

## ADSORPTION OF CARBON DIOXIDE ON MIL53(AL), CUBTC AND K- NAX ZEOLITE

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### ABSTRACT

CO<sub>2</sub> adsorption on K exchanged NaX zeolites, and metal organic frameworks (MOFs), namely Cu-BTC and MIL53 (Al) was studied at 5 °C and 25 °C. Exchange via ultrasonic and traditional methods, was conducted at 50 °C and 70 °C. The maximum replacement of Na<sup>+</sup> ion with K<sup>+</sup> ion in the extra framework of zeolite was increased from 76% to 83% with increasing temperature from 50 °C to 70 °C in the ultrasonic method which is more effective than traditional one. Compared with the zeolites, the MOF adsorbents used in this work have higher Langmuir specific surface area values namely 1278, 1473 and about 1000 m<sup>2</sup>/g for MIL 53, Cu-BTC and zeolite adsorbents respectively. The resulting CO<sub>2</sub> isotherms can be well represented by the Toth equation. Comparison of the isosteric heat of adsorption at zero loading shows that CO<sub>2</sub> was adsorbed more weakly on MOFs than zeolites.

**Keywords:** CO<sub>2</sub> , adsorption, Ultrasound, NaX zeolite, MOF

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### 1. INTRODUCTION

Global warming resulting from the emission of greenhouse gases, especially CO<sub>2</sub> has become a widespread concern in recent years. Adsorption of CO<sub>2</sub> is caused by van der Waals between adsorbate and adsorbent, as well as by electrostatic interactions between the large quadrupole of CO<sub>2</sub> ( $14.29 \times 10^{-40} \text{ C m}^{-2}$ ) and the ionic or polar sites of the solid adsorbent surface. Adsorbent selection is very important for the rational design of the adsorption processes such as pressure swing adsorption, vacuum swing adsorption and thermal swing adsorption. During the last decade, MOFs as a new family of nanoporous materials<sup>1</sup> are assembled by directly bonding metal clusters with organic linkers. A variety of adsorbents have been investigated as potential CO<sub>2</sub> adsorption materials including microporous and mesoporous materials such as metal aluminum silicates, aluminum phosphates and metal organic frameworks (MOFs).<sup>2-13</sup> In contrast to the tetrahedral building blocks in zeolites which are silicons or aluminum oxides, MOFs can be comprised of inorganic clusters (e.g. square-shaped, trigonal, tetrahedral and octahedral) and organic linkers (e.g. carboxylates, imidazolates and tetrazolates). With very high surface area (up to 6500 m<sup>2</sup>/g) MOFs have been considered versatile materials for adsorption<sup>14</sup>. MOFs have higher capacity (11 mmol/g to 32 mmol/ g) at 30 atm pressure and

298 K; however, at atmospheric pressures their capacity (0.95 mmol/g) is lower<sup>13</sup> as compared to zeolites<sup>3, 9, 11, 12</sup> and aluminum phosphate.<sup>5</sup> Zeolites, especially NaX, are commonly used adsorbents for CO<sub>2</sub> adsorption at 1 atm.<sup>11, 12.</sup>

Acidic CO<sub>2</sub> molecules can be adsorbed on the basic sites of the zeolite surfaces, the strength of which was increased along with an increase of the aluminum content. The presence of aluminum atoms in zeolites introduces negative framework charges that are compensated with exchangeable cations (extra framework cations) such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Na<sup>+</sup>. According to Walton et al.<sup>15</sup> the introduction of small univalent molecule via ion exchange enhances the adsorption of CO<sub>2</sub> on the X zeolites with the order of:



Even the adsorption of CO<sub>2</sub> in conventional ion-exchanged X zeolites has been studied previously.<sup>15-17</sup> There has not been an investigation of ultrasound effect in the preparation of K exchanged NaX zeolite and its effect on CO<sub>2</sub> adsorption. In literature, ultrasonic method as compared to the traditional exchange method was found to be very effective on the exchanged amount at equilibrium.<sup>18</sup>

In this paper, we studied CO<sub>2</sub> adsorption on two types of adsorbents: K exchanged NaX zeolites (KNaXs) which were prepared with ultrasonic and traditional methods and commercial metal organic frameworks (MOFs): Cu-BTC and MIL53 (Al).

