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CO_2 capture on diethanolamine-grafted NaY zeolite

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In this study, NaY zeolite with molar ratio Si/Al=2.5 was chemically grafted with diethanolamine (DEA) and was characterized by XRD, IR, TGA, FE-SEM, EDAX, N_2-BET and CO_2-TPD. After grafting and changing in surface nature of NaY a significant increase in CO_2 adsorption capacity was registered. As the temperature raises the CO_2 adsorption capacity increases. The mechanism of CO_2 adsorption on NaY is usually a physical interaction, but it seems that after amine functionalization, the chemical mechanism is dominant for the interaction between CO_2 and amine groups. The adsorbents were characterized by CO_2-TPD technique. The results showed that the functionalized NaY zeolites have an excellent potential for CO_2 adsorption at high temperatures.

Keywords: NaY, diethanolamine, grafted amine, CO_2-TPD

INTRODUCTION

The concentration of CO_2 in the Earth's atmosphere is about 380 ppm, [1]. After Industrial Revolution an increase of approximately 110 ppm was registered [2]. The combustion of fossil fuels is the main source of energy for many years to come [3]. However, as more fossil fuels are combusted, the amount of greenhouse CO_2 emitted to the atmosphere will continue to increase, leading to global climate change from which we have already started seeing the consequences [4]. The development of CO_2 capture and separation technologies is the solution of this global problem. Aqueous amines have been used commercially for CO_2 removal in industries [5]. However, amine-based homogeneous chemical absorption as have disadvantages, including the need for a large equipment size and high regeneration energy [6]. Therefore, as an alternative selection, CO_2 capture with solid sorbents (heterogeneous adsorption) has attracted much attention in recent years [7,8]. Solid adsorbents are acceptable candidates because the significantly smaller heat capacities of solids may reduce the heat required for regeneration. In addition, solvent loss and corrosion problems resulting from the use of aqueous amines would be minimized if solid adsorbents were utilized instead [9]. Currently, aqueous amines are used industrially to separate CO_2 from gas mixtures with high CO_2 partial pressures like natural gas, but solid adsorbents are used to remove CO_2 from mixtures with very low CO_2 partial pressures. Amine-modified porous silica can be divided in two classes according to the different synthesis methods, namely impregnation and grafting. For the impregnated adsorbents, high adsorption capacity for CO_2 can be achieved by loading a large amount of amines onto the support. However, weak interaction between amines and supports leads to poor thermal stability of these materials, which spoiled their application in practical processes [10]. By contrast, the grafted ones are more stable, due to the formation of chemical bonds between the surface silanols of silica and the aminosilanes. Mesoporous silicas and zeolites with different pore structures have been employed to synthesize various amine-grafted adsorbents [11,12].

Temperature-programmed desorption (TPD) is a sensitive technique for characterization of the interaction between adsorbed molecules and solid surface [13-15]. It is one of the most straightforward surface science experiments for the determination of the thermodynamic and kinetic parameters of a reaction and it can be a measure of the amount of chemisorption [16]. In this study after grafting NaY zeolite with diethanolamine we used CO_2-TPD technique to determine the chemisorbed amount of CO_2 on NaY and amine-functionalized NaY.

EXPERIMENTAL

Chemicals and reagents

Analytical grade $CHCl_3$, 3-(chloropropyl)-trimetoxysilane, diethanolamine were obtained from Merck Company (Germany). NaY nanozeolite with Si/Al=2.5 was purchased from Zeolyst Company (USA). Deionized water was used to prepare all solutions.

Instruments

The characterization of the crystal phase of the synthesized adsorbents was performed by means of

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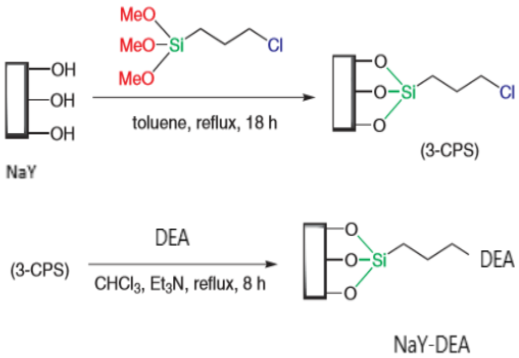
X-ray diffraction (XRD) with the Philips 1830 instrument. The surface functional groups of the adsorbents were assessed using Fourier transform infrared spectroscopy (FTIR) (DIGILAB FTS 7000 spectrometer). Scanning electron microscopy FE-SEM (KYKY-EM 3200) was applied for investigating zeolites' morphology. Thermal program desorption of functionalized zeolites measured by Belcat-A. Micromeritics BET (Brunauer, Emmett and Teller) was used to measure the specific surface area of a sample comprising the pore size distribution.

