

Improving CO₂ adsorption with new amine-functionalized Y-type zeolite

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ABSTRACT

In this work, a new synthesized Y-type zeolite with an Si/Al molar ratio of 2.5 (NaY) was modified with amines, in order to probe the influence of the modification of the adsorbent's surface on CO₂ adsorption. The three selected amines were diethanolamine, tetraethylenepentamine, and 2-methylaminoethanol. The surface nature of NaY was changed after amine modification, which causes a significant increase in the CO₂ adsorption capacity. The CO₂ adsorption capacity of the amine-modified NaY increased with temperature. The mechanism of CO₂ adsorption on NaY is usually a physical interaction, but it seems that after amine modification, chemical mechanism is the dominant mechanism for the chemical interaction between CO₂ and amine groups. The adsorbents were characterized by surface area and porosity analysis, X-ray diffraction, Fourier transform infrared spectroscopy, thermal gravimetric analysis, and scanning electron microscopy. The CO₂ adsorption capacity was measured by the volumetric method at 298 and 348 K. The CO₂ adsorption capacity of TEPA-NaY, DEA-NaY, and 2-MAE-NaY at 298 K was 60.63. The CO₂ adsorption capacity of TEPA-NaY, DEA-NaY, and 2-MAE-NaY at 348 K were 92.9, 78, and 85.42, respectively. These results showed that amine-functionalized NaY zeolites have excellent adsorption potential for CO₂ adsorption at high temperatures.

Keywords: CO₂ Adsorption, Y-Type Zeolite, amine modification, chemisorption, physisorption.

Introduction

The rapid expansion of industrialization on earth has caused serious problems in the environment like the greenhouse effect leading to global warming. Carbon dioxide, chlorofluorocarbons, N₂O, and methane are the major greenhouse gases. However, the major cause is carbon dioxide. CO₂ behaves like a blanket and entraps the infrared radiations coming from the earth's atmosphere and results in an increase in the earth's surface temperature. The concentration of CO₂ has increased from about 280 ppm to the current amount of 380 ppm.¹ The development of CO₂ capture and

separation technologies is the solution to overcome this global problem. Amine-based chemical absorption has been used commercially for CO₂ removal in industries.² However, the liquid amine-based processes have a number of disadvantages, including the need for a large equipment size and high regeneration energy.³ Therefore, as an alternative approach, CO₂ capture with solid sorbents has attracted much attention in the recent years.⁴⁻⁸ The solid sorbents for CO₂ capture include carbon molecular sieves,^{9,10} alkali-based sorbents,¹¹ activated carbons,¹² carbon nanotubes,^{13,14} polymers,^{15,16} zeolites,¹⁷⁻²⁰ and metal-organic frameworks (MOFs).²¹⁻²⁵ However, in these adsorbents, physical adsorption is the main factor in the adsorption of CO₂. It has been observed that the adsorption capacity decreases as the temperature increases. Consequently, these adsorbents should be

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modified so as to make easy chemical adsorptions on these adsorbents. Thus, there is an increasing need to design highly selective adsorbents, which can work at high temperatures.²⁶ An efficient technique is the integration of organic amines into porous supports for CO₂ adsorption.^{27,28}

This work explores the modification of the surface of a new synthesized Y-type zeolite by amine functional groups. Diethanolamine (DEA), tetraethylenepentamine (TEPA), and 2-Methylaminoethanol (2-MAE) have been selected as modification materials for NaY zeolite. The objectives of this study are to explore the adsorption capacity of the amine-modified zeolites using the volumetric method, and to analyze the microstructures and properties of the modified zeolite. The effect of the temperature at 25 °C and 75 °C on the CO₂ adsorption is also discussed.

Materials and Methods

Experimental section

Fumed silica and sodium aluminate (Merck) were used as silica alumina sources, respectively. Deionized (DI) water and sodium hydroxide (NaOH > 99.999%, Merck) were also

used to prepare a synthetic solution of zeolite. The amines used for the modification of the adsorbents were DEA (Merck), TEPA (Merck), and 2-MAE (Merck). The solvent used was methanol that came from Merck.

