Kinetic and thermodynamic investigation of CO_2 adsorption-desorption on polyethyleneimine - mesoporous silica

[1]M.M. Khader, [1]Mohammed J. Al-Marri, [1]Y.O. Kuti, [2]M. Khraisheh, [3]E.P. Giannelis

[1]Gas Processing Center, College of Engineering, Qatar University, P.O. Box 2713 Doha, Qatar

[2]Department of Chemical Engineering, College of Engineering, Qatar University, P.O. Box 2713 Doha, Qatar

[3]Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA.

ABSTRACT

Two CO_2 solid sorbents based on polyethyleneimine, PEI (432 and 10k) impregnated into mesoporous silica (MPS) foam were synthesized and tested for CO_2 capture. At ambient pressure, the amount of CO_2 captured by these solid sorbents was less than the theoretical calculated from the stoichiometry. At higher pressures, the CO_2 adsorption capacity increased following Langmuir adsorption isotherm relationship. When the MPS foam was treated with the non-ionic surfactant, Span 80, the CO_2 adsorption capacity at ambient pressure was further increased. The CO_2 adsorption was interpreted using the double exponential kinetic model.

Keywords: Adsorption of CO_2, desorption of CO_2, polyethyleneimine, mesoporous silica and Span 80.

** corresponding author: Email:mmkhader@qu.edu.qa,*

1. Introduction

Increasing levels of CO_2 emissions have precipitated a serious environmental concern. The main sources of CO_2 emissions stem from natural gas streams and burned fossil fuels, so, attempts of removal of CO_2 from these sources has been gaining widespread interest [1-3]. A wide range of technologies for capturing CO_2 from natural gas streams have been proposed. They are based on different physical and chemical processes including absorption, adsorption, membranes and cryogenics. Chemical absorption by liquid amines, is the most applicable industrial technology for CO_2 scrubbing[4,5]. This technology has several drawbacks, e.g. requiring large amounts of energy to break the strong C\N bonds of the formed carbamates in regenerating the amine for further use[4-6], corrosiveness of the utilized tools and equipment, volatilization and degradation of amines, and disposal of the spent scrubber. To avoid the problems encountered with liquid amine solvents, CO_2 solid sorbents have been researched as possible alternatives [7,8]. One subset is based on the development of inorganic – organic hybrid sorbents [8-10]. In most of these sorbents, the inorganic substrate is usually in the mesoporous form, where it provides both substantial pore volume and high surface area into and onto which the active organic groups are incorporated [11-14]. The most widely inorganic mesoporous support used till now is mesoporous silica [11-17]. Among the adsorption techniques, capturing CO_2 on immobilized amine sorbents has been considered as one of the most promising approaches [18-21]. So far, amines immobilized on mesoporous silica (MPS) have shown to have the highest CO_2 adsorptivity, high desorption rate, negligent corrosion problems, and low energy consumption during regeneration [20,21]. To date a series of amine supported mesoporous silicas have been prepared and investigated [5,6,11-13,17,20]. Furthermore, when high molecular weight polyethyleneimine (PEI) is employed the volatilization and/or decomposition are expected to be minimal because of the relatively high melting temperature of such a high molecular weight material [5,17].

In the present work, we report on the effectiveness of PEI/MPS for capturing CO_2. As part of our objective to enhance the capture capacity of the sorbent we performed CO_2 adsorption experiments at higher pressures. Furthermore, the solid sorbents were treated with the non-ionic surfactant Span 80 with the objective of enhancing and accelerating the rate CO_2 capture. Finally the experimental results were subjected to a thermodynamic and kinetic analysis to evaluate the relevant adsorption parameters and further optimize the sorbent.

2. Experimental

The mesoporous silica (MPS) support was prepared as reported previously [11,12,34]. Polyethylenimine PEI 432 and PEI-10k (10,000 g/mol) were impregnated into the mesoporous silica. In a typical batch, a certain amount of PEI was added into 10 mL of dry ethanol. The obtained samples are referred to as PEI432-MPS and PEI 10k-MPS, respectively. Further treatment with the nonionic surfactants Span 80 was attempted using two different methods. In both methods the PEI and the nonionic surfactant loadings were 70% and 5%, respectively. In the first, the PEI and surfactant were mixed together and then impregnated to the silica foam. The product is denoted as (PEI and surfactant/MPS). In the second, the MPS foam was first treated by the surfactant, and then the PEI was impregnated into the surfactant/MPS mixture. The resulting product is denoted as (PEI on the surfactant /MPS).