Thermogravimetric analysis (TGA) of adsorbents was performed using the TGA 8000 Perkin Elmer instrument by scanning up to 800 ºC with a heating rate of 10 ºC/min.

Experimental methods

NaY zeolite and 3-(chloropropyl)-trimetoxysilane were used for synthesis of 3-CPS. The amine used for the modification of the adsorbents was diethanolamine (DEA) (Scheme 1).



Scheme 1. Preparation of functionalized NaY zeolite.

DEA was chemically grafted on NaY zeolites. Finally, the NaY zeolite powders were separated from the solution through filtration and were dried in an oven at 50-60 ºC for 1 hour.

RESULTS AND DISCUSSION

The XRD patterns of NaY and DEA-grafted NaY zeolites are displayed in Fig. 1. The XRD patterns of the zeolite did not change significantly after the amine attachment, however, a decrease in the intensity of the signal located in the 6.0-6.5 range of the 2θ scale reported in the case of silica was attributed to the stress caused by the presence of the amines within the pores of the silica, in this case, of the NaY zeolite.

The FT-IR spectra of NaY and amine-grafted NaY samples are shown in Fig. 2.

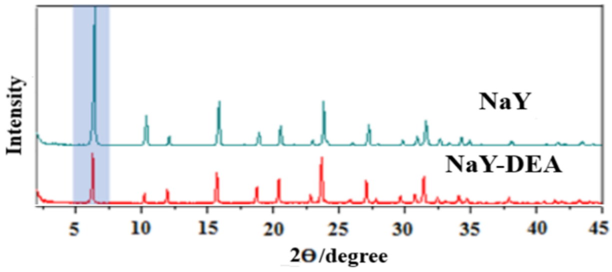


Figure 1. XRD patterns of NaY before and after amine grafting.

The amine-NaY spectra differed from those of pure NaY and showed several peaks. After modification of NaY, the adsorption peaks at 1500–1600 cm^{-1} were related to the stretching vibrations of -NH_2. The absorption band at 2800–2900 cm^{-1} shows the stretching of CH from the $CH_2CH_2CH_2NH_2$ groups. Therefore, the IR spectrum of the amine-modified NaY proved the absorption of amine inside the NaY channels.

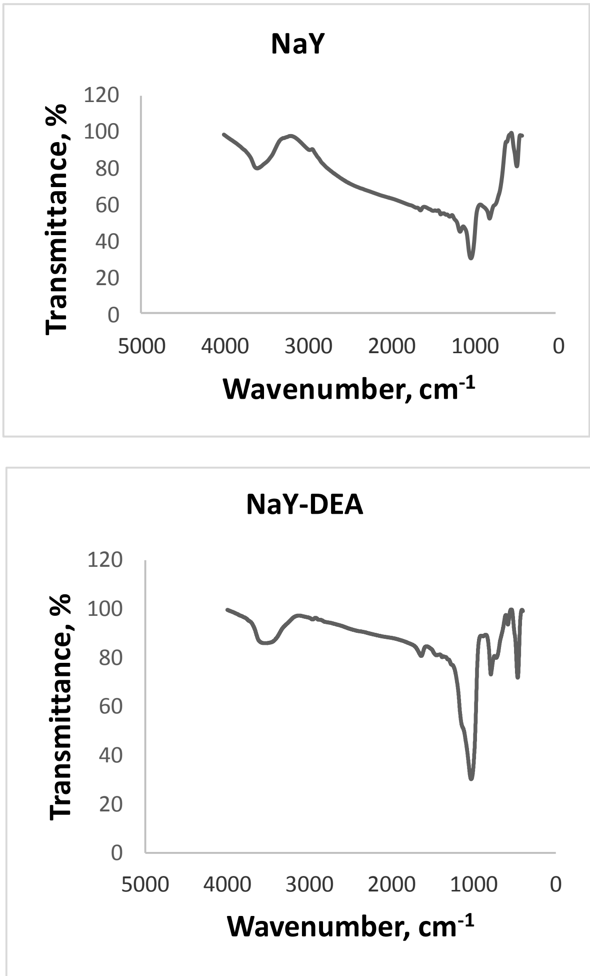


Figure 2. FT-IR spectra of NaY and NaY-DEA

Figure 3 represents the FE-SEM images corresponding to NaY, NaY-DEA with a magnification of 25 000 at 25 KV acceleration voltage. The outcome of FE-SEM showed that the NaY-DEA was grafted effectively by the amine groups. The results of the EDAX analysis of NaY and NaY-DEA are shown in Table 1, confirming that the amines are successfully grafted.

