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Mesostructured Zeolites Prepared by One-Pot Top-Down Synthesis Route for Carbon Dioxide Adsorption

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With the increasing emphasis on circular economies, biogas has gradually become an important energy source, but the refinement of biogas to reduce CO_2 concentrations and impurities is required. This study reports on a one-pot top-down route to easily obtain mesostructured zeolites for CO_2 adsorption during the biogas refinement process. Combining surfactants with an acid/base treatment achieved a perforation effect and generated mesopores in the zeolite structure. The zeolite structure and the presence of mesopores in the material were confirmed via XRD and a pore-size distribution analysis. The CO_2 adsorption process which took place at room temperature (30 °C) and under various pressures, showed significant improvement in selectivity (CO_2/CH_4) as well as adsorption rate due to the increase in pore size and pore volume obtained via the presence of the mesopores. The adsorption rate constant of the mesostructured zeolite was higher than that of the original zeolite and 92.4 % of the CO_2 capacity can be recovered during a 20 min regeneration in a vacuum at room temperature.

1. Introduction

Biogas is a gas mixture generated from the decomposition of organic substances in an anaerobic environment. It consists primarily of CH_4, CO_2, and small amounts of H_2S, N_2, O_2, and so on. Biogas has attracted worldwide attention due to its economic efficiency and environmental applications, such as renewable energy production (Rupf et al., 2017) and reductions in harmful emissions (Paolini et al., 2018). CO_2 and inert impurities in biogas can cause erosion of the pipes used to transport biogas (Saadabadi et al., 2019) or be emit directly into the environment after the combustion process (Qian et al., 2017). Biogas purification (reducing the concentrations of CO_2 and other impurities) is considered to important when biogas is to be used as a fuel for internal combustion engines as well as in other processes. Purification reduces the CO_2 emission rate and lowers the carbon footprint, while the CO_2 that is removed can be reused in other industries (Li et al., 2017). Physical adsorption is a promising technology for capturing CO_2 and can be accomplished with various adsorbents (microporous organic polymers (Liu et al., 2017), metal-organic frameworks, carbonaceous material (Puthiaraj and Ahn, 2017), and so on.).

These materials have great potential in CO_2 separation, but they also exhibit limitations such as high production costs, further activation costs due to the need for high-temperature heat treatments, and high energy requirements during the desorption process (Sánchez-Zambrano et al., 2018). The development of highly cost-effective adsorbents is needed for this technology to be applied widely in practice.

Zeolites are among the most commonly known adsorbents used in CO_2 capture and gas purification.

The separation of gases with zeolites depends on three factors: the structure and composition of the framework, cationic form, and zeolitic purity (Arami-Niya et al., 2017). Zeolites have large specific surface areas, making them ideal for adsorption, and their uniform pore sizes help prevent larger particles from entering their crystal lattices.

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The electric fields of their structural cations favor the adsorption of gases with large energetic dipoles and quadrupole moments, which means that gases with higher quadrupole moments and polarizability will be adsorbed more easily ($CO_2>N_2>CH_4>H_2$) (Pham et al., 2016). Microporous structures can also significantly reduce the amount of CO_2 adsorbed and result in a long recycling period and high regeneration costs (Chen et al., 2017).

According to the IUPAC definition (Sing et al., 1985), porous materials are divided into 3 types: microporous (<2 nm), mesoporous (2-50 nm), and macroporous (>50 nm) materials. Mesoporous zeolite has significant advantages, including a high specific surface area and large pore size, which can encourage mass transfers to occur faster within its crystal lattice. The energy required for the desorption of the adsorbate from its surface is relatively lower that required for microporous zeolite (Gunawan et al., 2018). Enlarging the pore size can potentially reduce the adsorption selectivity for some specific gases, and the kinetic data associated with the adsorption are rarely mentioned in the literature.

Additional relevant studies are needed to confirm the superiority of mesoporous zeolite in gas separation and purification.

In this study, a one-pot top-down route was used to synthesize mesoporous zeolites from LTA zeolite (LTA-Z) and FAU zeolite (FAU-Z) (Azmi et al., 2019). The modified materials were characterized by physicochemical analysis, and their CO_2 and CH_4 adsorption capacities, adsorption kinetics, and regeneration efficiencies were measured experimentally. The CO_2/CH_4 selectivity and CO_2 adsorption rate constants are also reported.