The CO_2 sorption–desorption cycles of the prepared PEI/MPS sorbents were monitored using a Pyris 6 TGA Perkin Elmer thermal gravimetric analyzer (TGA) from the weight increases/decreases during the sorption and desorption process in pure CO_2.

Rubotherm Magnetic Suspension Balance (MSB) was utilized for the high pressure CO_2 adsorption capacity determination.

3.0 Results and discussion

Though, the SEM investigation has shown that the PEI/MPS samples exhibited porous morphology, which allows access into the porous matrix [20], the stoichiometric

calculation revealed that the sorption capacity of the PEI/MPS at ambient conditions was not reached. Two possible explanations are proposed: first, the amine droplets blocked some of the pores and/or the micro channels between the pores that prevent eventually access of CO_2 to the PEI molecules inside these blocked pores and/or channels. Second, the reduced adsorption could be due to the deposition of PEI inside and outside the pores in the form of liquid droplets, which due to the skin formation also prevent complete exposure to CO_2. The PEI porous blocking and droplet formation can, in principle, decrease the CO_2 sorption capacity and diffusivity into the solid sorbent. In order to overcome these two limitations, two approaches were attempted: first carrying out the CO_2 sorption at higher pressure and, second, the sorbent was treated by a non-ionic surfactant that might assist with better wetting and spreading of the PEI droplets.

3.1. Effect of CO_2 pressure: Figure 1 shows the amount of CO_2 adorbed on PEI423/MPS and PEI/10k/MPS. In both cases, most of the CO_2 adorption ocuured at lower pressure. Indeed, increasing the pressure did not enhance the extent of adsorption significanty; typically this is a chemisorption phenomena which is best desribed by Langmuir relation.

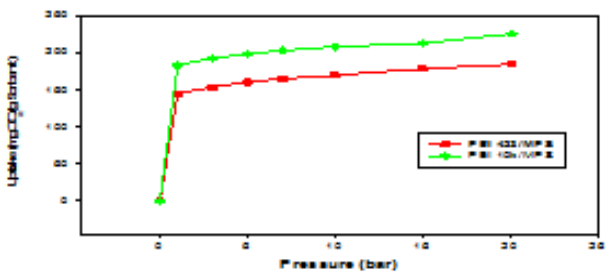

Figure 1: *Comparison of CO_2 adsorption between PEI-423/MPS and PEI-10k/MPS.*

Langmuir equation is written as:

$$\frac{p}{n} = \frac{1}{n_m} b + \frac{p}{n_m} \qquad (1)$$

Where p is pressure, n is the amount of CO_2 adsorbed, n_m is the sorbent monolayer capacity, and b is the coefficient of adsorption specific to the adsorbate/adsorbent relationship. When $\frac{p}{n}$ was plotted vs p good straight lines were obtained with the their intercept as the coefficient of adsorption (b) while the inverse of the slope is monolayer (n_m) – (as given in Tables 1).

Table 1: The adsorption coefficient b and monolayer coverage as deduced from Eq. 1.

T (^oC)	Polyethylen imine – Mesoporous Silica			
	PEI 423		PEI 10K	
	b	(n_m) (mg)	b	(n_m) (mg)
55	0.0023	172.41	0.0016	172.41
65	0.0023	172.41	0.0016	192.31
75	0.0029	185.19	0.0022	227.23
85	0.0024	188.68	0.0021	250.00

The experimental results showed that there is a significant differences between the amount of gas adsorbed at 1 bar and 20bar for both PEI 423 and PEI 10k sorbents. The monolayer coverage of CO_2 to PEI 10k/MPS increased as the sorption temperature increased, this is becaue PEI 10k/MPS molecule has bent structure, so as the temperature increased the molecule is straightened out, i.e. its exposure to the gas increased, consequently the monolayer coverage increased. On the other hand, the monolayer of PEI 423/MPS is about constant at all temperatures, simply because PEI 432 molecule is a straight mollecule and is not effected by temperature.

Under an isosteric condition, we estimated the enthalpy (ΔH) and entropy (ΔS) of CO_2 adsorption on the sorbents PEI 10K/MPS, PEI423/MPS via below equation:

$$In(p) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \qquad (2)$$

The above expression is derived is from relationship of enthalpy (H) with gibbs energy (G) and entropy (S) of any given system: $\Delta G^o = \Delta H^o - T\Delta S^o$ (3)

The gibbs energy of a chemical reaction is zero at equilibrium, when we considered the above reaction at equilibrium, hence the equation will take the following form: $\Delta G^o = -RTlnK$ (4)

Where G is free energy at any moment. By plotting In(p) vs 1/T the intercept of the graph is equal (ΔH)/R where R = 8.314J/ mol. K. From the graphs of ln(p) vs 1/T the enthalpy of adsorption for the sorbents PEI 423, PEI 10K, were estimated to be 55kJ/mol and 61kJ/mol (Fig. 3). Similarly, the entropies were estimated to be 2065.6 J/K, 2066.4J/K, for PEI-10K/MPS and PEI-423/MPS respectively.

