**NHẬN XÉT**

Tiêu đề bài báo: Evaluation on the stability of amine-mesoporous silica adsorbents used for CO2 capture.

**1) Tính mới và tính cập nhật của nội dung khoa học, tính trùng lặp về kết quả nghiên cứu:**

Trong bối cảnh phát thải CO2 toàn cầu không ngừng gia tăng, phát triển các công nghệ hỗ trợ việc tuần hoàn hoặc giảm lượng phát thải là vô cùng cần thiết. Bài báo có tính mới, có ý nghĩa khoa học và thực tiễn. Theo người nhận xét được biết thì bài báo không trùng lặp.

**2) Những kết quả nhận được đã đủ hàm lượng khoa học và khối lượng của một bài báo Khoa học đăng trên Tạp chí Khoc học ĐHQGHN, Chuyên san Các Khoa học Trái đất và Môi trường chưa?**

Kết quả chủ đạo của bài báo là về khả năng hấp phụ CO2 của hai vật liệu PEI-MPS và APTES-MPS. Các kết quả này mặc dù khá sơ sài (duy nhất ở hình 4) tuy nhiên có ý nghĩa và có triển vọng để phát triển/ứng dụng. Các kết quả thí nghiệm bổ trợ thiếu hoặc sơ sài, ví dụ: chỉ có kết quả phân tích TGA ở hình 3, nhưng dùng kết quả này để biện luận cho các phản ứng có thể diễn ra trong reactor là không hợp lý. Nếu được, nên bổ sung thêm một số kết quả để bài báo có hàm lượng khoa học tốt hơn, đáp ứng được yêu cầu của tạp chí Khoa học ĐHQGHN.

**3) Tính đầy đủ, tính trung thực trong phần tổng quan tài liệu, phương pháp và số liệu**

Tổng quan tài liệu đầy đủ; vật liệu nghiên cứu mô tả chưa đầy đủ (ví dụ: nguồn gốc CO2 và N2 sử dụng trong thí nghiệm; các hạt “silica bead” bổ sung để “enhance mass and heat transfer” có nguồn gốc ở đâu, tính chất thế nào và liệu có gây “tác dụng phụ” đối với phản ứng hấp phụ CO2? Phần phương pháp chưa được trình bày thật tường minh. Cần viết, cấu trúc lại phần phương pháp nghiên cứu cho hợp lý và logic hơn. Một số nội dung đáng lý thuộc phần phương pháp, nhưng lại được trình bày ở kết quả nghiên cứu.

**4) Trích dẫn tài liệu hợp lý, đầy đủ chưa?**

Trích dẫn tài liệu nhìn chung hợp lý. Lưu ý các lỗi typo trong phần tài liệu tham khảo.

**5) Hình vẽ, bảng biểu có hợp lý không?**

Một số hình vẽ được hợp lý hoặc thiếu thông tin: Hình 2 nên bổ sung SEM của vật liệu gốc MPS; hình 3 cần sửa PS thành MPS; hình 4 bố cục các đường chưa thực sự hợp lý, các vật liệu “dry” và “humid” xuất hiện đường đột vì không giới thiệu ở phần Materials & Methods.

**6) Bố cục bài báo có hợp lý không?**

Bố cục bài báo nhìn chung hợp lý.

**Cuối cùng đề nghị PGS cho kết luận:**

Có thể xem xét cho đăng sau khi “chỉnh sửa lớn”. Các tác giả xem thêm góp ý chi tiết được track change. Ngoài các lỗi ngữ pháp đã được sửa, đề nghị các tác giả tiếp tục rà soát cẩn thận để bài báo được hoàn thiện hơn.

**PHẢN BIỆN LẦN 2:**

Các tác giả đã thực hiện việc chỉnh sửa cẩn thận và chất lượng bài báo đã được cải thiện. Bài báo có thể chấp nhận cho đăng.

Tuy nhiên, các tác giả cần rà soát và chỉnh sửa lỗi typo công thức hóa học, ví dụ: tiêu đề mục 2.4; tài liệu tham khảo số 7, 17.

