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STUDIES OF ADSORBENTS AND PRESSURE/VACUUM SWING ADSORPTION FOR CO_2 CAPTURE

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Abstract

The capture of carbon dioxide via Pressure/Vacuum Swing Adsorption (PSA/VPSA) has been examined experimentally and mathematically. The adopted method was a two bed/four step process, known as the Skarstrom Cycle. Pelletised and calcined SBA-15 powder has been modified with a monoamine, a diamine and a triamine and has been tested in a PSA configuration. The performance of the monoamine modified SBA-15 was more than doubled with the presence of immobilised polyamine groups (diamine/triamine modified SBA-15) extending the adsorption capacity of the material (chemisorption), but still not comparable to the performance of zeolite 13X (physisorption) in terms of performance, stability and reproducibility. These results will be compared to the performance of four Metal Organic Frameworks, ZIF-8, ZIF-67, UiO-66 and CuBTC which are innovative and promising materials with several applications. Experimentally, the performance of zeolites and amine modified mesoporous silicas has been investigated for different experimental conditions (cycle time, pressure ratio, feed/purge ratio). This work is further supported by theoretical studies of PSA which employs a mathematical model based on linear coupled macropore and micropore diffusion and, where appropriate, reaction. These simulations are performed using gProms.

Keywords: *CO_2 Capture, Pressure Swing Adsorption, SBA-15, MOFs*

1. Introduction

Carbon dioxide is one of the major anthropogenic greenhouse gases and its concentration level in the atmosphere has been rapidly increasing in the atmosphere particularly since the middle of the last century. Recently, the level of atmospheric CO_2 has reached the alarming level of 400 ppm, which corresponds to a 90 ppm uptake in the last sixty years.

Approximately 87% of all anthropogenic CO_2 emissions come from fossil fuels which are the dominant energy source at the moment. Since an immediate halt of carbon dioxide emissions is unlikely to happen, there is an urgent need for the development of new processes and technologies for the effective capture and utilization/sequestration of emitted CO_2.

Chemical absorption with solvents, cryogenic separation, membrane separation and adsorption in solid adsorbents are some of the proposed methods for the capture of CO_2. Adsorption separation is considered to be the less energy demanding, more effective in terms of cost and performance and the most adaptable for different pressures and temperatures.

Many adsorbents with different properties have drawn the attention of researchers over the last couple of decades. Zeolites in general and zeolite 13X in particular have been undoubtedly considered as the most efficient adsorbents in terms of adsorption capacity, performance and capital cost. However, there are significant disadvantages in this regard particularly in respect of moisture selectivity and the high energy demand for the regeneration of these adsorbents.

The need for new materials that combine high selectivity for CO_2 relative to N_2, low hydrophilicity and low energy requirements for operation and regeneration purposes has led to the investigation of new adsorbents such as amine impregnated mesoporous silicas, activated carbons and Metal Organic Frameworks (MOFs), bare or amine functionalized. The adsorption mechanism for MOFs and activated carbon is physical adsorption as in the case of zeolites. In the case of amine modified solid adsorbents the leading adsorption mechanism in chemisorption.

Ordered mesoporous silicas such as MCM-41, MCM-48, SBA-12, SBA-15 and SBA-16 are highly porous materials [11] with low selectivity for CO_2. After amine modification, there is a significant enhancement in the CO_2 binding affinity. The energy requirements for the regeneration of amine impregnated mesoporous silicas are very reasonable. However, there is a significant degree of toxicity and corrosiveness involved due to the organic components. Besides, these materials are expensive and not commercially viable at this time.

Metal Organic Frameworks (MOFs) are newly developed ultra-high surface area materials suitable for multiple applications, one of which is the separation and capture of carbon dioxide. MOFs could be used as physical adsorbents or as chemical adsorbents. MOFs are quite expensive materials but they are progressively becoming more commercially acceptable in recent years.

The CO_2 adsorption capacity of some of the aforementioned materials have been examined and listed on a pure component basis by Sumida et al.[16] (see Appendix, Table 1). However, no effort for real separation in fixed beds has been made due to the lack of pellet shaped material. In this work, pellet shaped materials suitable for the industrial application of CO_2 capture via Pressure Swing Adsorption have been prepared, examined and compared.