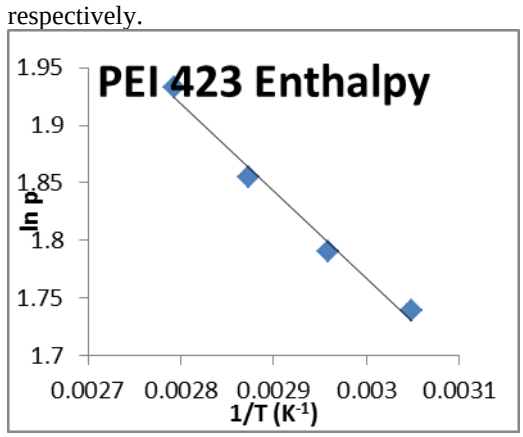

Figure 3: the relation between ln PCO2 and the reciprocal temperature at fixed surface cuverage of 10 mg CO2/g sorbent.

3.2.2. Influence of surfactants

The CO_2 adsorption-desorption cycles of PEI 423/MPS and PEI 423/MPS at 75℃ are shown in Fig. 2. It is clear that the CO_2 adsorption is a two stage process: the first step exhibited a sharp linear weight gain and took about 5-10 min followed by a second, much slower adsorption process that reached a maximum after about 2 hours of exposure to CO_2. The rate sorption capacity was increased with temperature till reached its maxima at 75℃ and 85℃ for PEI-423 and PEI-10k, respectively.

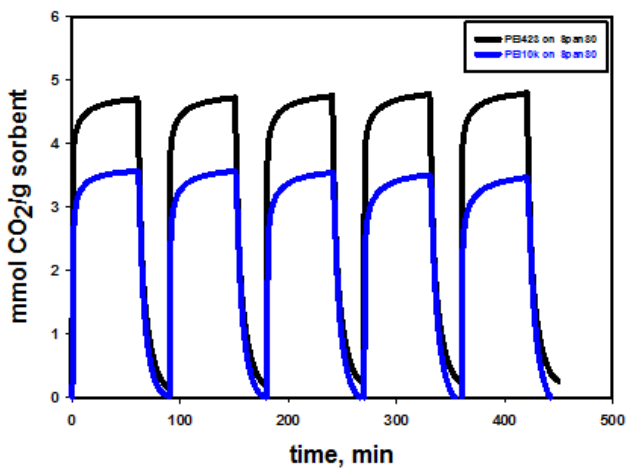

Figure 2: Adsorption-desorption of CO_2 on PEI423-Span 80/MPS and PEI 10k-Span 80/MPS at 75 ℃.

When the flow was switched from CO_2 into N_2, there was a noticeable mass loss, due to CO_2 desorption as shown in Fig. 1. In all experiments which were carried out under ambient pressure, the PEI-423 was more active than PEI-10k towards CO_2 adsorption. The activity of PEI-423 was due to the fact that this polymeric material had only primary and secondary amine groups, which were both active for CO_2 adsorption and both form carbamates according to reactions 5a and 5b.

$$CO_2 + 2RNH_2 \rightarrow RNHCO_2^- + RNH_3^+ \quad (5a)$$

$$CO_2 + 2R_1R_2NH \rightarrow R_1R_2NCO2^- + R_1R_2NH2^+ \quad (5b)$$

Under hydrous conditions ammonium bicarbonate is expected to form as expressed in Equation (5c) [35,36].

$$CO_2 + 2R{-}NH_2 + H_2O \rightarrow R{-}NH_3^+ \, HCO_3^- \quad (5c)$$

On the other hand, the PEI-10k in addition to having the active primary and secondary amine groups, it contains also the inactive tertiary amine with the ratio of the primary: secondary: tertiary amines of 1:2:1, respectively. Tertiary amine is active for CO_2 adsorption under hydrous conditions only [35-37]. Since the PEI-423/MPS and PEI-10k/MPS samples contain similar nitrogen contents, it is not surprising that the activity of PEI-423/MPS towards CO_2 adsorption was about 1.25 times higher than the activity of the PEI-10k/MPS (Fig. 2).

The surfactant effect on the adsorption process was studied by running adsorption experiments at 55, 65 and 75 and 85℃ with PEI/MPS. At all temperatures, the surfactant has an enhancing effect on CO_2 maximum absorptivity.

