol/g) for each sample was calculated at 100 kPa and 25 °C by converting the adsorbed CO₂ volume to mmol.

3.3 Adsorption equilibrium isotherm equations

This study utilizes four models to investigate the adsorbate-adsorbent interactions: Langmuir, Freundlich, Langmuir-Freundlich (Sips) and Toth models.

The Langmuir model assumes that adsorption takes place at specific, uniform sites on the surface of an adsorbent. Once a site is occupied by an adsorbate, no additional adsorption can occur at that same location.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e$$

where, q_m (mg g⁻¹) is the theoretical maximum adsorption capacity, K_L (L mg⁻¹) is the Langmuir isotherm constant, C_e is the equilibrium concentration (mg L⁻¹).

The Freundlich equation models a non-linear adsorption process over a range of adsorbate concentrations and effectively describes adsorption on surface sites with heterogeneous energy levels.

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f$$

where, K_f (L mg⁻¹) and n represent the Freundlich isotherm constant and heterogeneity factor, respectively.

The Toth isotherm model is a useful modification of the Langmuir model, improving the accuracy of predicted values compared to experimental results by considering sub monolayer coverage. It is used to describe adsorption on heterogeneous surfaces across a wide range of adsorbate concentrations.

$$q_e = \frac{q_m K_T C_e}{[1 + (K_T C_e)^{n_T}]^{\frac{1}{n_T}}}$$

where, q_m represent maximum adsorption capacity (mmol g⁻¹), K_T is Toth isotherm constant (bar⁻¹), n_T is heterogeneity factor (-). If the surface is homogenous, then n_T equals one, indicating that there is no difference in the relative energies of the various adsorption sites.

The Sips isotherm model (Langmuir-Freundlich) is a hybrid of the Langmuir and Freundlich model equations. It was created to predict heterogeneous adsorption systems while overcoming the limitations associated with increasing adsorbate concentrations that arise with the Freundlich isotherm model. Consequently, at low adsorbate concentrations, this model aligns with the Freundlich isotherm, while at

high concentrations, it predicts monolayer adsorption, characteristic of the Langmuir isotherm.

$$q_e = \frac{q_m (K_s C_e)^{\frac{1}{n_s}}}{1 + (K_s C_e)^{\frac{1}{n_s}}}$$

where, q_m is maximum adsorption capacity (mmol g⁻¹), K_s is Sips isotherm constant (bar⁻¹), and n_s is Sips isotherm exponent (-).