

Application of MEA, TEPA, and Morpholine Grafted NaY Zeolite as CO₂ Capture

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ABSTRACT: *In the current research, NaY zeolite with a molar ratio of Si/Al=2.5 was grafted chemically with amines like monoethanolamine, tetraethylenepentamine, and morpholine. The modified NaY zeolites were characterized by XRD, FT-IR, TGA, EDAX, BET, FESEM, CO₂-TPD, and Volumetric analysis. Modification of the NaY surface with amine groups led to a remarkable rise in CO₂ adsorption capacity. CO₂ adsorption studies of NaY and modified NaY zeolite by CO₂-TPD technique revealed that, the dominant mechanism involves the interaction of CO₂ with amine groups on the surface of NaY zeolite, at ambient pressure and at a temperature of 323 K. The volumetric method was also used to investigate CO₂ adsorption onto the amine grafted NaY zeolite at 5, 7 bar pressures and at temperatures of 298 and 343 K. The adsorption process is thermal dependence and results of adsorption studies indicate that increasing temperature leads to higher adsorption of CO₂ onto the amine grafted NaY zeolites.*

KEYWORDS: *CO₂-TPD; Monoethanolamine; Tetraethylenepentamine; Morpholine; Amine grafted NaY zeolite; CO₂ capture; Volumetric method.*

INTRODUCTION

Combining fossil fuels is and will continue to be the key resource of energy for many years to come [1]. Though, as a large number of fossil fuels are combusted, the level of greenhouse CO₂ released to the atmosphere will be enhanced continuously, so causing global climate alteration from which we have already observed the consequences [2]. The CO₂ concentration in the atmosphere of the earth has oscillated about 280 ppm over more than 10 thousand years. Though, a remarkable

increase in the carbon dioxide level in the atmosphere at the rate of 1.2 ppm per year has been reported since the second half of the 19-th century. Nowadays, the mean global atmospheric level of carbon dioxide is about 380 ppm [3]. The analysis performed on this subject by the intergovernmental panel on climate alteration show, amongst others, that human activity considerably involves raising the carbon dioxide concentration in the atmosphere. Accordingly, this anthropogenic carbon

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Table 1: Typical carbon dioxide concentration in different industrial flue gases.

Type of industry	Typical CO ₂ concentration In flue gases (%)	Ref
Power generation	9-13	[7]
Steel , Iron	20-40	[8]
Glass	35-45	[9]
Cement	14-33	[10]
Quicklime	20-28	[11-12]

Table 2: Different methods for CO₂ capture in Adsorption.

Adsorption	
Physical adsorption	Chemical adsorption
Carbonaceous Material (Graphene, Active carbon, Carbon Nano Tube)	Calcium Based Material
Metal Organic Frameworks (MOFs)	Lithium Based Material
Microporous Organic Polymer (MOPs)	Amine Based Material
Zeolite	1) Amine impregnated
Ordered Mesoporous Silica (OMS)	2) Amine grafted

dioxide causes climate alteration. Usual carbon dioxide concentration in diverse industrial flue gases are represented in Table 1 [4-6].

The improvement of CO₂ capture and separation approaches is one way to solve this global problem. Amine based chemical absorption has been utilized commercially to remove CO₂ in industries [13]. Though, the liquid amine based procedures as homogeneous absorber have several disadvantages like easy degradation and high regeneration energy [14]. Consequently, as an alternative method, CO₂ capture with solid sorbents (heterogeneous adsorber) has attracted much attention recently [15-19].

The solid adsorbents for capturing CO₂ are carbon molecular sieves [20,21], alkali based sorbents [22,23], carbonaceous materials [24-26], polymers [27,28], metal organic frameworks (MOFs) [29-33], and zeolites [34-37] (Table 2).