In order to quantify the surfactant effect on the rate of the CO_2 adsorption processes, the kinetics of adsorption was analyzed using the double exponential kinetic model. According to this model the mass of CO_2 adsorbed as a function of time is expressed by the following double exponential equation [20,38,39]:

$$\frac{M_t}{M_e} = A_S\left(1 - exp^{(-k_S t)}\right) + A_D\left(1 - exp^{(-k_D t)}\right) \quad (6)$$

In Eqn. 6, M_t and M_e represent the experimental mass gain due to CO_2 sorption at time t and after reaching equilibrium, respectively. The rate constants k_S, and k_D for the PEI/MPS and PEI-surfactant/ MPS are shown in Table 2.

Table 2: Kinetic parameters as obtaind from Eqn. 6.

T, ℃	PEI 10k(i)		PEI 10k on Span 80		PEI 423(i)		PEI 423 on Span 80	
	k_S	k_D	k_S	k_D	k_S	k_D	k_S	k_D
55	-	-	-	-	1.507	0.036	1.165	0.041
65	0.151	0.038	1.695	0.048	1.673	0.037	1.873	0.044
75	0.726	0.037	0.891	0.068	1.728	0.059	1.569	0.062
85	0.785	0.058	3.155	0.977	4.364	1.596	5.589	2.928
95	5.417	1.198	5.126	1.477	8.313	2.080	7.792	2.123

(i) From our published paper in Ref. 20.

It is clear that both the surface and diffusion rate constants were increased greatly due to treating the sorbents with the non-ionic surfactant Span 80. Possible explanations for the CO_2 enhancement could be due to 1) an improved dispersion of the PEI on the MPS surface due to prior deposition of the surfactant and 2) enhanced CO_2 diffusion through the amine coating layer.

Conclusions

We synthesized mesoporous silica foam, functionalized with PEI and used it as CO_2 sorbent. This sorbent exhibited high CO_2 adsorption capacity. When adsorption occurred at high pressures both the PEI 423/MPS and the PEI 10k/MPS exhibited enhanced sorpitivity.

The capacity towards CO_2 adsorption was also enhanced by depositing the nonionic surfactant Span 80 whether prior to PEI deposition or simultaneously with the PEI. The data obtained from double exponential kinetic model showed that the surfactant had increased both the surface and diffusion rate constants of CO_2 interaction with the solid sorbents.

ACKNOWLEDGMENTS

This paper was made possible by an NPRP Grant #5-1437-1- 243 from the Qatar National Research Fund (a member of Qatar Foundation). The statements made herein are solely the responsibility of the authors.

References:

(1) Rao, A. B.; Rubin, E. S. *Environmental Science and Technology* **2002**, *36*, 4467.

(2) Jones, C. W. *Annual Review of Chemical and Biomolecular Engineering* **2011**, *2*, 31.

(3) Wolsky, A. M.; Daniels, E. J.; Jody, B. J. *Environmental Progress* **1994**, *13*, 214.

(4) Conway, W.; Bruggink, S.; Beyad, Y.; Luo, W.; Melián-Cabrera, I.; Puxty, G.; Feron, P. *Chemical Engineering Science* **2015**, *126*, 446.

(5) Mandal, B. P.; Biswas, A. K.; Bandyopadhyay, S. S. *Chemical Engineering Science* **2003**, *58*, 4137.

(6) Mandal, B. P.; Bandyopadhyay, S. S. *Chemical Engineering Science* **2006**, *61*, 5440.

(7) Maurin, G.; Llewellyn, P. L.; Bell, R. G. *Journal of Physical Chemistry B* **2005**, *109*, 16084.

(8) Serna-Guerrero, R.; Belmabkhout, Y.; Sayari, A. *Chemical Engineering Journal* **2010**, *161*, 173.

(9) Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A. *Chemical Engineering Science* **2010**, *65*, 3695.

(10) Serna-Guerrero, R.; Belmabkhout, Y.; Sayari, A. *Chemical Engineering Science* **2010**, *65*, 4166.

(11) Qi, G.; Wang, Y.; Estevez, L.; Duan, X.; Anako, N.; Park, A. H. A.; Li, W.; Jones, C. W.; Giannelis, E. P. *Energy and Environmental Science* **2011**, *4*, 444.

(12) Qi, G.; Fu, L.; Choi, B. H.; Giannelis, E. P. *Energy and Environmental Science* **2012**, *5*, 7368.

(13) Chen, C.; Son, W. J.; You, K. S.; Ahn, J. W.; Ahn, W. S. *Chemical Engineering Journal* **2010**, *161*, 46.

