University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth & Environmental Research

EcoTER'22

Proceedings

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Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

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NEW STRATEGIES FOR DEVELOPMENT OF HIGHLY SELECTIVE MATERIALS FOR CARBON DIOXIDE CAPTURE

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Abstract

Selective separation of CO_2 is a field of intensive research due to emerging emissions from fire coaled and natural gas power plants. In the focus of development efforts is a design of regenerable CO_2 capture material where adsorption technologies and advanced solid adsorbents are again in the centre of interest. Short screening of composite zeolite/activated carbon material in the terms of its selectivity for CO_2 towards water is presented in this research. Adsorption rate of CO_2 and H_2O is determined and analysed at two different temperatures and equilibrium pressure of 3.5 kPa which corresponds to flue gases contents. The results imply the water should be removed from treated gas before CO_2 separation and capture. Design of advanced materials can be facilitated by implementation of DFT calculations. A preview of DFT analysed materials with higher affinity for CO_2 than for water adsorption is presented within this research. It underscores the possibility of defining future strategies for the design of novel carbon dioxide capture materials more resistant to water compared to currently used zeolites.

Keywords: CO_2 capture, adsorption, DFT theory

INTRODUCTION

Emerging emission of CO_2 implies a need for urgent implementation of CO_2 capturing technologies. Development efforts are significant, especially in field of separation from power and sour natural gas plants flue streams and from syngas [1]. Having in mind that any chemical employed to capture CO_2 will rapidly exhaust its global supplies if it is used in a once-through manner, and that any chemical produced from CO_2 as a reactant will rapidly saturate global markets for that chemical [2], the necessity of development of regenerable capture material is underlined.

Within CO_2 capture technologies by adsorption, advanced solid zeolite-based adsorbents with high capacity towards CO_2 represent an acceptable alternative [3]. In this case, where energy input for regeneration is the main criterion for evaluating the cost-effectiveness of CO_2 capture technology [4], current strategies include composites based on commercial zeolites

[5] and carbons [6]. Carbon component decreases the overall adsorbent capacity towards CO2, but as a conductive material it enables short and efficient regeneration by Joule effect using electric power [7,8].

One of the problems when capture the CO_2 with zeolite-based adsorbents is water content of 10–15 vol.% in flue gases of fire coaled and natural gas power plants [9]. Namely, zeolite-based materials have high affinity for water and efficient carbon capturing requires highly selective adsorption of CO_2 [10], with little or no adsorption of other combustion gas components (N_2, H_2O).

Within this research the adsorption rate of CO_2 and H_2O on zeolite/carbon composite material was analysed with the main goal to develop a strategy for a design of highly selective material for CO_2 capture. Design of novel, sophisticated materials can be facilitated by implementation of DFT calculations.

MATERIALS AND METHODS

Adsorption rates of pure gases (CO_2 and H_2O) were measured in automatic volumetric unit BELsorp-max II (Verder Scientific, Germany).

The composite material was prepared mixing the commercially available zeolite X13 (Chemiewerk Bad Köstriz, Germany) with acetylene carbon black (AlfaAesar, Heysham, UK) in ratio 80 wt.% : 20 wt.%. Prior to the experiments, the material was degassed at 150°C under vacuum for a period of 15 hours (heating ramp of 2°C/min).

Adsorption rates for both gases were measured at two temperatures, 30°C and 150°C, and equilibrium pressure of 3.5 kPa. The mass of adsorbent used in the water experiments was smaller to reduce the time of measurement (0.2851 g for CO_2 and 0.0804 g for H_2O).

RESULTS AND DISCUSSION

CO_2 and H_2O adsorption rate on zeolite/carbon composite

The adsorption rate of pure CO_2 and H_2O is determined at 30°C and 150°C. The first temperature (30°C) was chosen as the highest expectable during adsorption, and the second (150°C) as an acceptable limit for material thermo-stability. The results are presented in Figure 1, where C, C_{eq} and C_0 represent actual, equilibrium and initial concentration [kPa] of gas.

Higher adsorption rate of water is obvious at 30°C: H_2O reaches the equilibrium after approximately 100 s, while CO_2 is not in equilibrium even after 300 s. Very fast decrease of water concentration implies the binding on adsorption sites is strong and that water would first occupy available adsorption sites in the case of competitive adsorption (such as the separation of flue gases).

At 150°C adsorption rate of CO_2 and H_2O is approximately equal, which implies the adsorbent regeneration could be difficult in the case of competitive adsorption.

Water adsorption on zeolite involves chemisorption on multiple adsorption sites. For this reason, it is difficult to describe the adsorption rate by any of the simple kinetics models, and the same should be expected for the adsorption isotherm.