Zeolites are crystalline aluminosilicates widely used as adsorbents, catalysts and catalyst supports. The important properties of these materials are their adjustable acidic properties, high surface area, thermal stability and microporosity. With modification of these materials, their basicity can be increased and may improve their performance in adsorbing acidic gases such as carbon dioxide or sulphur dioxide [38]. The modification of zeolites with amines would increase their basicity,

thus enhancing the adsorption capacity of acidic gases. Amine impregnation and amine grafting are two different techniques for addition of amines to zeolites. In amine impregnation technique, amine diffuses into the porous cavity of zeolite [39]. *Chatti et al.* impregnated zeolite 13X matrix by monoethanolamine (MEA), isopropanol amine (IPPA) and observed that at 75 °C and 1 bar the adsorption capacity of zeolite impregnated by MEA (50 wt% loading) increased from 0.84 mmol/g to 1.10 mmol/g in comparison to 13X zeolite matrix [40]. In amine grafting technique, aminosilane reacts with the surface hydroxyl group of zeolite and form stable Si-O-Si chemical bonds. The amine grafted zeolites showed considerably greater thermal stability during adsorption and regeneration cycle. Madden et al. used the post-modification grafting method to graft (3-aminopropyl) trimethoxysilane (APTES) on zeolite β, which show CO₂ adsorption ability up to 4.4 mmol/g at 0.15 bar partial pressure and temperature of 35 °C [41]. Compared to other zeolites, NaY zeolite exhibits considerable high adsorption ability and stable structure [42].

In current study, we report a chemical modification of NaY zeolite via grafting of amines like monoethanolamine (MEA), tetraethylenepentamine (TEPA) and morpholine (MOR). We also investigated effect of amine modification of NaY zeolite on increasing CO₂ adsorption by dynamic

study (CO₂-TPD technique at 1 bar pressure and 323 K) and volumetric method at 5, 7 bar pressures and temperatures of 298 and 343 K.

EXPERIMENTAL SECTION

Chemicals

Analytical grade chloroform, 3-(chloropropyl)-trimetoxysilane, morpholine (99 %), monoethanolamine (99.5 %), tetraethylenepentamine (98 %), triethylamine were prepared from Merck company (Germany). NaY with Si/Al = 2.5 was purchased from zeolyst company (USA). Deionized water was used to prepare all the solutions.

Apparatus

The characterization of crystal phase of the synthesized adsorbents was performed by means of a X-ray diffraction (XRD) with the Philips 1830. Thermal program desorption of functionalized zeolites measured by Belcat-A. The surface functional groups of the adsorbents assessed using the Fourier Transform InfraRed (FT-IR) spectroscopy (DIGILAB FTS 7000 spectrometer). Thermogravimetric analysis (TGA) of adsorbents was studied using the TGA 8000 Perkin Elmer by scanning up to 600 °C with a heating rate of 10 °C/min. Scanning electron microscopy FESEM (KYKY-EM 3200) was applied for investigating the zeolites morphology. Micromeritics BET (Brunauer, Emmett and Teller) was used to measure the specific surface area of a sample comprising the pore size distribution.

Preparation of Amine-grafted NaY zeolite

Amine modification of NaY zeolite was performed via grafting technique. 2 g of NaY zeolite was stirred with 8 mL of 3-(chloropropyl)-trimetoxysilane at 70 °C in chloroform for 24 h to prepare 3-(chloropropyl)-trimetoxysilane functionalized NaY zeolite (3-CPS-NaY). After that 1 g of 3-CPS-NaY was stirred with 5 mmol of MEA (TEPA or MOR) at 70 °C in chloroform for 8 h in the presence of triethylamine. The mixture was filtered off and the residue was dried in an oven at 50-60 °C for 1 h to obtain amine grafted NaY zeolite (Fig. 1) [43,44].

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD) analysis

The XRD patterns of NaY and amine modified NaY zeolites showed in Fig. 2.

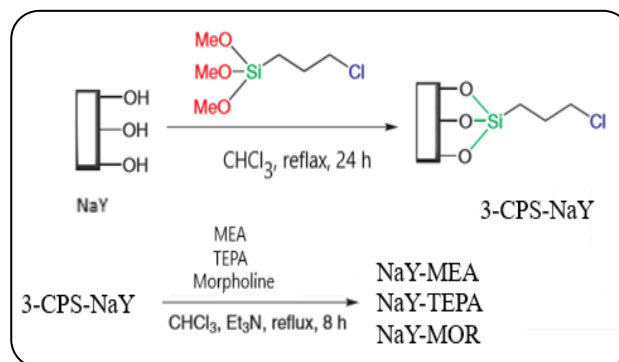


Fig. 1: Preparation of modified NaY zeolite.