(14) Labreche, Y.; Lively, R. P.; Rezaei, F.; Chen, G.; Jones, C. W.; Koros, W. J. *Chemical Engineering Journal* **2013**, *221*, 166.

(15) Knowles, G. P.; Graham, J. V.; Delaney, S. W.; Chaffee, A. L. *Fuel Processing Technology* **2005**, *86*, 1435.

(16) Kumar, P.; Guliants, V. V. *Microporous and Mesoporous Materials* **2010**, *132*, 1.

(17) Tsyganok, A.; Harlick, P. J. E.; Sayari, A. *Catalysis Communications* **2007**, *8*, 850.

(18) Das, D. D.; Harlick, P. J. E.; Sayari, A. *Catalysis Communications* **2007**, *8*, 829.

(19) Deng, S.; Li, H.; Li, S.; Zhang, Y. *Journal of Molecular Catalysis A: Chemical* **2007**, *268*, 169.

(20) Al-Marri, M. J.; Khader, M. M.; Tawfik, M.; Qi, G.; Giannelis, E. P. *Langmuir* **2015**, *31*, 3569.

(21) Cheung, O.; Bacsik, Z.; Liu, Q.; Mace, A.; Hedin, N. *Applied Energy* **2013**, *112*, 1326.

(22) Jia, Z.; Jiang, C. Y. In *ACS National Meeting Book of Abstracts* 2009.

(23) Kang, S. J.; Dou, T.; Gong, Y. J.; Li, Q.; Zheng, Y. Y. *Ranliao Huaxue Xuebao/Journal of Fuel Chemistry and Technology* **2006**, *34*, 625.

(24) Rashidi, N. A.; Yusup, S.; Hameed, B. H. *Energy* **2013**, *61*, 440.

(25) Guo, B.; Chang, L.; Xie, K. *Journal of Natural Gas Chemistry* **2006**, *15*, 223.

(26) Dantas, T. L. P.; Luna, F. M. T.; Silva, I. J.; de Azevedo, D. C. S.; Grande, C. A.; Rodrigues, A. E.; Moreira, R. F. P. M. *Chemical Engineering Journal* **2011**, *169*, 11.

(27) Shafeeyan, M. S.; Daud, W. M. A. W.; Houshmand, A.; Shamiri, A. *Journal of Analytical and Applied Pyrolysis* **2010**, *89*, 143.

(28) Auta, M.; Amat Darbis, N. D.; Mohd Din, A. T.; Hameed, B. H. *Chemical Engineering Journal* **2013**, *233*, 80.

(29) Chen, C.; Ahn, W.-S. *Chemical Engineering Journal* **2011**, *166*, 646.

(30) Thote, J. A.; Chatti, R. V.; Iyer, K. S.; Kumar, V.; Valechha, A. N.; Labhsetwar, N. K.; Biniwale, R. B.; Yenkie, M. K. N.; Rayalu, S. S. *Journal of Environmental Sciences* **2012**, *24*, 1979.

(31) Nafisi, V.; Hägg, M.-B. *Journal of Membrane Science* **2014**, *459*, 244.

(32) Kim, J.-Y.; Kim, J.; Yang, S.-T.; Ahn, W.-S. *Fuel* **2013**, *108*, 515.

(33) Dutcher, B.; Fan, M.; Cui, S.; Shen, X.-D.; Kong, Y.; Russell, A. G.; McCurdy, P.; Giotto, M. *International Journal of Greenhouse Gas Control* **2013**, *18*, 51.

(34) Bacsik, Z.; Ahlsten, N.; Ziadi, A.; Zhao, G.; Garcia-Bennett, A. E.; Martín-Matute, B.; Hedin, N. *Langmuir* **2011**, *27*, 11118.

(35) Wang, X.; Schwartz, V.; Clark, J. C.; Ma, X.; Overbury, S. H.; Xu, X.; Song, C. *The Journal of Physical Chemistry C* **2009**, *113*, 7260.

(36) Al-Marri, M. J.; Khader, M. M.; Giannelis, E. P.; Shibl, M. F. *Journal of Molecular Modeling* **2014**, *20*.

(37) Chandan, P. A.; Remias, J. E.; Liu, K. *International Journal of Greenhouse Gas Control* **2014**, *31*, 61.

(38) Kajiro, H.; Kondo, A.; Kaneko, K.; Kanoh, H. *International Journal of Molecular Sciences* **2010**, *11*, 3803.

(39) Fletcher, A. J.; Cussen, E. J.; Bradshaw, D.; Rosseinsky, M. J.; Thomas, K. M. *Journal of the American Chemical Society* **2004**, *126*, 9750.