2. Experiment

The zeolite LTA was synthesized from kaolin following the synthesis procedure of Somderam and colleagues (Somderam et al., 2019). The zeolite FAU (type X) was then prepared by using the procedure in a previous study (Nguyen et al., 2016). The preparation of the mesostructured zeolites was conducted in three steps within a single bottle. Each zeolite was first mixed with H_4EDTA 0.11 M and stirred at 100 °C for 3 h. Then CTAB and NaOH 0.2 M solutions were added to the mixture at a mass fraction CTAB/sample ratio of 2:5. The mixture was stirred at 65 °C for 0.75 h and then stirred at 100 °C for 1 h in the presence of Na_2H_2EDTA 0.11 M. After each step, the liquid was removed by centrifuge and decantation. Each sample was then washed with distilled water and dried at 80 °C for 8 h. Finally, the samples were calcined at 500 °C for 1 h in a static oven.

The crystalline structure of the prepared zeolites was analyzed by X-ray diffraction (XRD, diffraction D8), operating with Cu Kα radiation (=1.5418 Å) at 40 kV and 30 mA. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore size distribution of the materials were determined using the NOVA 2200e Surface area and Pore size analyzer (Quantachrome Corp.). This equipment was also used to measure CO_2, CH_4 adsorption of the prepared zeolites at room temperature (30 °C). Before each experiment, the materials were pretreated at 300 °C for 3 h and were cooled down at room temperature. The process was operated under vacuum condition. In the adsorption kinetics test, the adsorption amount of CO_2 overtime on the mesoporous zeolite as well as the “parent” zeolite was obtained by monitoring the change of CO_2 pressure at room temperature. Between each kinetic measurement, the samples were subjected to vacuum at room temperature for a certain time to check the regeneration condition of the mesoporous zeolites.

3. Results and Discussion

Figure 1a displays the adsorption and desorption curves of the prepared zeolites (FAU-MZ and LTA-MZ). For FAU-MZ, the adsorption/desorption isotherms exhibited a typical type IV curve, which confirmed that capillary condensation was caused by the new mesopores within the material. Figure 1b also shows the pores of FAU-MZ after concentrated denaturation at 3 - 4 nm, which is the size of the mesopores. The external surface area of the modified sample was nearly triple that of the original sample (from 54 m^2/g to 138 m^2/g), and the total pore volume increased significantly (from 0.339 cc/g to 0.508 cc/g). In the case of LTA-Z, after modification, the specific surface area was significantly reduced from 613 to 82 m^2/g, and the total pore volume decreased from 0.260 to 0.087 cc/g. LTA-Z may have lost its crystalline structure during the preparation process.

Figure 2 indicates that FAU peaks were generally present in FAU-Z and FAU-MZ, confirming the preservation of the crystal structure after the preparation of FAU-MZ. The absence of LTA peaks was observed in LTA-MZ, which showed that the crystalline structure of LTA-Z probably collapsed after the modification. The top-down method used in this study can be used to modify the FAU-Z but not LTA-Z.

Figure 3a illustrates CO_2 adsorption of the zeolites and the mesostructured zeolites. In the case of FAU-Z, it can be seen that the “parent” zeolite and the modified zeolite have nearly similar CO_2 capacities under the testing conditions. At a pressure of around 1 atm, the FAU-MZ can adsorb 74.2 $mL_{(CO2)}$/g, FAU-Z can adsorb 69.6 $mL_{(CO2)}$/g. For comparison, under similar adsorption conditions, the CO_2 adsorption capacities of other measured zeolites are 65.34 $mL_{(CO2)}$/g (Regufe et al., 2018) and 44.72 $mL_{(CO2)}$/g (Arami-Niya et al., 2017).

The FAU-MZ and FAU-Z samples have shown somewhat higher CO_2 adsorption capacities. The CO_2 adsorption capacity was significantly lower in the mesostructured LTA in comparison to the "parent" LTA zeolite. At a pressure of around 1 atm, the LTA-MZ can adsorb 6.7 $mL_{(CO2)}$/g, the LTA-Z can adsorb 26.4 $mL_{(CO2)}$/g. The CO_2 adsorption capacities of the FAU-Z and FAU-MZ are much higher than those of LTA-Z and LTA-MZ. LTA-Z had pore sizes of ~ 0.4 nm while FAU-Z had pore sizes of ~ 0.7 nm. The difference in their CO_2 adsorption capacities may be due to the difference in their pore structures.