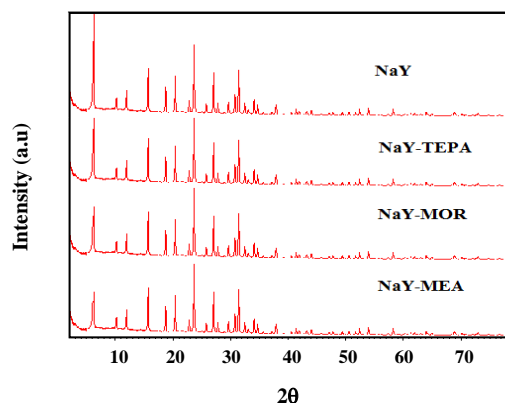


Fig. 2: XRD patterns of the NaY and amines grafted NaY zeolite.

Based on the XRD patterns, no significant changes are observed in the structure of NaY zeolite following the amines attachment. Though, the intensity of the signal at 2θ, 6.0-6.5 for amine grafted zeolites is reduced which could be related with the stress of the presence of amines within the NaY zeolite pores.

Fourier-Transform InfraRed (FT-IR) spectroscopy

The FT-IR spectra corresponding to amine attached NaY samples are represented in Fig. 3.

The spectrum of NaY exhibits the adsorption band at 500-1000 cm⁻¹ and 1000-1100 cm⁻¹ corresponding to the symmetric and asymmetric stretching vibrations of Si-O-Si. After modification of NaY, the adsorption peaks at 1500-1600 cm⁻¹ were related with the stretching vibrations of -NH₂. The broad bands at around 3500 cm⁻¹ can be assigned to the overlap peaks of surface hydroxyl groups and N-H symmetrical stretching vibration band. Therefore, the IR spectra of the amines modified NaY showed stable and confirmed the adsorption of amine onto the NaY structure.

Table 3: EDAX information corresponding to NaY and amine modified NaY.

Adsorbent	Element (Wt %)							
	O	Na	Al	Si	N	C	Au	Cl
NaY	61.42	6.18	7.76	24.64	0	0	0	0
NaY-MEA	48.41	4.26	5.81	13.91	6.99	15.04	5.23	0.35
NaY-MOR	35.27	8.98	12.30	30.50	2.00	9.69	0	1.26

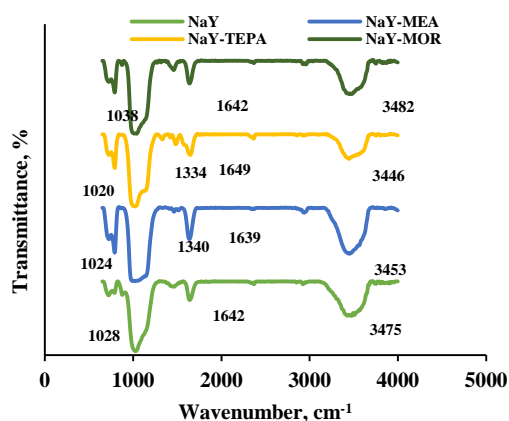


Fig. 3: FT-IR spectra of the NaY before and after modification.

Thermal gravimetric analysis (TGA)

Fig. 4 indicates the TGA corresponding to the NaY modified with diverse amines. Heating of samples from 30 °C to 600 °C was performed at a rate of 10 °C per minute. In TGA profile of NaY a weight loss of about 11% is observed in temperature range of 50-140 °C, which is related to the moisture content and the amount of water absorbed physically. In addition, another weight loss of about 9% is found in the temperature range of 140-240 °C, that is related to removal of water absorbed chemically. According to the TGA curve, NaY-MEA, NaY-TEPA and NaY-MOR had a weight loss of about 10% in temperature range of 50-250 °C that is related to removal of water in the sample. The following losses in 250-600 °C are due to the amount of amines deposited in the pores and on the surface of the zeolite, due to their respective thermal decomposition at different temperatures, obtaining residues about 77% for the contained zeolite grafted with MEA, TEPA and morpholine.

Energy dispersive X-ray spectroscopy analysis(EDAX mapping)

Results of EDAX analysis for NaY and NaY-MEA and NaY-MOR showed in Table 3.

The type and percentage of constituent elements are determined by this analysis. Of interest, the chemical composition given by EDAX revealing significant N content up to 6.99 wt% and 2.00 for NaY-MEA and NaY-MOR respectively. Nitrogen and carbon elements in EDAX analysis of NaY-MEA and NaY-MOR showed that NaY-MEA and NaY-MOR was grafted effectively by amines groups.