Synthesis of Sorbents

NaY zeolite was synthesized with an Si/Al molar ratio of 2.5. A synthesis mixture with a molar composition of Al₂O₃: 3 Na₂O: 5 SiO₂: 200 H₂O was used. Amine-modification of NaY zeolites by using the impregnation method was carried out under different approaches (Table 1). The amine solutions with a concentration of 10 wt % were prepared in methanol. The adsorbents were wetted with methanol prior to an agitation with the amine solutions, by agitating NaY-zeolite powder and methanol in a solid-to-liquid ratio of 1:2 for a period of 60 min. The wetted zeolites were air-dried and were kept in contact with the solutions under agitation at ambient temperatures, as recorded in Table 1. Finally, the NaY-zeolite powders were separated from the solution through filtration and were then dried in an oven at different temperatures for 3 hours (See Table 1).

Table 1. Summary of amine impregnation conditions on NaY zeolite

Adsorbent	Amine	Time of immersion in impregnate solutions	Solid liquid ratio	Drying temperature (°C)
NaY zeolite	DEA	30 min	1:2	110
	TEPA	120 min	1:10	140
	2-MAE	30 min	1:2	100

Characterization of adsorbents

The crystal phase of the prepared adsorbents was characterized by an X-ray diffraction (XRD) using the Philips 1830 diffractometer with a Cu-K radiation source. The XRD patterns were obtained in the 2θ range of 5–40 with a 2θ step size of 0.018 and a step time of 1 s. The surface functional groups of the adsorbents were evaluated by the Fourier transform infrared spectroscopy (FTIR) (DIGILAB FTS 7000 spectrometer). The thermal stability of the adsorbents in the air was determined by a thermo gravimetric analyzer (Mettler Toledo 851) at a heating rate of 10 °C per minute at 30–800 °C. Scanning electron

microscopy SEM (KYKY-EM3200) was used to examine the morphology of the zeolites. The porosity characteristics of the zeolites were determined by N₂ adsorption–desorption isotherms. Experiments were performed at 77 K on a micromeritics model ASAP 2010 sorptometer. This method gives data on the specific surface area and the pore diameters. The specific surface area was determined using the BET method.

CO₂ adsorption measurement

The adsorption capacity of the zeolites was evaluated using a volumetric method by the setup shown in Figure 1. At first, 0.5 g of a

sample was loaded in the sample cell (13) and attached to the system. The existing gas inside the system was swept out with helium. For degassing the system, the valves 3, 4, 5 and 6 were closed and the other valves were opened. Then, the vacuum pump was turned on and the system was vacuumed at a heating temperature of 120 °C for 1.5 h. After degassing, the system was cooled to the experiment temperature. Ultra-high purity carbon dioxide (99.999%) was introduced into the adsorption unit for the CO₂ adsorption measurements. To perform an adsorption test, the valve of the CO₂ cylinder

was opened and the CO₂ pressure was regulated at the desired value. Valves 7 and 8 were then opened to reach a pressure balance in the reference cell (12). Afterwards, valve 10 was immediately opened and the pressure decrease was recorded. The pressure of the adsorption cell decreased due to some dead volume and some CO₂ adsorption. The portion of the dead volume was calculated via helium tests and subtracted from the total pressure change. Finally, the exact pressure decrease resulting from the CO₂ adsorption could be calculated.