## 2. RESULTS AND DISCUSSION

### 2.1. Characterization of Adsorbents

#### 2.1.1. Zeolite Adsorbents

Textural properties and the Na exchange percent (number in the parenthesis in case of zeolites) of the adsorbents are given in Table 1. As seen in the table, the temperature was effective on the Na exchange method, and the maximum Na exchange percent obtained were 83% and 81% at 70 °C when ultrasonic and traditional methods were applied, respectively. The table also shows that K exchanged NaX have lower langmuir surface area, micropore volume and pore diameter than NaX zeolite. This can be explained with the restriction of available pores because K<sup>+</sup> ions are bigger ions than Na<sup>+</sup> (R<sub>K+</sub> > R<sub>Na+</sub>) ions. The micrographs of the surface obtained from the scanning electron microscope show that the spherical crystal size (2 μm) of NaX zeolite did not change with K<sup>+</sup> ion exchange applied (Figure 1). Comparison of the XRD spectra (Figure 2) of zeolite adsorbents shows that the NaX zeolite has the highest peak intensities and highly crystalline material but it is reduced with K<sup>+</sup> exchange as mentioned in the literature.<sup>19</sup> This confirms the migration of cations to zeolite extraframework sites without affecting the skeleton.

#### 2.1.2. MIL53 (Al) and Cu-BTC Adsorbents

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Metal organic frameworks namely MIL53 (Al) and Cu-BTC demonstrate higher surface area (1278 and 1473 m<sup>2</sup>/g, respectively) and micropore volume (0.4 and 0.43 cm<sup>3</sup>/g, respectively) than zeolites (about 1000 m<sup>2</sup>/g and 0.3 cm<sup>3</sup>/g, respectively). MIL53 (Al) adsorbent has smaller crystals than Cu-BTC adsorbent (Figure 3 and 4, respectively).

## 2.2. CO<sub>2</sub> Adsorption Studies

Figures 5a and 5b show the adsorption isotherm of CO<sub>2</sub> adsorption on the zeolites and MOFs obtained at 278K and 298K, respectively. As shown in the figures, similar and highly favorable adsorption isotherms which are of type 1, according to IUPAC classification, were observed for zeolite adsorbents while linear isotherms were noticed for the MOF adsorbents. Zeolites have similar and highly favorable adsorption isotherms which are of type 1, according to IUPAC classification, whereas MOF adsorbents have linear isotherms. The temperature increased the amount adsorbed by the adsorbents since adsorption is an exothermic process. NaX zeolite has the higher CO<sub>2</sub> adsorption than K exchanged NaX zeolite, due to its higher electropositivity and ionic radius of Na<sup>+</sup> ion than those of K<sup>+</sup> ion. NaX is the most basic surfaces among the zeolites. The CO<sub>2</sub> adsorption data were fitted to Langmuir, Freundlich, Toth and Sips models (as representatively shown in Figure 6). Among them Toth model equation,

$$q = \frac{q_m b P}{(1 + (bP)^t)^{1/t}} \quad (1)$$

was the best method to describe the experimental data as discussed by Yerkesikli.<sup>20</sup> Where  $q$  and  $q_m$  represent the amount adsorbed and monolayer adsorption capacity (mmol/g adsorbent),  $P$ (kPa) is the gas pressure inside the pores at equilibrium. Parameter “ $t$ ” and “ $b$ ” (kPa<sup>-1</sup>) of the model equation characterize the heterogeneity of the CO<sub>2</sub>-adsorbent system and the affinity of adsorbent to CO<sub>2</sub>, respectively. Table 2 shows the Toth’s parameter and the errors defined. It was concluded that the sum of square error (SSE), in harmony with regression coefficient, is less sensitive than the standard error (SE). As stated by Do<sup>21</sup> the parameter “ $t$ ” deviates from unity, suggesting that the system was "apparently" more heterogeneous. Among the zeolites, CO<sub>2</sub>-NaX pair is the most heterogeneous; the heterogeneity of the CO<sub>2</sub>-KNaXs systems decreases with increasing exchange percentage. Our results agree with the results obtained by Walton et al.<sup>15</sup> Among the adsorbents, CuBTC has the lowest heterogeneity. Parameter “ $b$ ”, the affinity constant, decreases as the temperature increases; zeolite adsorbents have higher  $b$  values than MOF adsorbents showing that CO<sub>2</sub> molecule is preferentially attracted onto the zeolite surfaces. Among the zeolite adsorbents NaX zeolite was the most attractive adsorbent for CO<sub>2</sub>.