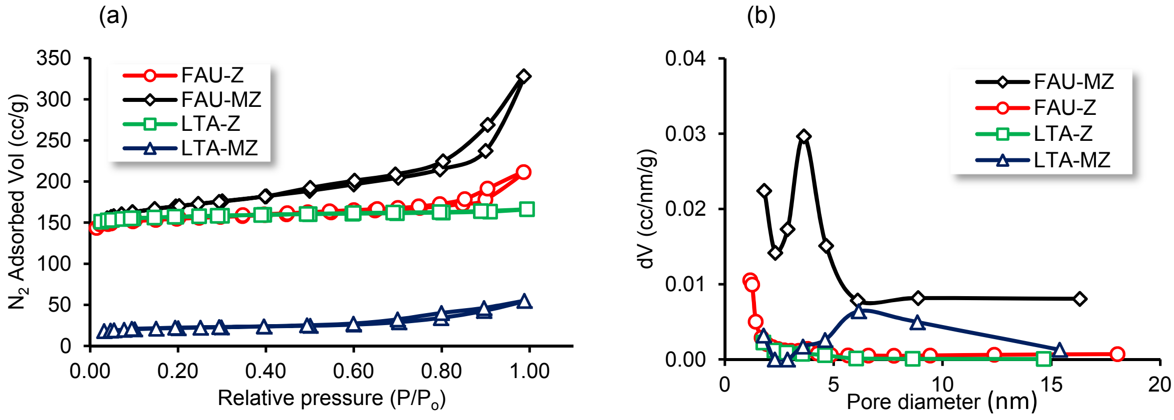

Figure 1: (a) N_2 adsorption-desorptioncurves and (b) BJH pore size distribution of the prepared zeolites

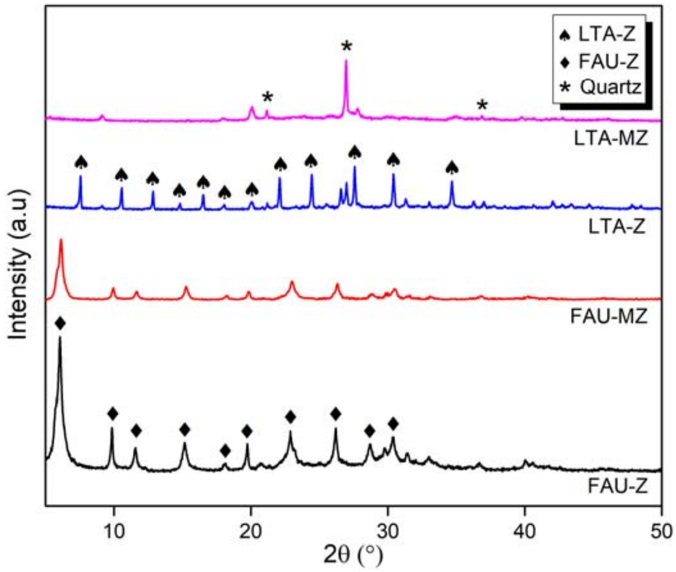

Figure 2: XRD patterns of FAU-Z, LTA-Z, mesostructured FAU-MZ and LTA-MZ

The capacities of FAU-Z and FAU-MZ for CH_4 adsorption are shown in Figure 3b and indicate that both samples adsorbed a much lower amount of CH_4 than of CO_2. At a pressure of around 1 atm, FAU-MZ can adsorb 7.4 $mL_{(CH4)}$/g, while FAU-Z can adsorb 9.4 $mL_{(CH4)}$/g. The kinetic diameter of the CO_2 is 0.33 nm, while that of the CH_4 is 0.38 nm (Kulprathipanja, 2010). CO_2 is more condensable than CH_4 since its critical temperature is 31.1 °C, which was much higher than that of CH_4 (-73.6 °C). Higher adsorption capacities for CO_2 have been observed on the micropores/mesopores of the FAU zeolite.