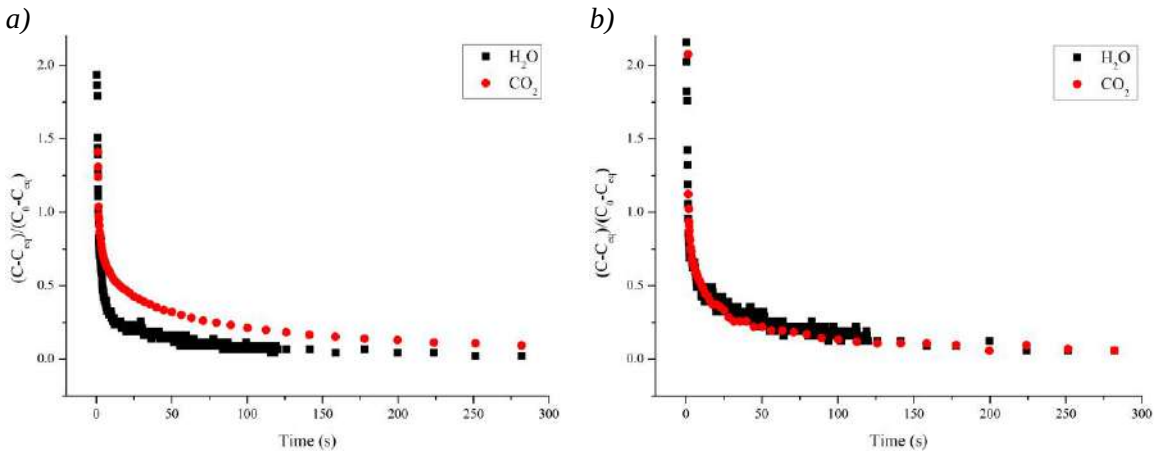

Figure 1 *Adsorption rate of CO_2 and H_2O on zeolite/carbon composite a) at temperature 30°C; b) at temperature 150°C*

Overview of DFT calculated adsorption energies of CO_2 and H_2O on various materials

Plenty of literature data on co-adsorption of water and CO_2 on various materials are already available. There are numerous materials with considerably higher affinity for CO_2 than for water adsorption. Some of them are presented in Table 1.

Table 1 *DFT calculated adsorption energies (E_{DFT}) of CO_2 and H_2O on various materials*

Material	$E_{DFT,CO2}$	$E_{DFT,H2O}$	Reference
As_2O_3	-52 kJ/mol	-144 kJ/mol	[11]
graphene	-17.9 kJ/mol	-20.2 kJ/mol	[12]
graphite	-16.5 kJ/mol	-14.9 kJ/mol	[13]
zeolite (faujasite) [a]	-21–36 kJ/mol	-58–88 kJ/mol	[14]
CaO	-243 kJ/mol	-146 kJ/mol	[15]

[a] multiple adsorption sites.

As can be seen from Table 1, it is possible to find existing materials with lower affinity for water adsorption compared to CO_2 adsorption. Initial design and preparation of the novel materials with controlled H_2O and CO_2 adsorption properties can be guided by DFT calculations. Besides the selectivity, the novel materials should also meet the requirements for CO_2 capture, such as good adsorption capacity or good conductivity.

CONCLUSION

Strong physical and chemical binding of water on zeolite 13X reduces adsorbent capacity for CO_2 and efficiency of regeneration on low temperatures (up to 150°C) that significantly affect the overall cost-effectiveness of separation process (i.e. CO_2 capture). It is possible to define future strategies for the design of novel carbon capture materials, more resistant to

water compared to currently used zeolites. DFT theory can contribute to the prediction of adsorption properties and guide the sophisticated design of the materials.

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REFERENCES

[1] P. Madejski, K. Chmiel, N. Subramanian, *et al.*, Energies; 15 (3) (2022) 887.

[2] D.M. D'Alessandro, B. Smit, J.R. Long, Angew. Chem., Int. Ed. Engl; 49 (35) (2010) 6058–6082.

[3] J.Y. Lai, L.H. Ngu, S.S. Hashim, Greenh. Gases: Sci. Technol; 11 (5) (2021) 1076–1117.

[4] A. Cousins, P. Feron, J. Hayward, *et al.*, IEAGHG Technical Report, April 11th, Melbourne, Australia (2019).

[5] E. Khoramzadeh, M. Mofarahi, C.H. Lee, J. Chem. Eng. Data; 64 (12) (2019) 5648–5664.

[6] J. Wang, Q. Pu, P. Ning, *et al.*, Greenh. Gases: Sci. Technol; 11 (2) (2021) 377–393.

[7] J.S. Lee, J.H. Kim, J.T. Kim, *et al*., J. Chem. Eng. Data; 47 (5) (2022) 1237–1242.

[8] M.J. Regufe, A.F.P. Ferreira, J.M. Loureiro, *et al.*, Adsorption; 24 (3) (2018) 249–265.

[9] J.H. Copen, T.B. Sullivan, B.C. Folkedahl, *et al.*, Proceedings of the International Symposium POWER-GEN, December 6–8th, Las Vegas, Nevada (2005) 13.

[10] O. Cheung, Z. Bacsik, N. Fil, *et al.*, ACS Omega; 5 (39) (2020) 25371–25380.

[11] P. Hu, Q. Weng, D. Li, *et al*., J. Hazard. Mater; 403 (2021) 123866.

[12] Z. Gao, Y. Ding, J. Mol. Model; 23 (6) (2017) 187.

[13] M. Rubeš, J. Kysilka, P. Nachtigall, *et al*., Phys. Chem. Chem. Phys; 12 (24) (2010) 6438.

[14] E.P. Hessou, W.G. Kanhounnon, D. Rocca, *et al*., Theor. Chem. Acc; 137 (12) (2018) 161.

[15] X. Ma, Y. Li, W. Zhang, *et al*., Chem. Eng. J; 370 (2019) 10–18.