### 2.2.1. Isotheric heat of adsorption

In addition to the surface area, pore volume, and adsorption capacity, the isosteric heat of adsorption is an important parameter to evaluate the adsorption performance of adsorbents. Therefore the Van’t Hoff equation

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$$-\frac{q_{st}}{RT^2} = \left[ \frac{\partial \ln P}{\partial T} \right]_V \quad (2)$$

and Toth equation were used to obtain isosteric heat of adsorption as a function of adsorbate loading.<sup>21</sup>

$$q_{st} = q_{st} \Big|_{q \rightarrow 0} - t(\alpha RT) \left[ \ln \left( \frac{q}{q_m^t - qt} \right)^{1/t} \right] - \frac{\ln(q_m)}{1 - (q/q_m)t} \quad (3)$$

Where,  $q_{st} \Big|_{q \rightarrow 0}$ , R, T and P are the isosteric heat of adsorption at zero loading, the gas constant (8.314(LkJPa/mol K)), temperature(K), and pressure(kPa), respectively. Figure 7 shows the variation of the isosteric heat of adsorption with the amount adsorbed, q. As expected for heterogeneous systems the CO<sub>2</sub> adsorbent interaction decreases with increasing amount adsorbed, since the stronger binding sites would be occupied first. However, this change does not point out the source of heterogeneity, whether it is the solid structural property, energetic property of the solid or the sorbate. In other words, heterogeneity is not a solid characteristic alone but rather it is a characteristics of the specific solid and adsorbate pair.<sup>16, 21</sup>

The isosteric heat of adsorption at zero loading ( $q_{st} \Big|_{q \rightarrow 0}$ ) of NaX (55 kJ/mol) is higher than KNaX zeolites. This is attributed to the strongest interaction between the large quadrupole moment of CO<sub>2</sub> and the cations. The isosteric heat of adsorption at zero loading for Cu-BTC and MIL53 (Al) (40 kJ/mol and 38 kJ/mol, respectively) has lower value than zeolites. This low isosteric heat indicates that CO<sub>2</sub> molecules weakly interact with MOFs. The isosteric heat of adsorption of MOFs obtained in this study is comparable with the measured value (34kJ/mol) of MOF-5 in the literature.<sup>2</sup>

### 3. EXPERIMENTAL

#### 3.1.1. Preparation of the adsorbents

Binderless NaX zeolite (Cas# 63231-69-6) from Aldrich with unit cell formula of Na<sub>86</sub>(Al<sub>86</sub>Si<sub>106</sub>O<sub>384</sub>) 264H<sub>2</sub>O, and Si/Al:1.23 was used. Commercial metal organic frameworks MIL53 (Al) and Cu-BTC (Basolite A100 and Basolite C300, respectively) were supplied from Aldrich. In preparation of KNaX, ultrasound is employed as an alternative method to traditional ion exchange method as given detailed in the previous study.<sup>18</sup> 2 g of zeolite were mixed with 20 mL of 1 M KCl solution for 2h at 50 °C or 70 °C with water bath shaker (GFL 1092) at 130 rpm (in traditional method) or ultrasonic processor (Sonics-Vibracell-VC 505) at 16 kHz frequency (in ultrasonic method). The mixtures were centrifuged and then zeolite phases were washed with water until Cl<sup>-</sup> free solutions were obtained. The solutions were analyzed by using

inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES 96, Varian) to calculate

$$\text{Na exchange percentage, } \eta_{Na}; \quad \eta_{Na} = \left( \frac{q_o - q_{Na}}{q_o} \right) \times 100 \quad (4)$$

where  $q_o$  and  $q_{Na}$  ( $\text{mg g}^{-1}$ ) are the initial and equilibrium (after 2h) amount of  $\text{Na}^+$  ions into zeolites, respectively. In Na exchanged zeolite codes, U and S represents the ion exchange methods: ultrasound and traditional respectively; 50 and 70 are temperatures in  $^{\circ}\text{C}$  unit; the number in the parenthesis is Na exchange percent (%). All chemicals are analytical grade and were purchased from Aldrich.

### 3.1.2. Characterization of Adsorbents

Mineralogy and crystallinity of the adsorbents were determined by X-ray diffraction (Philips X-Pert Pro Diffractometer) using  $\text{CuK}\alpha$  radiation at 45 kV and 40 mA in the  $2\theta$  range of  $5\text{--}70^{\circ}$  with  $0.2^{\circ}$  step size. The micrographs of the adsorbents were taken by using scanning electron microscopy (SEM, Philips XL 30S). Chemical composition of the zeolite adsorbents was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, 96, Varian). Textural properties of adsorbents were determined by using a volumetric  $\text{N}_2$  adsorption instrument (Micromeritics, ASAP 2010M) at 77K. Prior to adsorption, the samples were degassed at  $350^{\circ}\text{C}$  for 24 h under vacuum better than  $10^{-5}$  mbar.

### 3.1.3. $\text{CO}_2$ Adsorption

Adsorption of  $\text{CO}_2$  on the adsorbents were measured in a volumetric adsorption instrument (Micromeritics ASAP 2010M) at 278 and 298 K. Toth adsorption models were used to correlate the  $\text{CO}_2$  adsorption. The fitting of the isotherm data to the model equations was carried out by using Sigma Plot 6.01 statistical software program.