**Evaluation on the stability of amine-mesoporous silica adsorbents used for CO2 capture**

**Abstract**

Amine-mesoporous silica has been considered as a promising CO2 adsorbent with high potential for the reduction of energy consumption and CO2 capture cost, however, its stability could greatly vary with synthetic method. In this study, adsorbents prepared by impregnating different amines including polyethylenimine (PEI) and 3-aminopropyltriethoxysilane (APTES) onto mesoporous silica were used to evaluate the effect of amines selection on the stability of adsorbents used in CO2 capture process. Results revealed that APTES impregnated mesoporous silica (APTES-MPS) is more stable than PEI-impregnated mesoporous silica (PEI-MPS); APTES-MPS was thermally decomposed at ≈280 oC, while PEI-MPS was thermally decomposed at ≈180 oC only. PEI-MPS was particularly less stable when operating under dry condition; its CO2 adsorption capacity reduced by 22.1% after 10 adsorption/regeneration cycles, however, the capacity can be significantly improved in humid condition. APTES-MPS showed a greater stability with no significant reduction in CO2 capture capacity after 10 adsorption/regeneration cycles. In general, APTES-MPS adsorbent possesses a higher stability compared to PEI-MPS thanks to the formation of chemical bonds between amino-functional groups and mesoporous silica substrate.

*Keywords:* Mesoporous silica; CO2 capture; Adsorption; Regeneration; Emission.

1. **Introduction**

CO2 emission from human activities has been considered as a major cause of the increase in the concentration of CO2 in the air, which has reached 410 ppm [1]. Such high atmospheric concentration has never been observed and it could involve in global warming and climate change [2]. A large fraction of emitted CO2 relates to burning fossil fuels for electricity production, industrial activities, and transportation. To mitigate the environmental consequences of climate change, the reduction in CO2 emission should be taken into account. While burning fossil fuels cannot be stopped due to the high demand for energy, CO­2 capturing and storing could be a good option that allows one to continue using fossil fuels effectively [3, 4]. Several technologies that have been proposed for capturing CO2 include pre-combustion capture, post-combustion capture, and oxygen fuel combustion capture, of which the post-combustion CO2 capture is the most appropriate technology that can be retrofitted to existing power plants without any significant change or improvement of the plants [5].

Aqueous amine-based CO2 capture technology has been well-known and applied to remove CO2 from natural gas [6]. This technology, however, is not practical for capturing CO2 from flue gas since the aqueous amine solution is a highly corrosive and rapidly degradative solution and it consumes large energy for regeneration. Consequently, the cost of electricity increases significantly as CO2 capture and storage technology is retrofited to power plant [7]. Numerous studies have been conducted to find out a feasible approach to reduce the cost of capturing CO2 from flue gas [8]. One of the promising way is to replace aqueous amine solution by a solid sorbent [9]. Accordingly, amine compounds, major components that adsorb CO2 are loaded on a porous substrate instead of dissolving in water. Low heat capacity is an advantage of solid sorbent due to the avoidance of solvent usage. The sorbent, therefore, has high CO2 adsorption capacity. The solid sorbent has become an ideal candidate for CO2 post combustion capture thanks to its possibility to reduce the energy consumption. Recent studies indicated that energy consumption by a CO2 capture process based on polyethylenemine impregnated mesoporous silica (PEI-MPS) can reduce 44 % compared to conventional aqueous amine used ethanolamine (30%) [10, 11].

PEI-MPS material possesses a high CO2 capture capacity, however, its drawbacks are unstable; PEI can be leached out and vaporized during operation, particularly when adsorption is operated in a fluidized bed reactor (FBR) [12-14]. Numerous solid sorbents have been synthesized and examined to find a more stable adsorbent for CO2 capture application; however, the reported adsorbents usually face certain problems such as low CO2 adsorption capacity or difficult for large scale production [15-19]. Therefore, some important parameters including stability, adsorption capacity, and recyclability must be considered when developing novel CO2 adsorbents. Those adsorbents should have the high density of amino functional groups, the possibility of large production, and cost effectiveness. In fact, the stability of reported adsorbents is variable depending on synthetic methods and amine precursors; however, their influence on the stability and CO2 adsorption performance of adsorbent has barely been investigated. Therefore, the major objective of this study is to evaluate the influence of amine precursors used to impregnate onto mesoporous silica on the stability and recyclability of resulting adsorbents.