2. Experimental

2.1. Preparation and amine modification of SBA-15 pellets

2.1.1. Preparation of pellets

SBA-15 pellets were prepared for the investigation of the adsorption capacity of the bare and amine modified material. A binder (methylcellulose) and a cement (bentonite) were added to the SBA-15 powder (Glantreo Ireland Limited, Cork) to produce a mixture of the following mass ratio: (deionized Water) 10: (silica) 3: (bentonite) 1: (methylcellulose) 1 and extracted by a Makin's clay extruder (diameter 1.7mm). The pellets were cut to the desirable length (4 mm), fully dried and then calcined at 600^{o}C for 6 hours. For the regeneration of the hydroxyl groups, the pellets were boiled in water for 16 hours, as proposed by Dugas and Chevalier [4].

2.1.2. Amine modification

Three amines with the same linker group were selected for the amine modification of the SBA-15 pellets (see Appendix).

According to Yong Li et al. [8], amine impregnated materials have extended CO_2 adsorption capacity over amine grafted, co-condensed or post-grafted materials, due to the larger amount of physically and chemically loaded amines.

The method used for the amine modification of SBA-15 and MOFs was wet impregnation. Ethanol was used as the solvent. The amine-ethanol solution was prepared by mixing 50 ml of amines with 200 ml of ethanol (20% amine solution) and shaking carefully for 5 minutes. Finally, the SBA-15 pellets were introduced in the solution and stirred for 72h at 100 rpm at 50°C. The pellets were then washed with ethanol and dried at room temperature.

2.2. Preparation of MOF pellets

Three different MOFs were selected for the preparation of pellets: HKUST1 (or CuBTC), ZIF 8 (MOF Technologies, Belfast, UK) and UiO-66 (MOFapps, Levalloit-Perret, France). The mass ratio of the mixture was: (deionized Water) 2: (MOF) 1: (bentonite) 0.15: (methylcellulose) 0.15 and the process employed was the same as in the case of SBA-15.

2.3. Breakthrough tests

The breakthrough curve represents the evolution of the gas concentration as a function of adsorption parameters, such as operating pressure and temperature, gas concentration etc. [11]

A 10% CO_2/ 90% N_2 gas mixture was used for the completion of the breakthrough experiments. The column was filled with regenerated pellets and 1000 sccs/min of the gas mixture was introduced into it. The breakthrough curve was measured by an infrared CO_2 detector at the exit of the column. The operating pressure was 4.5 bara and was measured at the exit of the column. The temperature of the experiments was maintained constant at 25^{o}C.

2.4. Pressure/Vacuum Swing Adsorption

The PSA process considered in this study consisted of two beds and four steps, otherwise known as Skarstrom cycle. Pressurization and adsorption were cyclically followed by depressurization and desorption (see Figure 1). The experimental conditions were the same as in the case of the breakthrough experiments.

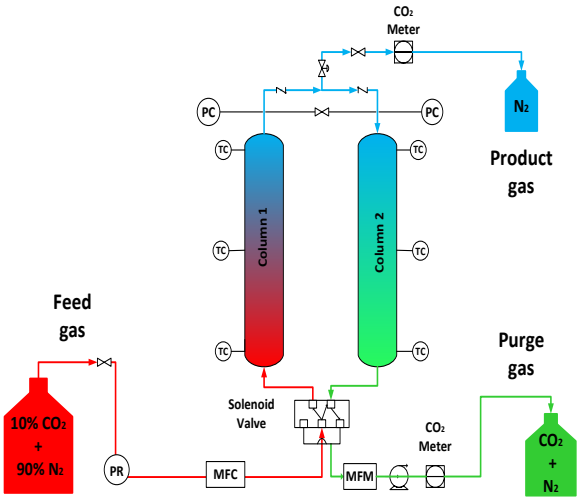


Figure 1. Simplified configuration of PSA system

3. Results and Discussion

3.1. BET surface area

The surface area and the pore radius of the pellet shaped adsorbents were compared to the properties of the pure materials (powder), using a Quantachrome BET surface area analyser (Table 1).

In the case of SBA-15, the surface area of the pellets was dramatically decreased compared to the powder. Further decrease in the surface area was recorded in the amine modified materials with the amount of amines having an inversely proportional effect on the surface area.

In the case of MOFs, the pelletisation process had a significant effect on ZIF 67 and HKUST 1, with the surface area being close to the surface area of zeolite 13X. The pellets with the highest surface area were measured for ZIF 8 (1471 m^2/g).