## 4. CONCLUSION

$\text{K}^+$  ion exchange on NaX zeolite was conducted at  $50^{\circ}\text{C}$  and at  $70^{\circ}\text{C}$  by means of traditional and ultrasound methods. The ultrasonic method was found to be more effective on the exchange due to the cavitation effect of ultrasound field. Additional to KNaX zeolites, MIL53 (Al) and Cu-BTC adsorbents were evaluated as a potential adsorbent for  $\text{CO}_2$  adsorption.  $\text{CO}_2$  adsorption data fitting to the theoretical models lead us to the conclusion that  $\text{CO}_2$ -adsorbents are heterogeneous systems; isosteric heat of  $\text{CO}_2$  adsorption on zeolite and MOF adsorbents decreases with loading. Compared with the zeolites, the MOF adsorbents used in this study have higher Langmuir specific surface area and lower isosteric heat of adsorption at zero loading. This is essential for adsorption application because of the large energy requirement associated with the regeneration (i.e. desorption) of the adsorbents.

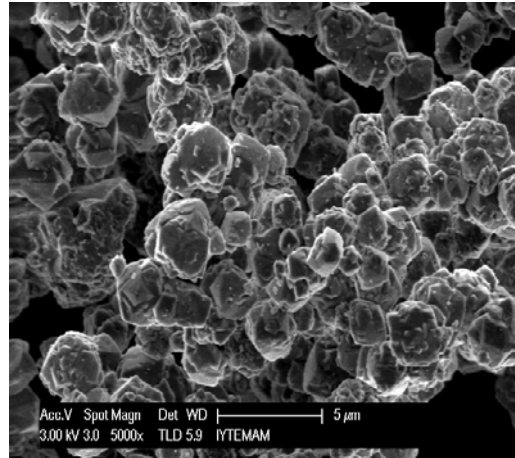
## ACKNOWLEDGMENT

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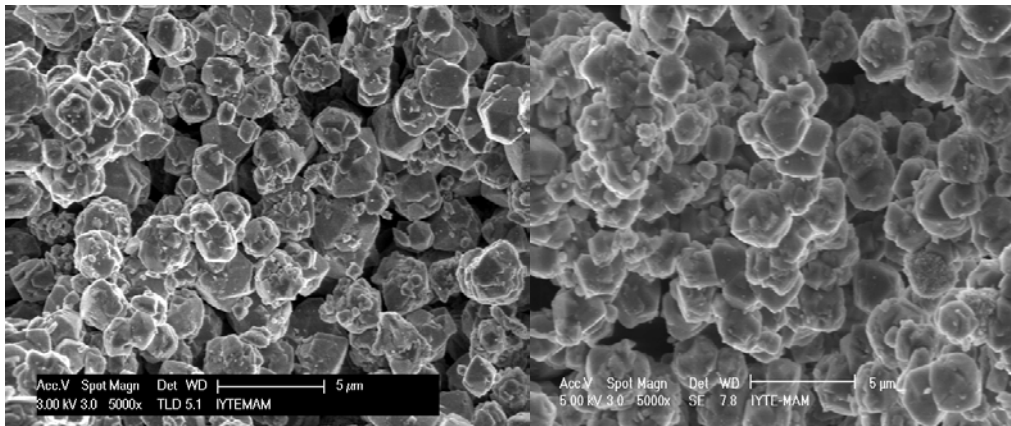
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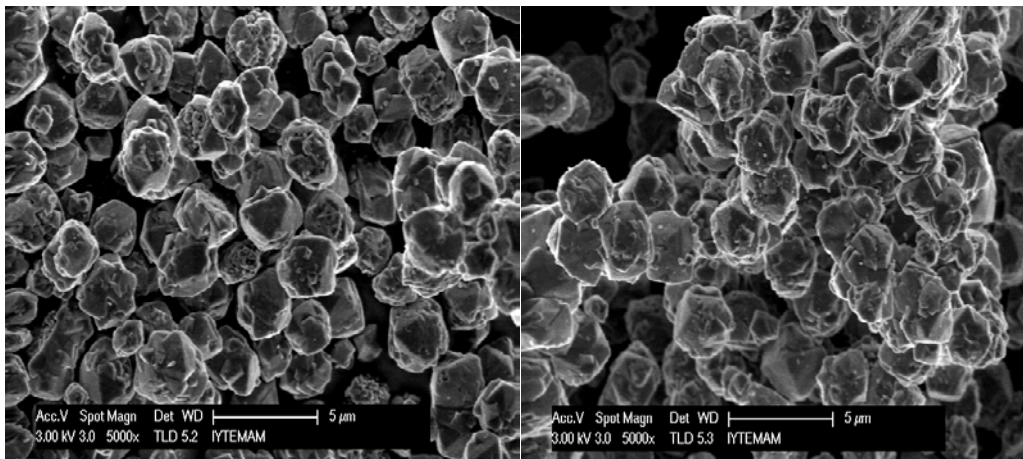
(a)