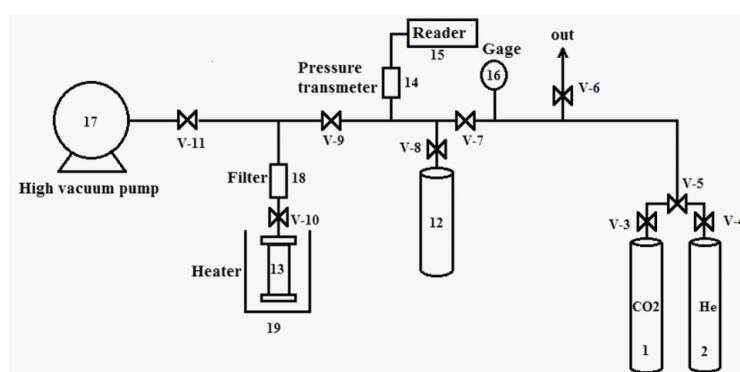


Fig. 1. Schematic diagram of volumetric set up for adsorption test

Results and Discussion

Adsorbent Characterization

The XRD patterns of NaY and amine-modified NaY zeolites are displayed in Figure 2. The XRD patterns of zeolite did not change significantly after the amine attachment, implying that the pore structure order was not affected by amines. However, the intensity of

the diffraction peak became slightly weak. The peak intensity is a function of the scattering contrast between the zeolite walls and pore channels and decreases with the decreasing scattering contrast after the attachment of amino groups to the pore surface. Hence, the observed decrease of the XRD peak intensity is probably due to the pore filling by amine groups.²⁹

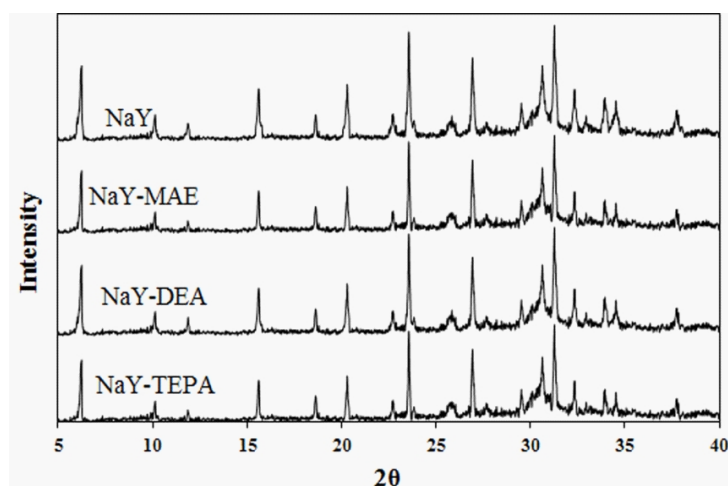


Fig. 2. XRD patterns of the NaY before and after different amines loading

The FT-IR spectra of NaY and Amine-attached NaY samples are shown in Figure 3. The amine-NaY differed from the pure NaY and exhibits several peaks. After the NaY was modified, the adsorption peaks at 1500–1600 cm^{-1} were associated with the stretching vibrations of $-\text{NH}_2$. The absorption band at 2800–2900 cm^{-1} represents the stretching of CH from the $\text{CH}_2\text{CH}_2\text{CH}_2\text{-NH}_2$ groups. Thus, the IR spectra of the amine-modified NaY confirmed the integration of amine inside the NaY channels.

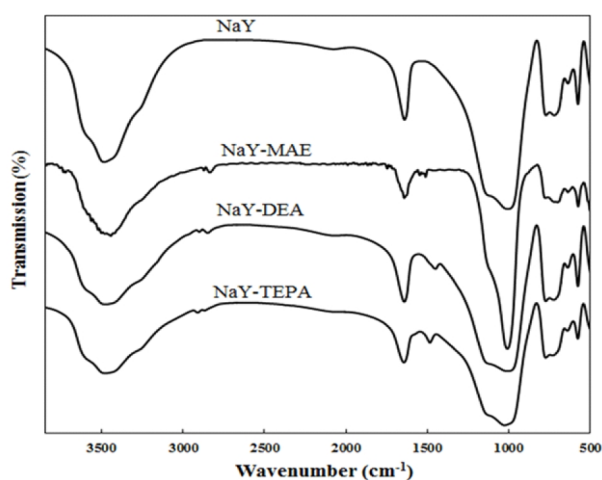


Fig. 3. IR spectra of NaY and amine-modified NaY

Figure 4 shows the TGA of the NaY modifying with the different kinds of amines. The samples were heated from 30 °C to 800 °C by a speed of 10 °C per minute. The TGA profile of NaY shows a weight loss that occurred near 100 °C and a sharp weight loss that appeared at 150 °C and could be attributed to the desorption of moisture. The heating of pure NaY from 150 to 800 °C underwent much weight loss