N₂-adsorption/desorption analysis

The Barrett-Joyner-Halenda (BJH) technique on the basis of the pore condensation phenomena is appropriate only for the mesoporous or microporous materials. Fig. 5 shows the N₂ adsorption-desorption isotherms of NaY and the amine modified NaY at 77 K

According to the IUPAC classification these isotherms may be classified as Type I. In this type, the adsorption is limited to few molecular layers and then chemisorption is expected [45]. For NaY, high volume of nitrogen adsorbed within very low relative pressures indicated microporous characteristics. Also a second sharp increase in relative pressure of 1.0 showed macropores property. Other isotherms indicate that amines grafted NaY zeolite practically have no macropores, possibly because they were completely filled with amine.

The structural features of the samples have been represented in Table 4. Furthermore, the BET surface area and pore volume reduced clearly, which proves the occupation of the zeolite pores by amines.

The BET surface area of NaY was found to be 810.64 m²/g while for NaY-MEA, NaY-TEPA and NaY-MOR decreased to 229.41, 57.40 and 5.23 m²/g respectively. These data indicate, as expected, a considerable reduction in the surface area and of pore volume with respect to the unmodified NaY zeolite. These observations may be due to saturation of zeolite pores by amine which resulted in reduction of surface area.

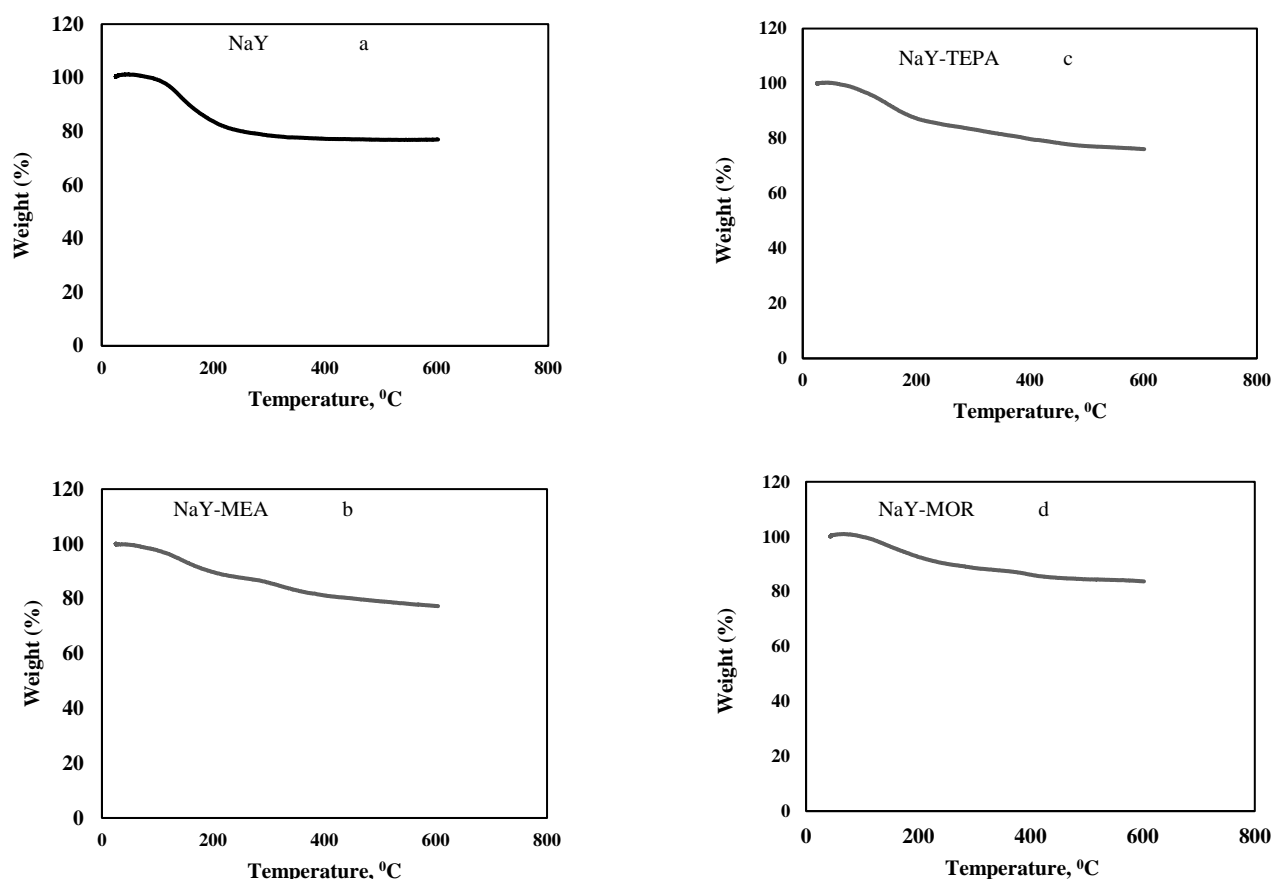


Fig. 4: TGA of (a): NaY, (b): NaY-MEA, (c): NaY-TEPA, (d): NaY-MOR.