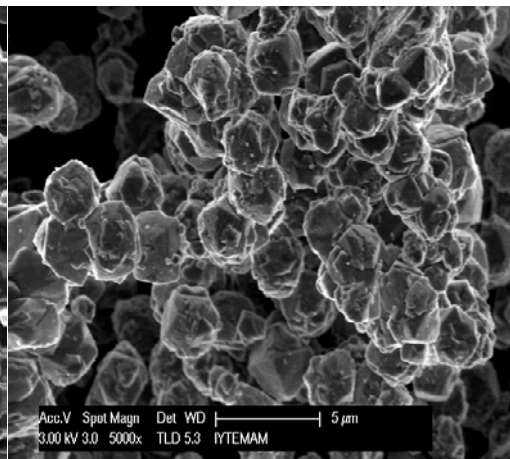
(b)



(c)



(d)



(e)

Figure 1: Scanning Electron Micrographs of the zeolites surfaces



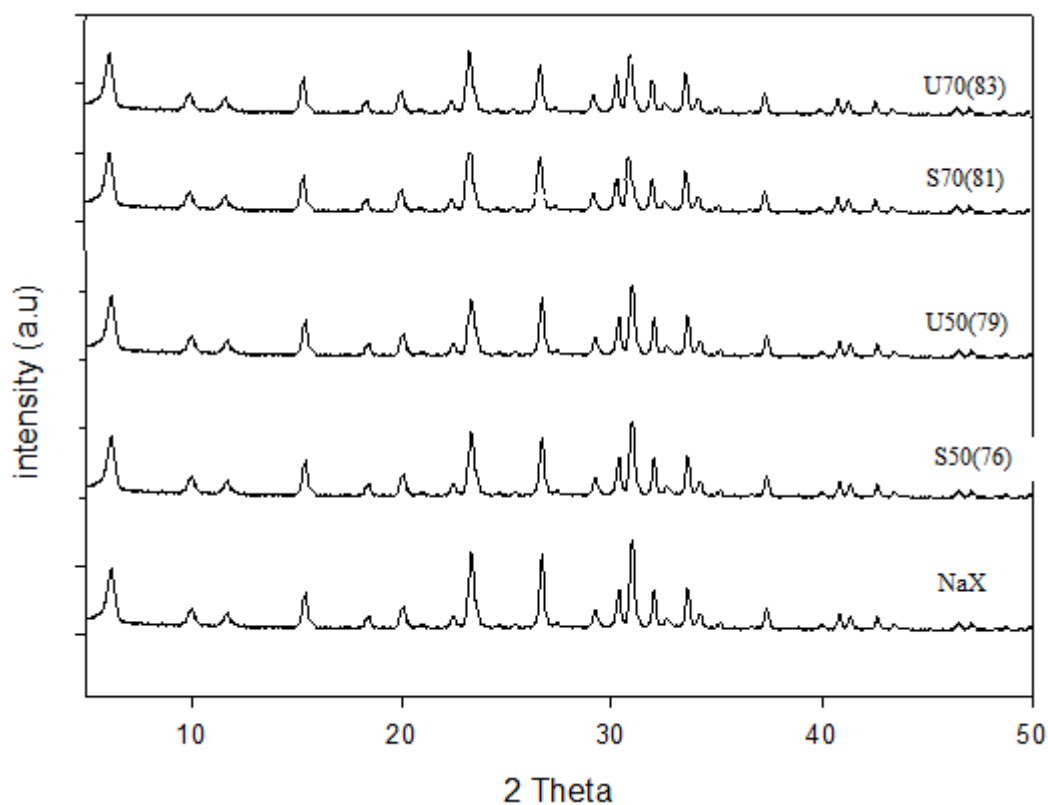


Figure 2: X-ray diffractogram of the zeolite adsorbents