3.2. Breakthrough curves

3.2.1. Amine functionalised SBA-15

Breakthrough tests were conducted for the amine modified materials (Figure 2). Initially, polyamine functionalised materials showed significantly stronger adsorption capacity compared to the monoamine modified SBA-15. Moreover, the lack of sharp curves in the case of the polyamine materials indicated the slower kinetics compared to the monoamine material. However, the CO_2 adsorption capacity was progressively decreased after different regeneration strategies (air or nitrogen flow treatment at high temperature, vacuum regeneration) and the initial adsorption profile of diamine SBA-15 was never fully recovered (Figure 3). A similar behaviour was observed for triamine functionalised SBA-15.

There are several explanations for the behaviour of the polyamine adsorbents. Depending on the sensitivity of the amino-chain, amino groups could undergo oxidation to oxime or imine species during thermal treatment and lead to structural damage [2]. The formation of urea in the absence of water [15], amine degradation and amine loading [5] are also possible explanations for the irreversibility in the behaviour of these two adsorbents, marking some of the limitations of chemisorption.

This behaviour was not observed in monoamine modified SBA-15 and the breakthrough profile of this adsorbent was reproducible after different regeneration strategies (Figure 4). The achievement of complete regeneration of the adsorption capacity of the adsorbent at 100°C for 60 min is of significant importance due to the low energy consumption, compared to zeolites. Zeolite 13X, which is the dominant adsorbent for the capture of CO_2 with PSA, requires regeneration for 12 hours at 200°C.

In the presence of moisture, the adsorption capacity is expected to be doubled due to the formation of one carbonate for each amine, instead of one carbamate for every two amines in the case of a dry stream (see Appendix, Figure 1). In order to explore this fact, the monoamine modified pellets were partially moisturized by exposure to open air for 5 and 20 minutes respectively. The adsorption capacity of the moisturized pellets was increased by 11% and 26% respectively (see Figure 5), clearly indicating that the presence of moisture enhances the CO_2 adsorption capacity. Further extension of the breakthrough time (and hence adsorptive capacity) is expected in the presence of a constant level of moisture in the feed gas. This is another advantage over zeolite 13X, the CO_2 adsorption capacity of which is lowered in the presence of moisture.

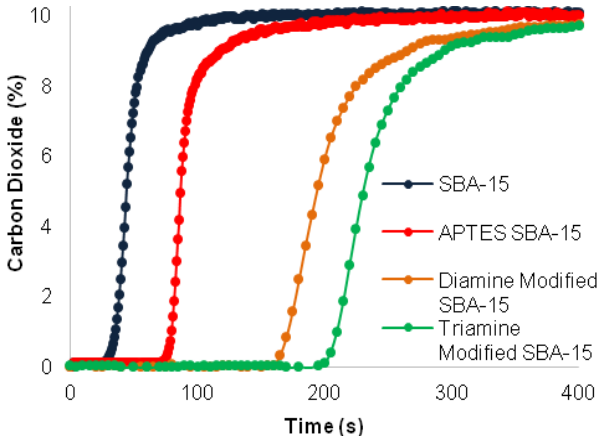


Figure 2. Comparison of adsorption capacity of SBA-15 and amine functionalised SBA-15 adsorbents.

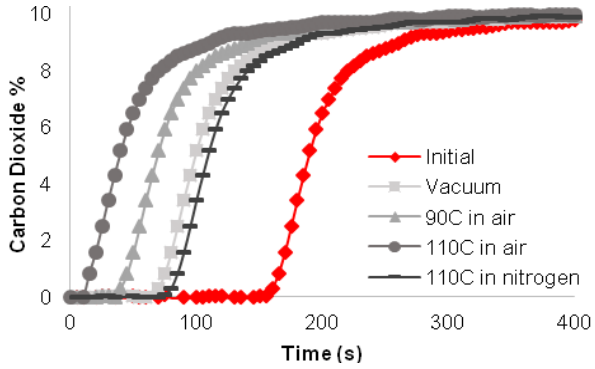


Figure 3. Comparison of adsorption capacity of Diamine SBA-15 after different regeneration strategies.