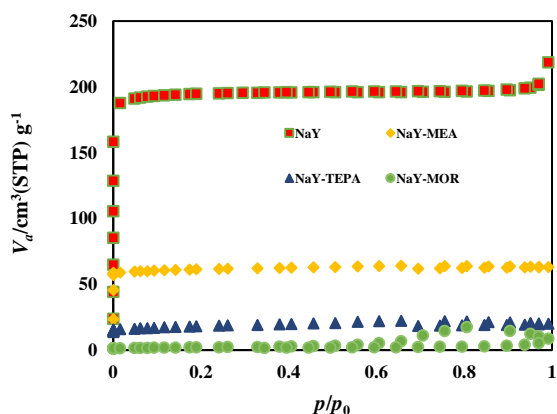


Fig. 5: N_2 adsorption-desorption isotherms of NaY and amines grafted NaY zeolite.

Field Emission Scanning Electron Microscopy (FESEM) analysis

Fig. 6 represents the FESEM images corresponding to NaY, NaY-MEA and NaY-MOR under a magnification of 25,000 at 25 KV acceleration voltage.

The SEM images confirmed that the NaY was grafted successfully by the amine groups. For all three samples, particles with uniform size were obtained. Further, the surface morphology of NaY-MEA and NaY-MOR were found to be similar to that of NaY.

Thermal Program Desorption (TPD)

Thermal programmed desorption method is appropriate for determination of zeolite CO_2 desorption and it was utilized in current research (CO_2 -TPD) (Fig. 7).

The pre-treatment of each adsorbent was performed at $120^\circ C$ for 1 h under 50 mL/min of He, then it was cooled to $50^\circ C$ with He and prior to saturation with CO_2 (10 v/v % in He) for 60 min at a rate of 5 mL/min. Flushing of the CO_2 saturated samples was performed using He gas for 30 min at a speed of 50 mL min^{-1} to completely eliminate physically adsorbed CO_2 . Then TPD program was started by heating from $35^\circ C$ (the specific adsorption temperature) to $650^\circ C$ at a rate of $5^\circ C/min$.

Table 4: Structural properties of NaY, NaY-MEA, NaY-TEPA and NaY-MOR.

Adsorbent	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Mean Pore Diameter (nm)
NaY	810.64	0.336	1.658
NaY-MEA	229.41	0.099	1.722
NaY-TEPA	57.40	0.034	2.388
NaY-MOR	5.23	0.026	19.969