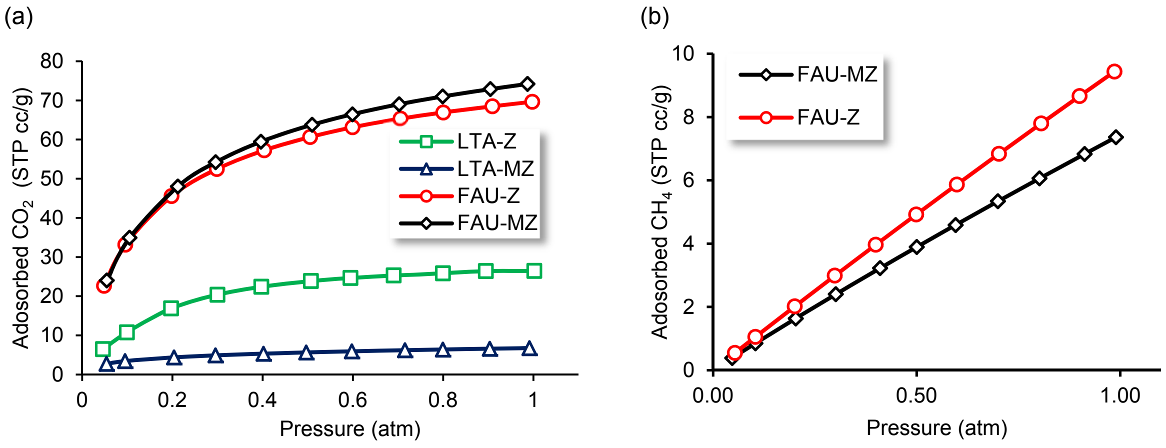

Figure 3: CO_2 adsorption on (a) zeolites and mesostructured zeolites at 30 °C and (b) CH_4 adsorption on zeolite FAU and mesostructured zeolite FAU

The CO_2/CH_4 selectivity was calculated by using ideal adsorption solution theory (IAST) (Walton and Sholl, 2015). The results of the selectivity calculations are shown in Figure 4. The CO_2 concentration of the gas mixture affected the CO_2/CH_4 selectivity. In particular, for FAU-Z, the CO_2/CH_4 selectivity dropped from 36 to 12 when the CO_2 molar fraction increased from 0.1 to 0.5. Similarly, in the case of FAU-MZ, the selectivity changed from 47 to 16 when the CO_2 molar fraction increased from 0.1 to 0.5. Noticeably, the selectivity of FAU-MZ was higher than that of FAU-Z for all the reported CO_2 molar fractions. Higher selectivity, in practice, can lead to lower CH_4 loss during the adsorption process. The higher selectivity of FAU-MZ makes this material better for biogas purification.

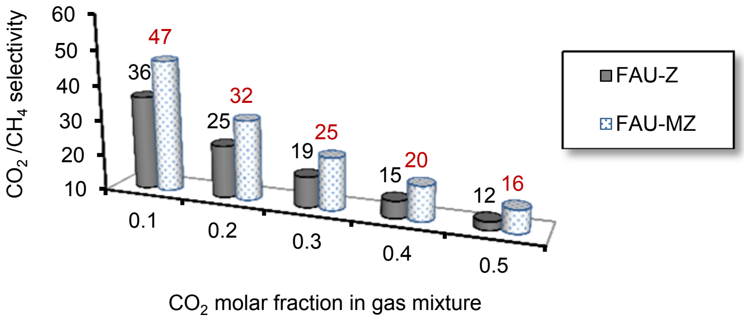

Figure 4: Adsorption selectivity of zeolite FAU and mesostructured zeolite FAU

Time was a vital factor in evaluating the kinetics of the adsorption process, and the results are shown in Figure 5. The saturated adsorption time of FAU-MZ was approximately 100 s, while it took FAU-Z quite a bit more time to reach saturation (about 150 s). This time could be referred to as the preparation of FAU-MZ to obtain a mesoporous structure, leading to the easy diffusion of CO_2 into the material. FAU-MZ possesses a fast adsorption rate compared to the rate for FAU-Z. Two kinetic models have been tested for FAU-MZ's CO_2 adsorption:

Pseudo 1st-order: $dq_t/dt = k_1(q_e - q_t)$

Pseudo 2nd-order: $dq_t/dt = k_2(q_e - q_t)^2$

The kinetic parameters of the adsorption process are shown in Table 1. Base on the R-square values, it can be concluded that the pseudo 1st-order model is more appropriate than the pseudo 2nd-order model for both the mesostructured zeolite and "parent" zeolite. In particular, the rate constant (k_1) of FAU-MZ and FAU-Z are 0.0319 (1/s) and 0.0279 (1/s). The adsorption rate of FAU-MZ is clearly higher than that of FAU-Z.