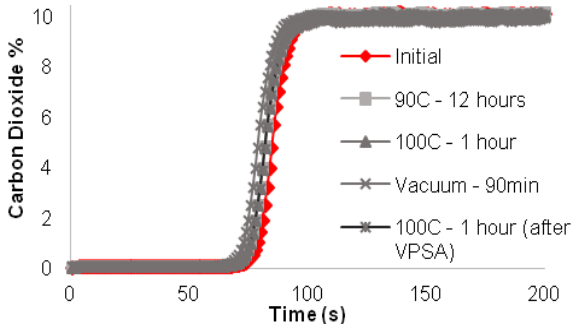


Figure 4. Comparison of adsorption capacity of Monoamine SBA-15 after different regeneration strategies.

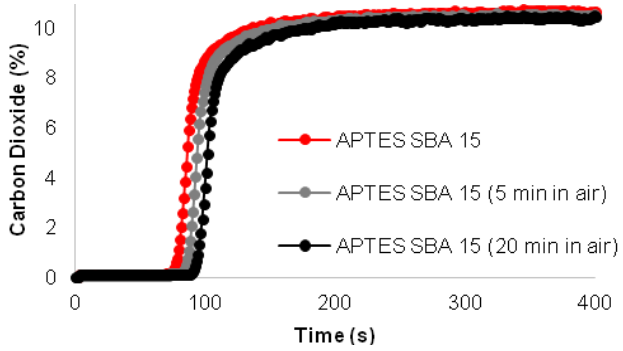


Figure 5. Adsorption capacity of SBA-15 with and without moisture

3.2.2. Metal Organic Frameworks (MOFs)

The adsorption capability of ZIF 8, HKUST 1 and APTES-HKUST 1 was examined and is illustrated in Figure 6. ZIF 67, due to its high toxicity and dramatic loss of surface area, was not examined.

Although the time-to-break was almost the same in each case, the shape of the breakthrough curve indicates that the adsorption mechanism is quite different.

The CO_2 adsorption capacity of HKUST 1 and ZIF 8 powder was measured by Sumida et al. as 19.8 wt% and 4.3 wt% respectively. However, it appears that the pellet shaped HKUST 1 does not have the same properties as the powder. The presence of water, binder and cement has significantly transformed the pore structure of HKUST 1. The surface area of the pellet shaped material has been greatly decreased (Table 1) while its structure has dramatically changed (see Figure 7).

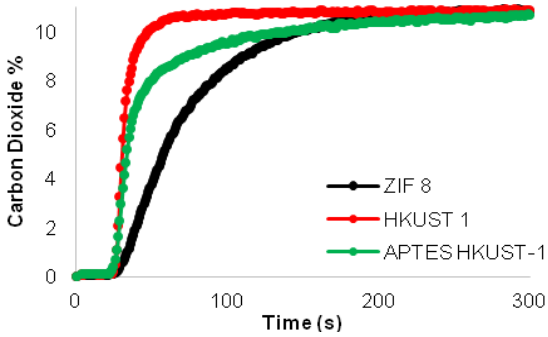


Figure 6. Adsorption capacity of MOFs

The shape and structure of the particles of ZIF 8 were maintained after the pelletization process (see Figure 8), which is in accordance with the modest loss in the surface area of the pelletized material. However, despite the high surface area, the CO_2 adsorption capacity at low pressures was very poor.

Table 1. Comparison of properties of the different types of adsorbents

Adsorbent Type	BET Surface area m^2/g		Pore radius Å
	Powder	Pellet	
Zeolite 13x	-	658	10
SBA-15	726	314.25	24.61
Monoamine SBA-15	-	197.8	24.7
Diamine SBA-15	-	188.62	24.75
Triamine SBA-15	-	175.24	24.73
HKUST 1	1271.2	605	
ZIF 8	2047.1	1471.5	14.75
ZIF 67	1789.6	464.4	-
UiO 66	1110.8	787.4	-

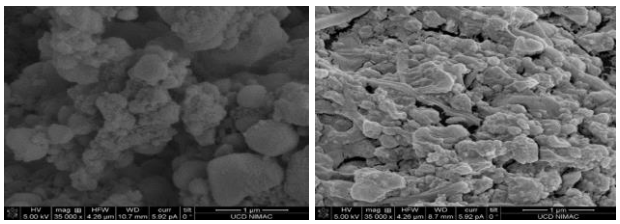


Figure 7. SEM for HKUST 1 powder (a) and pellet (b)