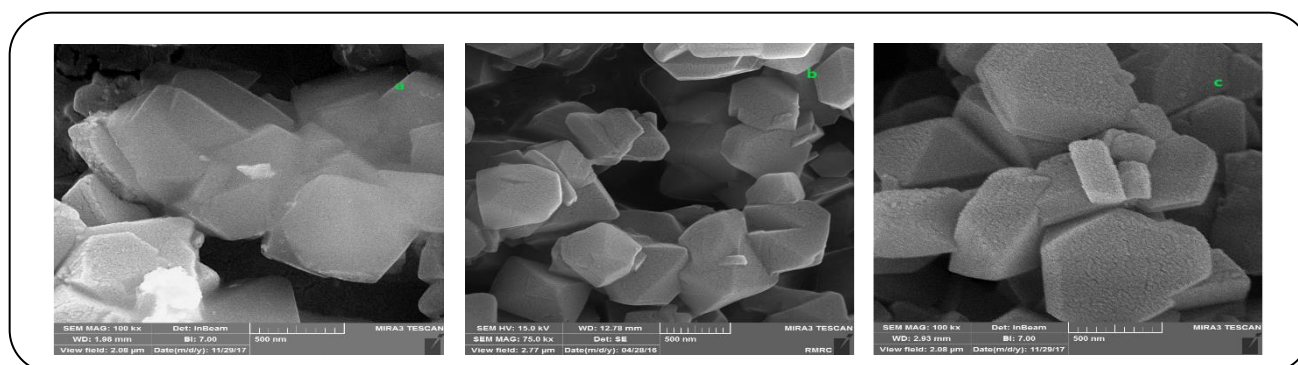
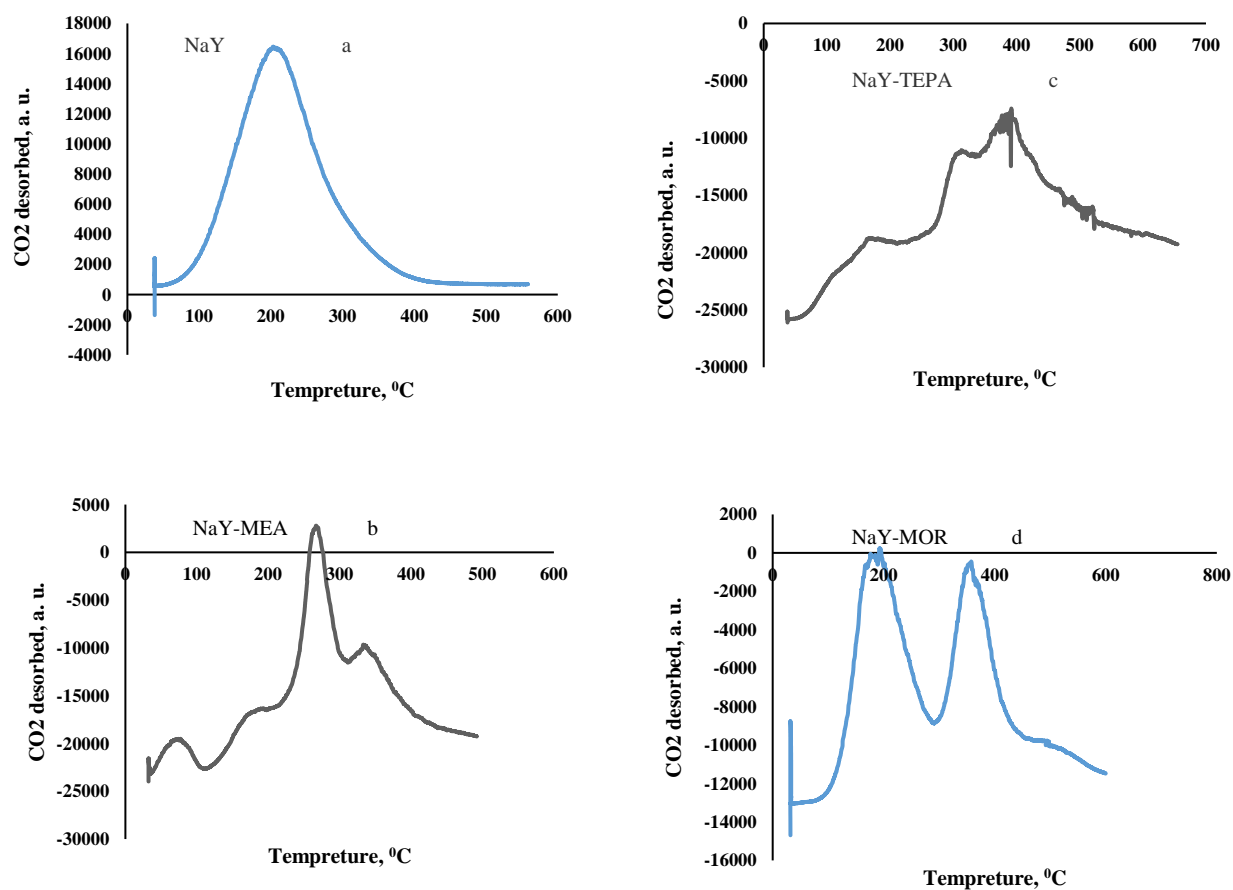
**Fig. 6: E-SEM images corresponding to (a) NaY, (b) NaY-MEA, (c) NaY-MOR.****Fig 7: CO₂-TPD isotherms corresponding to (a): NaY, (b): NaY-MEA, (c): NaY-TEPA, (d): NaY-MOR.**

Table 5: CO₂ desorption capacity of NaY and amine modified NaY.