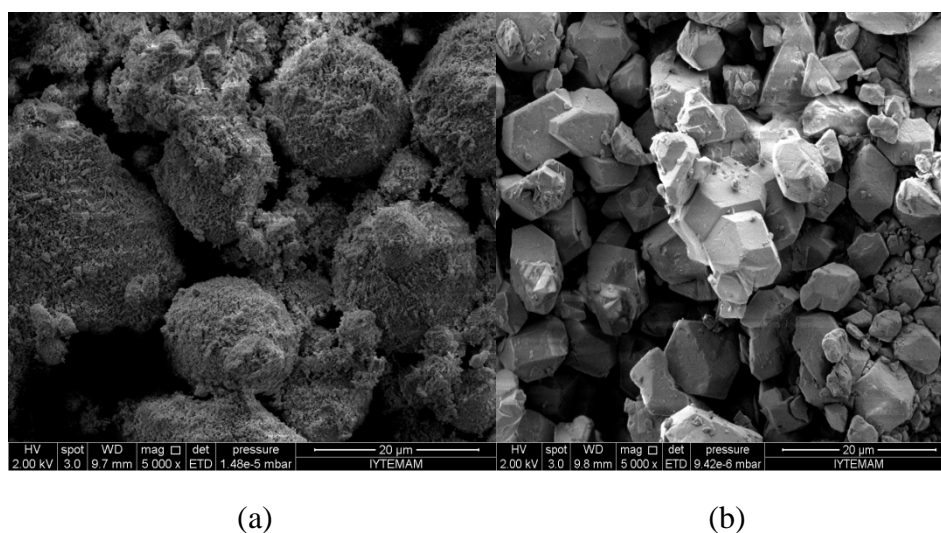


Figure 3: Scanning Electron Micrographs of the (a) MIL53(Al) and (b) CuBTC surfaces

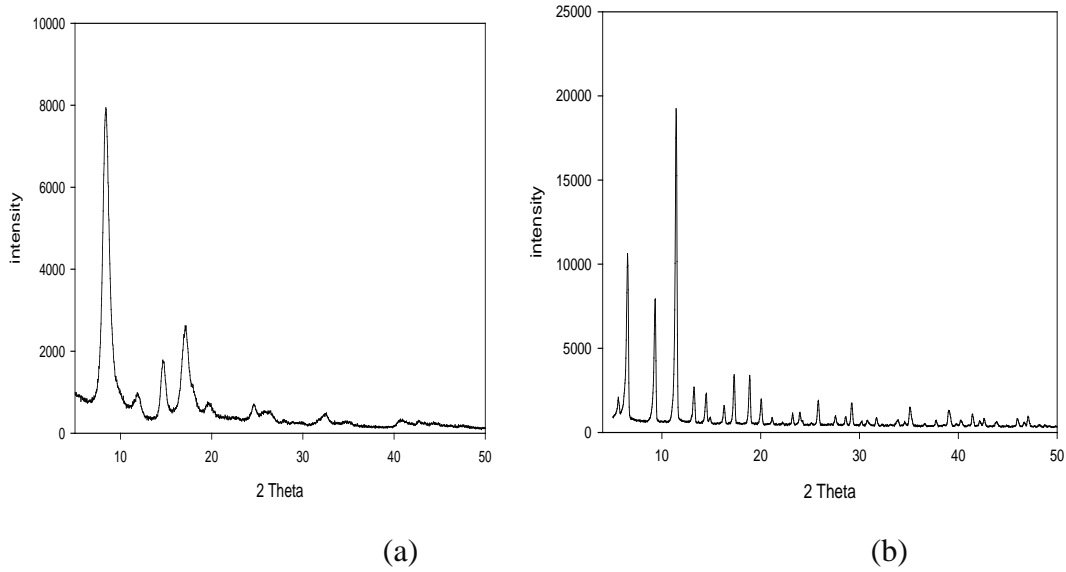
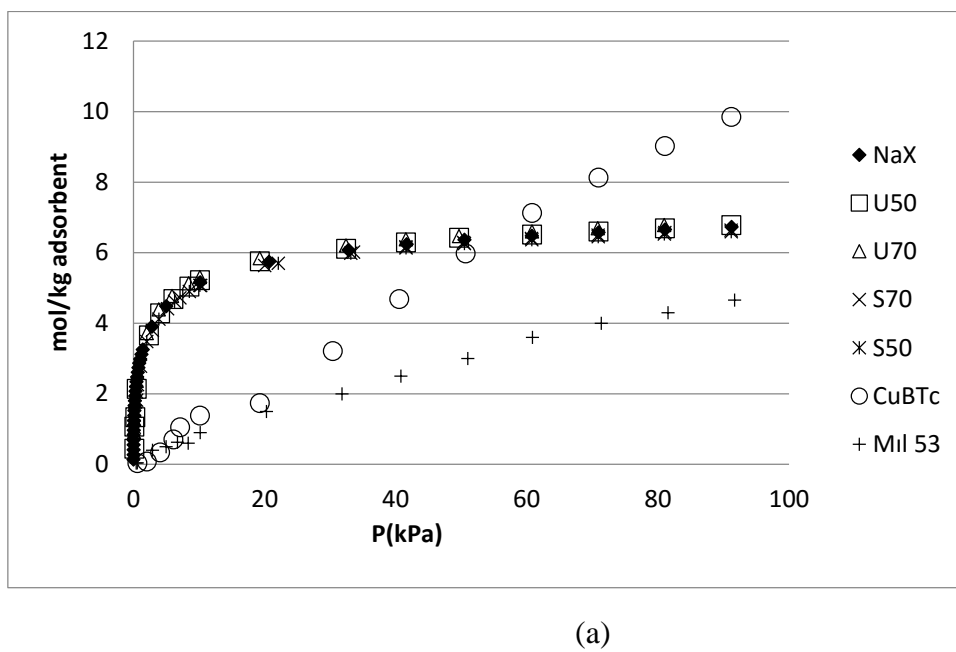
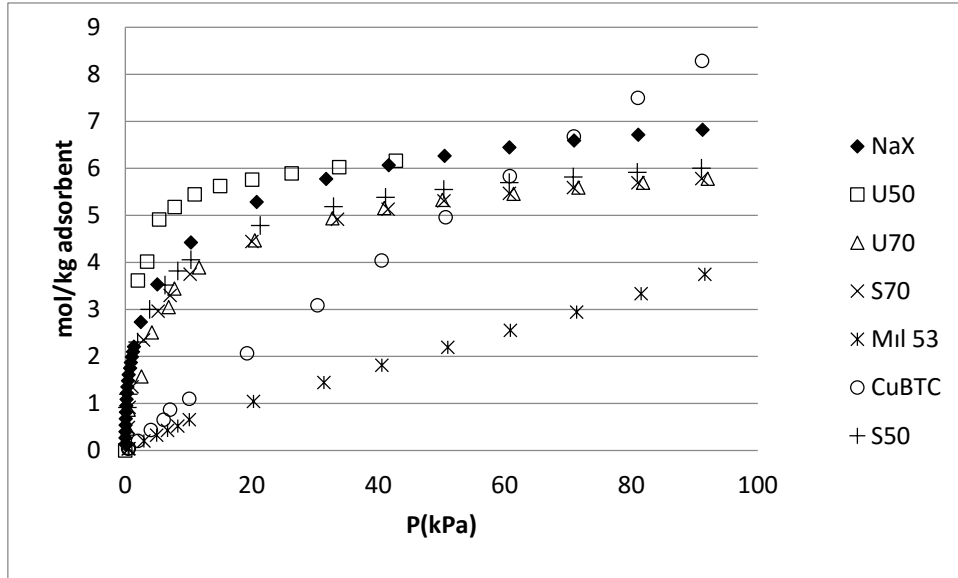