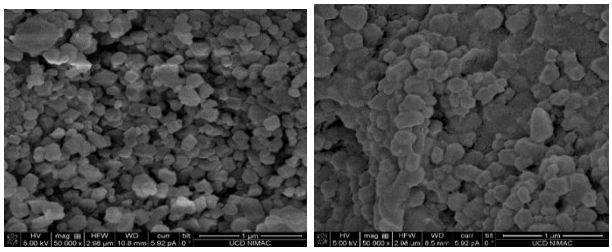


Figure 8. SEM for ZIF 8 powder (a) and pellet (b)

3.2.3. Comparison with zeolite 13x

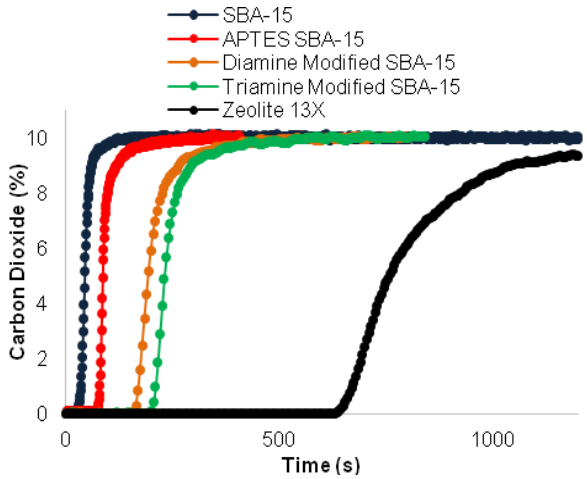


Figure 9. Comparison of adsorption capacities of different adsorbents.

The CO_2 adsorption capacity of the aforementioned materials is very low compared to zeolite 13x which is the dominant adsorbent in CO_2 capture with PSA (see Figure 9). The breakthrough time of zeolite 13X was 7 times higher compared to APTES SBA-15 and almost 35 higher compared to the MOFs.

3.3. PSA/VPSA

3.3.1. Zeolite 13X

CO_2 PSA tests were conducted for zeolite 13X. The experimental purity and recovery for the simple Skarstrom cycle were relatively low given the potential of the adsorbent but they were matching with the values mentioned in the literature [3].

In order to investigate the effect of the operating temperature in the case of zeolite 13X, a mathematical model based on linear coupled macropore and micropore diffusion was employed. Having obtained good agreement of the experimental and simulated data at 293K, the temperature range was expanded up to 373K, showing a significant improvement in the recovery and purity (see Figures 10&11). This increase in the adsorption properties at high temperatures is of significant importance for industrial purposes since the cooling of the gas is an unnecessary expense.

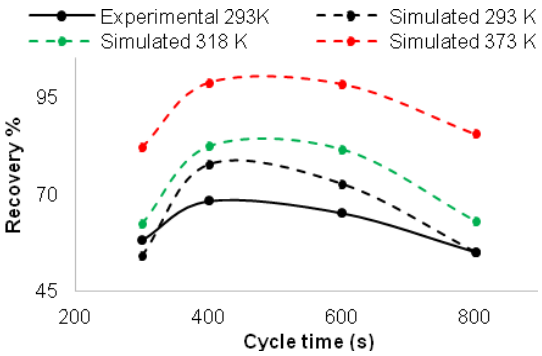


Figure 10. Experimental and simulated PSA recovery for zeolite 13X.

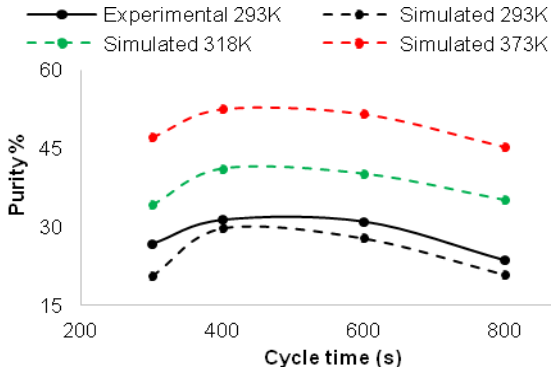


Figure 11. Experimental and simulated PSA purity for zeolite 13X.