Adsorbent	Temperature, °C with CO ₂ desorption capacity, mmol g ⁻¹			
	NaY	202 °C 2.174	-	-
NaY-MEA	73 °C 0.170	191 °C 0.363	267 °C 1.606	334 °C 1.346
NaY-TEPA	164 °C 0.750	312 °C 1.151	391 °C 2.836	-
NaY-MOR	180 °C 1.481	356 °C 1.267	-	-

Table 6: Comparison of CO₂ sorption capacity.

Sorbents	CO ₂ sorption capacity (mmol/g)	Temperature (°C)	Pressure (bar)	Reference
NaY	2.40	25	1	[49]
NaY	2.17	50	1	This work
NaY_MEA	3.48	50	1	This work
NaY-MEA (Amine impregnation method)	1.55	30	1	[50]
NaY-TEPA	4.74	50	1	This work
NaY-TEPA (Amine impregnation method)	2.11	75	1	[51]
NaY-MOR	2.75	50	1	This work
MEA/DMA-Ash (Amine impregnation method)	6.89	30-60	1	[52]
PAN/PVDF nanofibers	2.21	25	1	[53]
Activated carbons prepared from Argan fruits shells	5.63	25	1	[54]

Yu et al. used CO₂-TPD for determination of the chemisorption of CO₂ onto NaY and amine modified NaY. The concentration of desorbed CO₂ should be equal to the concentration of CO₂ adsorbed on the sample through chemical mechanism [46].

Table 5 represents the CO₂-TPD data of NaY and amine modified NaY zeolites.

The NaY zeolite showed one desorption peak for CO₂ at 202 °C that indicating a CO₂ adsorption capacity of 2.174 mmol/g. In NaY-MEA there were four desorption peaks for CO₂ at 73 °C, 191 °C, 267 °C and 334 °C respectively. NaY-TEPA exhibited three desorption peaks for CO₂ at 164 °C, 312 °C and 391 °C, and finally NaY-MOR, displayed two CO₂ desorption peaks at 180 °C and 356 °C.

At ambient pressure and temperature, CO₂ would diffuse relatively slow in amine grafted zeolites and its uptake would appear unusually low [47-51]. But at the same pressure and at temperature of 323 K (50 °C), the reaction kinetics becomes more important and the adsorption capacity enhances with increasing the temperature. This feature of amine grafted zeolites

make them as potential adsorbents for CO₂ capture from flue gas. Table 6 compares the CO₂ sorption capacity of NaY, NaY-MEA, NaY-TEPA and NaY-MOR measured by CO₂-TPD method with some other sorbents reported in the literature.

As it is seen in Table 5, CO₂ sorption capacity of NaY at 50 °C (2.17 mmol g⁻¹) is lower than NaY at 25 °C (2.40 mmol g⁻¹) conforming the CO₂ physisorption onto the NaY.

Activated carbons prepared from argan fruits shells showed good CO₂ adsorption. Higher adsorption capacity of monoethanolamine/dimethylamine modified ash (MEA/DMA-Ash) (6.89 mmol g⁻¹) is due to impregnation technique of amine onto ash. This is worth to mention that amine modified ash (or zeolite) made by impregnation method can only be used in dry medium.

Experimental set up of volumetric equipment

A schematic diagram of experimental setup of volumetric equipment consisting reference cell (FV), Sample cell (SC), a set of valves and a high precision pressure transducer that is showed in Fig 8.

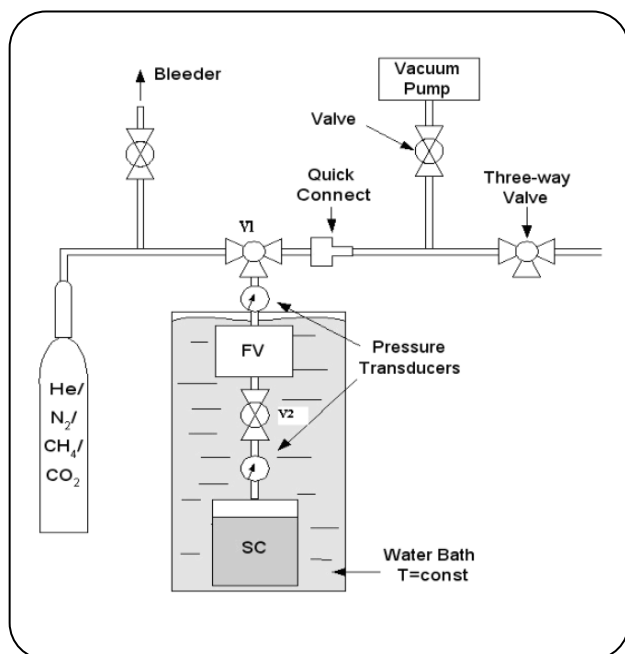


Fig. 8: Schematic diagram of experimental set up of volumetric equipment.