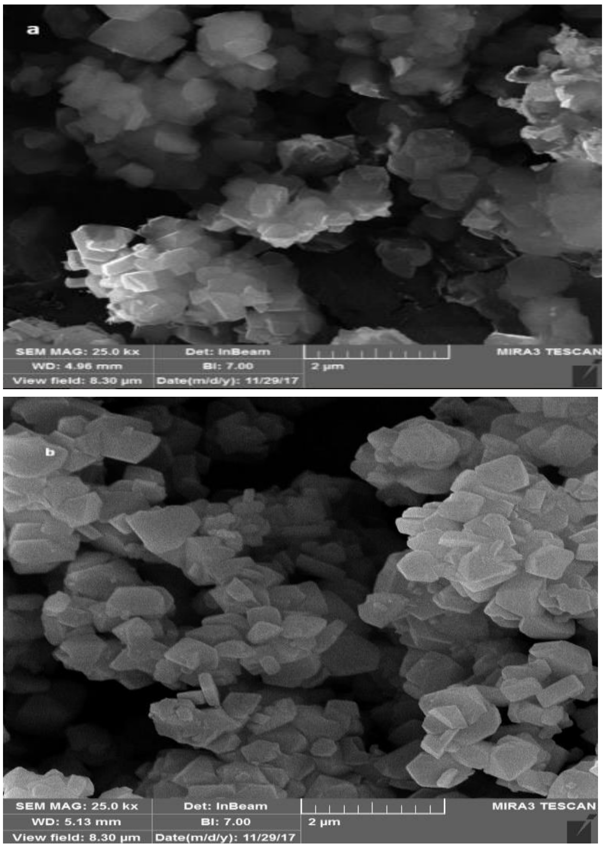


Figure 3. E-SEM images corresponding to (a) NaY, (b) NaY-DEA .

Table 1. EDAX information corresponding to NaY- and amine- modified NaY

Element Adsorbent	O Wt%	Na Wt%	Al Wt%	Si Wt%	N Wt%	C Wt%
NaY	61.42	6.18	7.76	24.64	0	0
NaY-DEA	37.44	6.01	7.76	22.92	2.64	23.23

Nitrogen physisorption is a technique which provides information about porous materials, like specific surface area and pore diameters. In physisorption tests, an activated porous or excellently divided solid is equilibrated with a permanent gas like nitrogen or a vapour at a fixed temperature [17,18].

The Barrett-Joyner-Halenda (BJH) technique on the basis of pore condensation phenomena is appropriate only for mesoporous or microporous materials (Fig. 4).

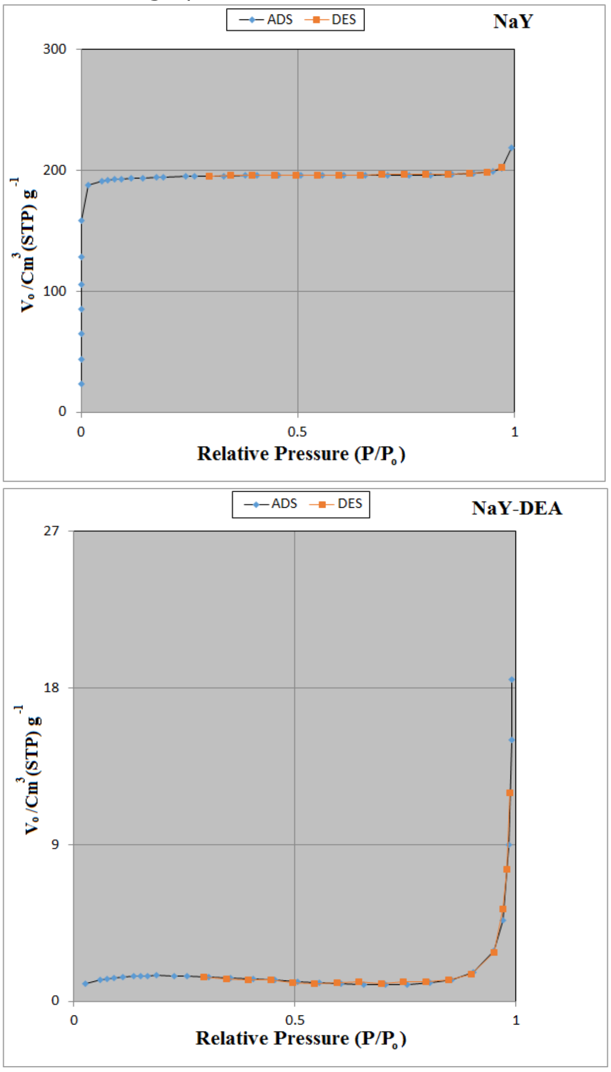


Figure 4. N_2 adsorption–desorption isotherms corresponding to NaY and amine-grafted NaY.