4. Conclusions

The purpose of this work was the investigation of the CO_2 adsorption capacity of pelletized adsorbents and their comparison with zeolite 13X, the dominant adsorbent for CO_2 capture in PSA. In the case of SBA-15, there was a significant loss in the surface area of the pelletized material compared to the powder, which was further reduced after the amine modification process. The poor performance of the “bare” SBA-15 pellets was dramatically enhanced in the presence of amino-groups. However, the lack of reproducibility of the breakthrough profiles for amines other than APTES, a monoamine, as a result of amine loading and degradation, urea formation and oxidation highlighted the limitations of chemisorption. The monoamine modified SBA-15 was stable with energy efficient regeneration properties (60 min at 100^{o}C) and promising properties in the presence of moisture (up to a factor of two higher adsorption capacity due to the formation of carbonates instead of carbamates, in the absence of moisture). The adsorption capacity of the pellet shaped HKUST 1 was very poor compared to the properties of the HKUST 1 powder in the literature, indicating that the pelletization process affects the crystal and surface structure of this MOF. ZIF 8 was robust and consistent in its adsorption capacity before and

after pelletization with the amount of the adsorbed CO_2 remaining at 4 wt%.

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References

[1] Agarwal, A., Biegler L. T., Zitney S. E. Superstructure-based optimal synthesis of pressure swing adsorption cycles for precombustion CO_2 capture. *Industrial & Engineering Chemistry Research*, 2009, **49**(11): 5066-5079.

[2] Calleja, G., Sanz R., Arencibia A. et al. Influence of drying conditions on amine-functionalized SBA-15 as adsorbent of CO_2. *Topics in Catalysis*, 2011, **54**(1-4):135-145.

[3] Cavenati, S., Grande C A, Rodrigues A E. Removal of carbon dioxide from natural gas by vacuum pressure swing adsorption. *Energy & fuels*, 2006, **20**(6):2648-2659.

[4] Dugas, V., Chevalier Y. Surface hydroxylation and silane grafting on fumed and thermal silica. *Journal of colloid and interface science*, 2003, **264**(2): 354-361.

[5] Hedin, N., Andersson L., Bergström L. et al. Adsorbents for the post-combustion capture of CO_2 using rapid temperature swing or vacuum swing adsorption. *Applied Energy*, 2013, **104**: 418-433.

[6] Hu, B., Chen, J. & Zhang, F.-Q., 1993. Concentration and Recovery of C02 from Flue Gas by Pressure Swing Adsorption. *Industrial & Engineering Chemistry Research*, **32**: 2714–27–20. Available at: http://www.ncbi.nlm.nih.gov/pubmed/22241938.

[7] Ko, Y. G., Shin S. S., Choi U. S. Primary, secondary, and tertiary amines for CO_2 capture: Designing for mesoporous CO_2 adsorbents. *Journal of colloid and interface science*, 2011, **361**(2): 594-602.

[8] Li, Y., Sun N., Li L. et al. Grafting of amines on ethanol-extracted SBA-15 for CO_2 adsorption. *Materials*, 2013, **6**(3): 981-999.

[9] Liu S. H., Wu C. H., Lee H. K. et al. Highly stable amine-modified mesoporous silica materials for efficient CO_2 capture. *Topics in Catalysis*, 2010, **53**(3-4): 210-217.

[10] Mello, M. R., Phanon D., Silveira G. Q. et al. Amine-modified MCM-41 mesoporous silica for carbon dioxide capture. *Microporous and Mesoporous Materials*, 2011, **143**(1): 174-179.

[11] Mihaly, M., E. Andreiadis, E. Pincovski, *Determination of Breakthrough Curves Parameters on Online Solid-phase Extraction Cartridges*, UPB Scientific Bulletin, Series B, 2005, **67**: 57-64.

[12] Serna-Guerrero, R., Belmabkhout Y., Sayari A. Modeling CO_2 adsorption on amine-functionalized mesoporous silica: A semi-empirical equilibrium model. *Chemical Engineering Journal*, 2010, **161**(1): 173-181.

[13] Serna-Guerrero, R., Sayari A. Modeling adsorption of CO_2 on amine-functionalized mesoporous silica. 2: Kinetics and breakthrough curves. *Chemical Engineering Journal*, 2010, **161**(1): 182-190.

[14] Serna-Guerrero, R., Dana E., Sayari A. New insights into the interactions of CO_2 with amine-functionalized silica, *Ind. Eng. Chem.* Res., 2008, **47**: 9406–9412.

[15] Subagyono, D. J. N., Marshall M., Knowles G. P. et al. CO_2 adsorption by amine modified siliceous mesostructured cellular foam (MCF) in humidified gas. *Microporous and Mesoporous Materials*, 2014, **186**: 84-93.