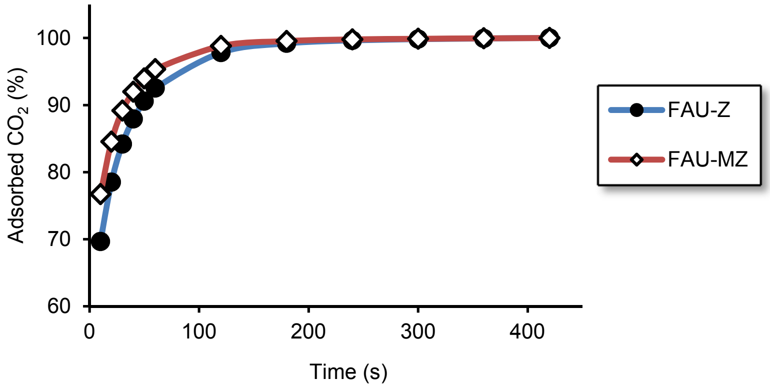

Figure 5: Time's effect on CO_2 adsorption of zeolite FAU and mesostructured zeolite FAU

Table 1: Kinetic parameters of the CO_2 adsorption process of FAU-Z and FAU-MZ

Sample	Pseudo 1st order		Pseudo 2nd order	
	k_1 (1/s)	R^2	k_2 (1/s(mmol/g))	R^2
FAU-Z	0.0279	0.9943	0.384	0.9350
FAU-MZ	0.0319	0.9927	1.417	0.9249

Figure 6 shows the effect of regeneration (vacuum time) on the recovery of the CO_2 adsorption capacities of FAU-Z and FAU-MZ. It can be seen that the recovery percentage is higher for FAU-MZ than it is for FAU-Z. For example, the FAU-MZ recovered 83.6 % of its capacity after regeneration in a vacuum for 5 min, while FAU-Z recovered 78.2 % of its capacity under the same conditions. Remarkably, both materials have fast regeneration. After 20 min under a vacuum at room temperature, about 90 % of the CO_2 adsorption capacity can be recovered in both samples.

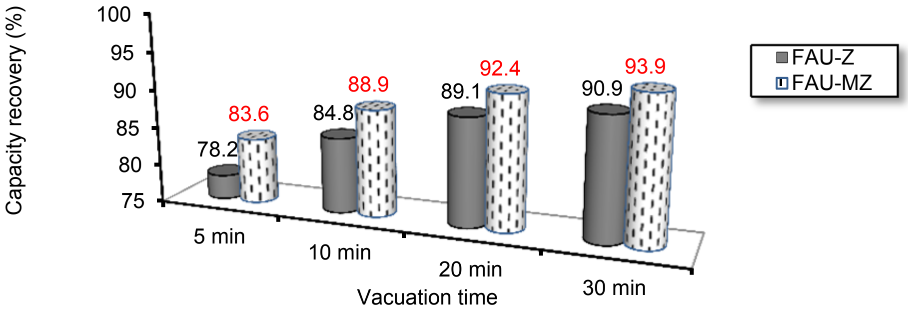

Figure 6: Time's effect on the CO_2 capacity of the regenerated zeolite FAU and mesostructured zeolite FAU

4. Conclusions

In this study, mesostructured FAU zeolite was successfully prepared via the one-pot top-down method using some common chemicals. The obtained zeolite material possessed mesopores (3 - 4 nm) while retaining its structure. Higher CO_2/CH_4 selectivity and a higher adsorption rate constant have been obtained for the mesostructured zeolite in comparison with the original zeolite. The mesostructured FAU zeolite also exhibited a fast regeneration time under a vacuum. This material can recover over 90 % of its CO_2 adsorption capacity under a vacuum at room temperature in approximately 20 min. The one-pot top-down method was not suitable for LTA zeolite, and further improvements will be necessary in future research.

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