Figure 4: XRD Pattern of the (a) MIL53(Al) and (b) CuBTC adsorbents





(b)

Figure 5: CO<sub>2</sub> adsorption isotherm of the zeolites and MOFs at 278K (a) and 298K (b)

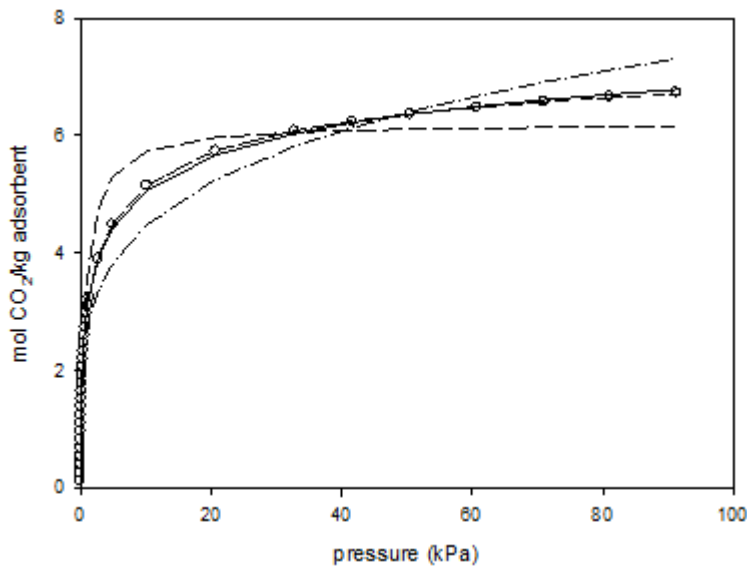


Figure 6: Adsorption isotherms of CO<sub>2</sub> at 278 K of NaX zeolite (points: experimental, model: curve fittings Langmuir: - - - Freundlich: - · - · - Sips: · · · · - Toth: ———)