indicating the high thermal stability of NaY. The TEPA, DEA, and 2-Methylaminoethanol had flash points of 193 °C, 138 °C and 76 °C, which indicate that both TEPA-NaY and DEA-NaY have two weight losses. The first weight loss region (for TEPA-NaY <120 °C and for DEA-NaY <100 °C) is due to the evaporation of the adsorbed water. The second region (for TEPA-NaY 120-200 °C and for DEA-NaY 100-150 °C) can be mainly attributed to the elimination of $-\text{NH}_2$. NaY modified with 2-Methylaminoethanol has only one weight loss prior to reaching 100 °C that is due to the evaporation of the adsorbed water and the elimination of $-\text{NH}_2$.

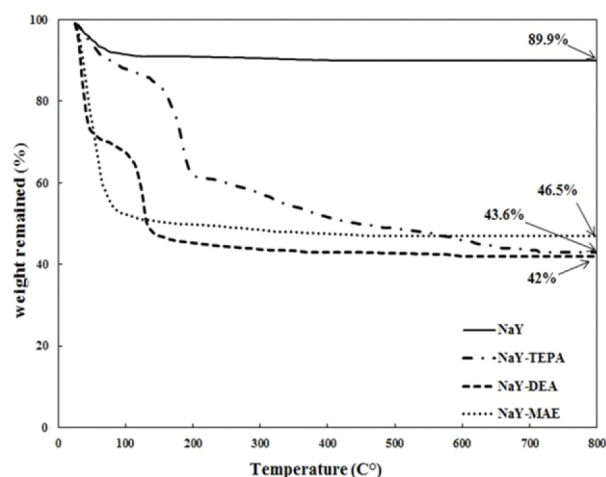


Fig. 4. TGA curves of NaY and amine-modified NaY

The SEM images of NaY and TEPA-NaY under a magnification of 20,000 at 25 KV acceleration voltage have been shown in Figure 5. The result of the SEM confirmed that the TEPA-NaY was grafted successfully by the amine groups.