To maintain constant temperature, Both of reference cell and the sample cell are kept in a water bath. After degassing, the system was cooled to the experiment temperature. Ultra-high purity carbon dioxide (99.999%) was passed into the adsorption unit for the CO₂ adsorption measurements. Therefore, valve V1 was opened to reach a pressure balance in the reference cell. After that, valve V2 was instantly opened and the pressure decrease was recorded. The pressure of the adsorption cell decreased because of some dead volume and some CO₂ adsorption. The portion of the dead volume was calculated with helium tests and then subtracted from the total pressure change. Eventually, the exact pressure decrease resulting from the CO₂ adsorption could be calculated.

Results of volumetric method analysis for NaY, NaY-MEA and NaY-TEPA shown in Table 7.

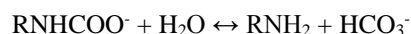
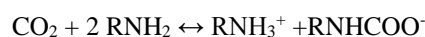
For NaY zeolite, by increasing adsorption temperature to 70 °C at pressure 5 bar, CO₂ adsorption capacity decreased.

Mahanta et al. reported that increasing temperature simply gives more internal energy to CO₂ molecules in the gas phase. Then the increasing energy allows gaseous molecules to diffuse at a greater rate, but, at the same time, it reduces the chance for the CO₂ to be restrained or trapped by fixed energy adsorption sites on the adsorbent

surface [55].

For NaY-MEA and NaY-TEPA, by increasing adsorption temperature to 70 °C at pressure 5 bar, CO₂ adsorption capacity increased.

Lee et al. reported that by increasing adsorption temperature, chemical reactions take place between the amino groups and CO₂ to form the carbamate species based on the following equations:



It is believed that CO₂ is chemisorbed on the intrinsic lewis basic sites related with the lattice oxygen in the NaY framework. In other word, in the modified zeolites, the adsorption of CO₂ occurs on both the intrinsic basic sites on NaY and amine groups through chemical sorption[56].

The dominant procedure at low temperatures can be physisorption and the higher adsorption value of amine grafted NaY at higher temperature could indicate chemical adsorption of CO₂ onto the amine grafted zeolite [55-57]. In this regard, CO₂ adsorption for NaY-MEA and NaY-TEPA at low temperature can be physisorption, whereas at higher temperature, the adsorption can be chemisorption.

The results exhibit that the amount of adsorbed CO₂ increased with increasing pressure. For NaY zeolite The higher CO₂ uptake at 7 bar pressure, can be attributed to the interaction of CO₂ and NaY zeolite with more energy, whereas for amine grafted NaY zeolite at high pressures show interaction with more energy between CO₂ and amine group [58].

CONCLUSIONS

Zeolite NaY has been grafted with monoethanolamine (MEA), tetraethylenepentamine (TEPA) and morpholine. surface chemistry and texture of the products have been investigated by XRD, TGA, FTIR, EDAX, FESEM and N₂-BET. The analyses reveal that part of the loaded amine is firmly attached to the zeolite surface.

The ability of amine grafted zeolite as adsorbents was evaluated by CO₂ thermal program desorption (CO₂-TPD) and volumetric method. The CO₂ adsorption value of NaY, NaY-MEA, NaY-TEPA and NaY-MOR were measured and results showed that amine grafted zeolite are more potential adsorbent for CO₂ capture than NaY alone at higher temperature.

Table 7: CO₂ adsorption capacity of NaY and amine modified NaY.

Sorbents	Temperature (°C)	Pressure (bar)	CO ₂ adsorption capacity (mmolg ⁻¹)
NaY	25	5	2.338
	70	5	1.988
	25	7	2.592
NaY-MEA	25	5	3.861
	70	5	4.131
	25	7	4.187
NaY-TEPA	25	5	4.073
	70	5	4.756
	25	7	4.618

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