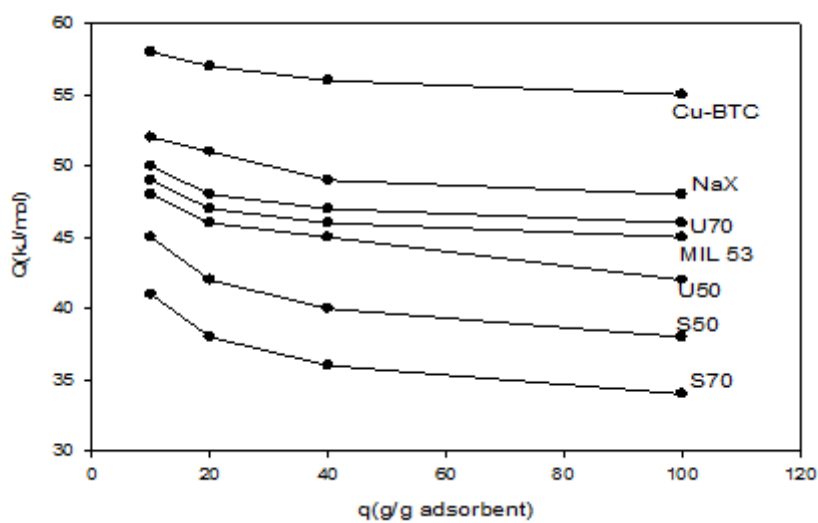


Figure 7: Comparison between isosteric heats calculated from Toth model equations for the adsorbents.

| Adsorbent codes* | $A_L/m^2 g^{-1}$ | $V_{mic}/cm^3 g^{-1}$ | $d_m/(\text{Å})$ |
|------------------|------------------|-----------------------|------------------|
| NaX              | 1058             | 0.37                  | 7.47             |
| U50 (79)         | 899              | 0.31                  | 6.55             |
| U70 (83)         | 1036             | 0.34                  | 5.67             |
| S50 (76)         | 902              | 0.31                  | 7.15             |
| S70 (81)         | 857              | 0.33                  | 6.48             |
| MIL 53           | 1278             | 0.4                   | 7.10             |
| CU-BTC           | 1473             | 0.43                  | 8.55             |

\*: Numbers in the parentheses are Na exchange amount%

$A_L$ : Surface area from Langmuir method;  $V_{mic}$ : micropore volume,  $d_m$ : median pore diameter from Howard–Kawazoe Method

Table 1: Textural properties of adsorbents

| Parameter     | NaX    |        | U70(86) |        | S50(76) |        | U50(79) |       | S70(81) |        | MIL 53 (Al) |        | Cu-BTC |
|---------------|--------|--------|---------|--------|---------|--------|---------|-------|---------|--------|-------------|--------|--------|
|               | 278K   | 298K   | 278K    | 298K   | 278K    | 298K   | 278K    | 298K  | 278K    | 298K   | 278K        | 298K   | 278K   |
| $q_m$         | 7.10   | 6.89   | 6.90    | 6.69   | 7.30    | 7.10   | 7.70    | 6.54  | 7.10    | 6.50   | 1.70        | 1.40   | 5.60   |
| $b(kPa^{-1})$ | 0.28   | 0.2    | 0.17    | 0.166  | 0.22    | 0.21   | 0.15    | 0.139 | 0.19    | 0.171  | 0.0009      | 0.0009 | 0.004  |
| $t$           | 0.24   | 0.29   | 0.54    | 0.61   | 0.35    | 0.4    | 0.67    | 0.69  | 0.43    | 0.5    | 0.71        | 0.82   | 0.24   |
| $R^2$         | 0.9973 | 0.9994 | 0.9994  | 0.9986 | 0.9993  | 0.9990 | 0.9999  | 0.995 | 0.9964  | 0.9994 | 0.99999     | 0.98   | 0.9998 |
| $SE$          | 0.09   | 0.04   | 0.04    | 0.07   | 0.05    | 0.07   | 0.02    | 0.13  | 0.13    | 0.04   | 0.0036      | 0.11   | 0.02   |
| $SSE$         | 0.13   | 0.02   | 0.02    | 0.06   | 0.10    | 0.14   | 0.007   | 0.21  | 0.026   | 0.01   | 0.001       | 0.001  | 0.007  |

$$SSE = \sum_{i=1}^m (Q_i - q_i)^2$$

Sum of square error:

$q_i$ : observation from the batch experiment  $i$ ,  $Q_i$  is the estimate from the isotherm for corresponding  $q_i$

Standard error:  $SE = \left[ \frac{1}{m-p} \sum_{i=1}^m (Q_i - q_i)^2 \right]^{0.5}$

$m$ : number of observations in the experimental isotherm,  $p$ : number of parameters in the regression model

$q_m$  = the amount adsorbed (mmole CO<sub>2</sub>/ g zeolite) at monolayer coverage

Table 2: Isotherm Model fitting for CO<sub>2</sub> adsorption data

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