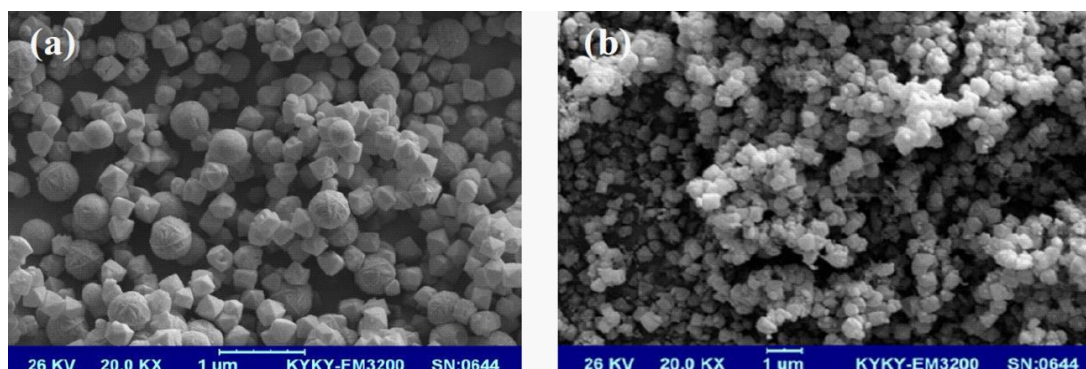


Fig. 5. SEM images of NaY before and after TEPA loading (a): NaY, (b) TEPA- NaY

Nitrogen physisorption is a method that gives the information about porous materials, such as the specific surface area and the pore diameters. The Barrett-Joyner-Halenda (BJH) method is based on the pore condensation phenomena which is applicable only for the mesoporous or microporous materials. Figure 6 illustrates the nitrogen adsorption-desorption isotherms of NaY and TEPA-NaY. As seen in Figure 6, N₂ adsorption isotherms are classified as Type I, in accordance with the characteristics of microporous materials. The structural properties of the samples are listed in Table 2. After amine modification, the nitrogen adsorption isotherm becomes an even line and the volume adsorbed decreases, distinctly. Also, an obvious reduction of the BET surface area and pore volume were observed, which confirms that amines have occupied the pores in the zeolite.

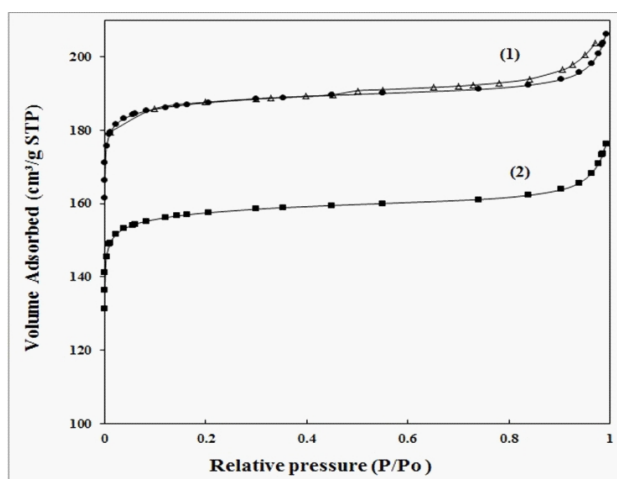


Fig. 6. N₂ adsorption-desorption isotherms of NaY (1) and TEPA- NaY (2) powders at 77 K

Table 2. Structural properties of NaY and TEPA- NaY

Adsorbent	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Mean pore diameter (Å)
NaY zeolite	212	0.213	7
TEPA- NaY	172	0.148	5.64

CO₂ Adsorption Measurement

The adsorption isotherms of CO₂ at 298 K and 348 K on NaY zeolite and amine-modified NaY zeolite are shown in Figure 7. As expected, these isotherms show a sharp increase in the CO₂ uptake at low partial pressures reaching a constant plateau at higher pressures. As is clear

from the adsorption isotherms, the amine-modified NaY zeolites present a lower CO₂ uptake at low temperatures as compared to the NaY zeolite. The reduction in the textural characteristics can justify the lower CO₂ uptake (see Table 2). As shown in Table 3, the CO₂ adsorption capacity of the NaY zeolite drops with an increase in the temperature. For modified zeolites at 298 K, the adsorption capacities are lower than that of unmodified zeolites. At low temperatures, physisorption is a dominant process and the adsorption capacity is directly proportional to the surface area of the adsorbent. With amines loading, the surface area of zeolite was reduced, significantly. This explains the decreased adsorption capacity of the modified zeolites at 298 K despite amine loading. The modified zeolites adsorb more CO₂ at 348 K. As the adsorption temperature is increased, chemical reactions occur between the amino groups and CO₂ to produce the carbamate species according to the following equations:



This adsorption behavior could be attributed to a strongly diffusion-controlled process. In other words, more sites inside the particles can react with CO₂ only when the CO₂ is diffused into the particles. At low temperatures, CO₂ would diffuse quite slowly in amine-loaded adsorbents and its uptake would seem unusually low, whereas at high temperatures, the kinetics of the reaction becomes significant and the adsorption capacity increases with the temperature. In the case of CO₂ capture from flue gas, which itself is at a higher temperature, it is important to have a higher adsorption capacity even at higher temperatures, and the amine-modified NaY zeolite shows promising results.