[16] Sumida, K. et al., 2012. Carbon dioxide capture in metal-organic frameworks. *Chemical Reviews*, **112**(2): 724–781.

[17] Wagner, A., Steen B., Johansson G. et al. Carbon Dioxide Capture from Ambient Air Using Amine-Grafted Mesoporous Adsorbents. *International Journal of Spectroscopy*, 2013, (Article ID 690186), http://dx.doi.org/10.1155/2013/690186

[18] Yan, X. et al., 2011. Amine-Modified SBA-15 : Effect of Pore Structure on the Performance for CO_2 Capture. *Ind. Eng. Chem. Res.*, 2011, **50**:3220–3226.

[19] Zelenaka, V., Halamova D., Gaberova L., et al. Amine-modified SBA-12 mesoporous silica for carbon dioxide capture: Effect of amine basicity on sorption properties. *Microporous and Mesoporous Materials*, 2008, **116**(1): 358-364.

[20] Zhang, Z. et al., 2012. MOFs for CO_2 Capture and Separation from Flue Gas Mixtures: The Effect of Multifunctional Sites on Their Adsorption Capacity and Selectivity. *Chemical Communications*, 2013, **49**: 653-661.

[21] Zheng, F. et al, Ethylenediamine-modified SBA-15 as regenerable CO_2 sorbent, *Industrial and Engineering Chemistry Research* 44 (2005), pp. 3099–3105.

[22] Zhuravlev, L. T. Concentration of hydroxyl groups on the surface of amorphous silicas. Langmuir, 1987, **3**(3): 316-318.

Appendix

A. CO_2 adsorption capacity for MOFs

Table 2. CO_2 adsorption capacities for MOFs [16]

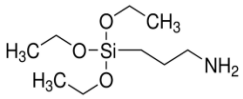
Name	BET Surface area (m^2/g)	CO_2 capacity (wt%)	Pressure (bar)	Temp. (K)
HKUST 1	1270	42.8	300	313
	1400	19.8	1	293
	-	18.4	1	298
	-	18.3	1	295
	1781	15.2	1	298
	1482	15	1	295
	-	10.6	0.8	298
	-	6.2	1	313
	857	6.2	1	295
ZIF 8	1135	4.3	1	298
UiO 66	-	24.3	18	303

B. Amines for SBA-15 modification

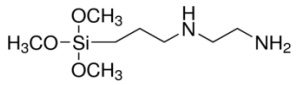
The three selected amines for the modification of SBA-15 are presented below. The linker group is the same in each case:

Monoamine (or APTES):

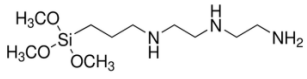
(3-Aminopropyl) triethoxysilane



- **Diamine:**
  [3-(2-Aminoethylamino)propyl] trimethoxysilane



- **Triamine:**
  N1-(3-Trimethoxysilylpropyl) diethylenetriamine



C. Dry and wet adsorption mechanism for SBA-15

The adsorption mechanism of CO_2 in APTES SBA-15 in the absence and presence of moisture is presented in Figure 1:

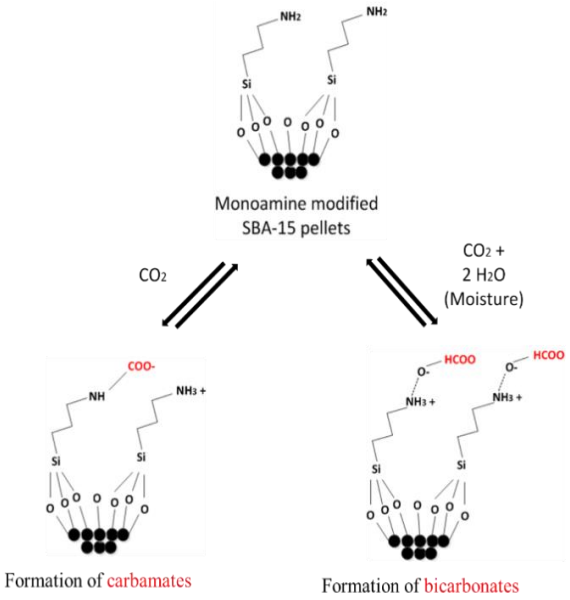


Figure 1. Formation of carbamates and bicarbonates

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