The structural features of the samples are represented in Table 2.

Table 2. Structural properties of NaY and amine-modified NaY

Adsorbent	BET Surface Area (m^2 g^{-1})	Pore Volume (cm^3g^{-1})	Mean Pore Diameter (nm)
NaY	810.64	0.336	1.658
NaY-DEA	5.45	0.025	18.384

Following the modification by the amine, the nitrogen adsorption isotherm becomes a straight line and the adsorbed volume reduces clearly. Furthermore, the BET surface area and pore volume are clearly reduced, which proves the occupation of the zeolite pores by amines.

To determine the amount of zeolite desorption a thermal desorption technique is suitable (Fig. 5).

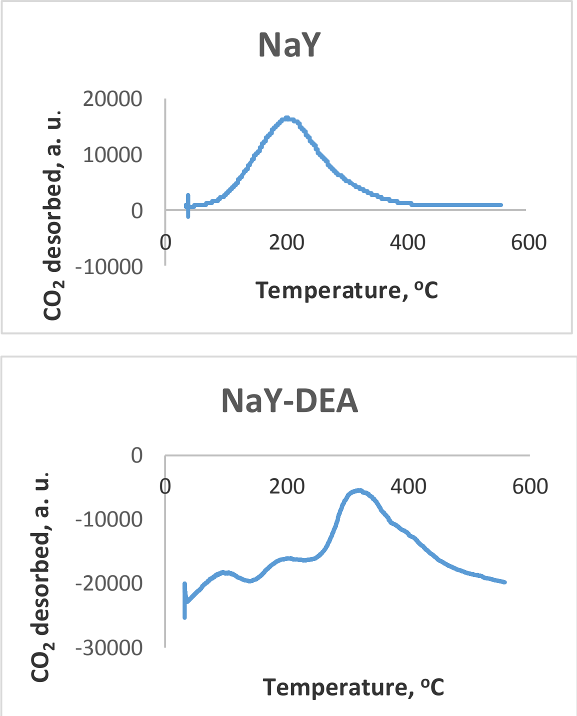


Figure 5. CO_2-TPD isotherms corresponding to NaY and NaY-DEA

The TPD-CO_2 technique was used for this study (Table 3).

Table 3. CO_2-TPD of NaY and amine-modified NaY

Adsorbent	Temp(^{0}C)/CO_2 desorption capacity(mmol/g)		
NaY	202^{0}C		
	2.174		
NaY-DEA	94^{0}C	202^{0}C	320^{0}C
	0.353	0.509	2.899

CO_2-TPD measurements were carried out to determine the chemisorbed amount of CO_2 on NaY and amine-functionalized NaY [19]. The adsorbent was first pre-treated at 120°C for 60 min in a He flow of 50 mL min^{-1} then cooled to the desired temperature (50°C) before being saturated with CO_2 for 1 h at a rate of 5 mL min^{-1}. The CO_2-saturated samples were flushed with 50 mL min^{-1} of He gas for 0.5 h to fully remove physically adsorbed CO_2. TPD program was then initiated by heating from the specific adsorption temperature (35 °C) to 380°C (for NaY) or 600°C (for NaY-DEA) at a rate of 0.1°C min^{-1}. The amount of desorbed CO_2 should be equal to the amount of CO_2 chemically adsorbed on the sample.

At low temperatures, physisorption is important and the adsorption capacity is directly proportional to the surface area of the adsorbent. With amines grafting, the surface area of zeolite was significantly reduced.

At high temperatures, chemical reactions occur between the amino groups and CO_2 to produce carbamate.

On the NaY zeolite CO_2 chemisorbed on the intrinsic Lewis basic sites is associated with the lattice oxygen in the NaY framework but in functionalized zeolite CO_2 can be chemically adsorbed on both the intrinsic basic sites in NaY and amine group. At low temperatures, CO_2 would diffuse quite slowly in amine-grafted 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. These results showed that amine-functionalized NaY zeolites have excellent adsorption potential for CO_2 at high temperatures and can be employed in the process of CO_2 capture from flue gas which is performed at high temperatures.

CONCLUSIONS

In this study, NaY zeolite was functionalized with DEA. The samples were characterized by XRD, IR, TGA, FE-SEM, EDAX, N_2-BET and CO_2-TPD analyses.

The functionalized adsorbents were also evaluated for their CO_2 desorption capacities and it was observed that the functionalized zeolites desorb less than the pristine material at low temperatures, but their CO_2 uptake increases with a rise in the temperature. Therefore, it can be concluded that the mechanism of CO_2 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-grafted NaY zeolites can be employed in the process of CO_2 capture from flue gas which is performed at high temperatures.

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