Comparison of the CO₂ adsorption capacities of the amine modification zeolites and other porous materials have been given in Table 4.

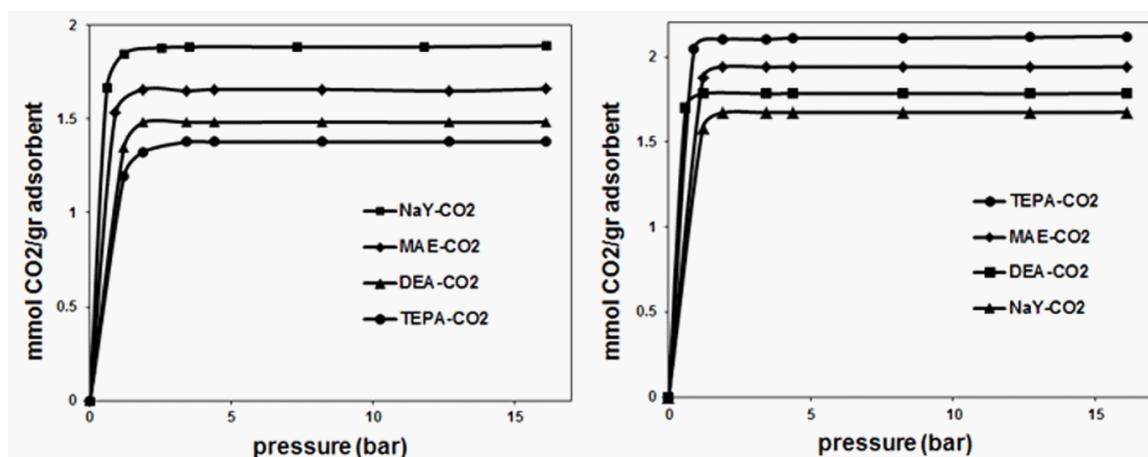


Fig. 7. Adsorption isotherms of CO₂ in pristine and modified zeolites at 298 K (a) and 348 K (b)

Table 3. CO₂ adsorption capacity of pristine and modified zeolites at two temperatures

Adsorbent	CO ₂ adsorption capacity (mg/g)	
	298 K	348 K
NaY zeolite	82.8	73.51
TEPA-NaY	60.63	92.9
DEA-NaY	65.21	78
2-MAE-NaY	72.93	85.42

Table 4. Comparison of the CO₂ adsorption capacity of the amine modification zeolites with other porous materials.

Adsorbent	CO ₂ adsorption capacity (mg/g)	Condition	Reference
Zeolite 13X	37.33	348 K	1
13X/MEA	48.64	348 K	1
MCM-48-PEHA-DEA	22.44	298 K	30
SAOP-43	47.08	298 K	31
ZSM-5	47.52	313 K	32
NaY zeolite	82.80	298 K	This study
NaY zeolite	73.51	348 K	This study
TEPA-NaY	92.90	348 K	This study

Conclusion

In this study, NaY Zeolite has been impregnated with DEA, TEPA, and 2-methylaminoethanol from methanolic solutions. The samples are characterized by BET, XRD, TGA, SEM, and FT-IR methods. Following the modification by TEPA, the BET surface area of NaY decreases from 212 m²/g to 172 m²/g. The nitrogen adsorption isotherm becomes an even line and the volume adsorbed decreases. This phenomenon suggests the occupation of the

pores by amine. The amine-modified adsorbents have also been evaluated for their CO₂ adsorption capacities and it has been observed that the amine-modified zeolites adsorb less than the pristine material at low temperatures, but their CO₂ uptake increases with a rise in the temperature. Therefore, it can be concluded that the mechanism of the CO₂ adsorption on NaY is entirely a physical interaction process but appears mainly attributable to a chemical interaction after the amine modification. This

suggests that the amine-modified NaY zeolites can be employed in the process of CO₂ capture from flue gas which is performed at high temperatures.

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