1. **Materials and methods**
	1. **Materials**

 Polyethyleneimine, branched (PEI, Mw ≈ 600), 3-aminopropyltriethoxysilane (97%, APTES), absolute ethanol, and mesoporous silica (MPS) were purchased from Sigma Aldrich. MPS has particle size from 75-150 µm, pore volume 1.15 cm3/g, pore size 11.5 nm, and surface area 300 m2/g. Thiếu mô tả các khí sử dụng (e.g, CO2 và N2) và vật liệu ‘silica bead’.

* 1. **Amine impregnation on mesoporous silica**

Desired amounts of amine and water were weighed and mixed in a 1 L flask followed by the addition of a designated amount of MPS and continued to stir until the mixture became homogenous. The mass of PEI, APTES, and MPS was pre-determined to generate a final product composition of 55 wt% PEI in PEI-MPS and 70 wt% APTES in APTES-MPS adsorbents. When mixture became homogenous, the flask was mounted onto a rotation evaporator (IKA RV 10 Rotovapor, USA) to remove water and generate solid adsorbents. PEI-MPS and APTES-MPS obtained were dried at 105 oC for 3 h in an oven and stored in containers for later characterization and evaluation.

* 1. **Adsorbent characterization**

Morphology of adsorbents was observed on a scanning electron microscope (SEM, Quanta 250). Thermogravimetric analysis (TGA) was conducted on a thermal analyzer (Netzsch STA 449 F3) from room temperature to 800 oC in atmospheric condition at ramping rate of 5 oC/min.

* 1. Determination of CO2 adsorption capacity

The cyclic adsorption capacity of adsorbent in different adsorption/regeneration cycles was analyzed by a packed bed reactor as shown in **Figure 1**. Simulated flue gas containing approximately 15 vol% of CO2 in balance with N2 was prepared by controlling N2 (MFC4) and CO2 flow rate (MFC5). In a typical experiment, approximately 2 g of adsorbent was mixed with ca. 4.5g silica bead to enhance mass and heat transfer, are loaded into a cylindrical reactor. The reactor was made of stainless-steel column with 1.27 cm inner diameter and 20 cm length. Feed gas was run through a humidifier (A), makeup vessel (B) and fed to the reactor (C) with a flow rate of 15 L/h using MFC6. Effluent gas was directed to condenser (D) to remove the moisture in collector (E) and then to CO2 analyzer. In an adsorption stage, the simulated flue gas was fed into the reactor at 30 oC for 1h. On the completion of adsorption, valve V8 and V9 were switched to by-pass following by MFC6 closure and MFC7 unlock. The regenerative gas (N2) blew all CO2 out of the line before it was directed into the reactor by controlling the valves V8 and V9. As long as the valve directs regenerative gas to the reactor, its temperature was gradually increased to regeneration temperature. Regeneration step ended when the level of CO2 in the effluent gas reached zero, but N2 was kept flowing until the temperature cools down to adsorption temperature for another cycle. All gas flow rates and CO2 concentration were recorded and used for the calculation of CO2 loading. In this study, the adsorption/regeneration were conducted at 75 oC/110 oC for PEI-MPS and 100 oC/120 oC for APTES-MPS and the CO2 loading was calculated based on regeneration data; it is the amount of CO2 desorbed in regeneration step per mass of adsorbent.



**Figure 1.** A schematic illustration of a fixed bed reactor for CO2 adsorption/regeneration tests

1. **Results and Discussion**

SEM images were used to investigate morphology and structure of the synthesized adsorbents. Mesoporous silica with porous structure created by the interconnection numerous silica nanoparticles. Pores are cavities and voids between those nanoparticles and are spaces for amine molecules to fill. As seen in **Figure 2**, MPS after impregnated with PEI (A) and APTES (B) still maintains its porous structure, even though, its large porous fraction was occupied by amine molecules. With highly porous structure, the adsorbents prepared by wet impregnation method is expected to have high CO2 capture capacity.



**Figure 2.** Adsorbents synthesized by wet impregnation of PEI (A) and APTES (B) on MPS.

The TGA profiles of the adsorbents were shown in **Figure 3**. All materials show mass loss from room temperature to 150 oC corresponding to the adsorbed water and gases on the adsorbents. Water adsorbed on MPS and adsorbents usually exists as a physical and chemical adsorption. The physically adsorbed water, which is considered as the moisture of materials, can be easily separated by heating up at a relatively low temperature or by changing dynamic conditions. Thus, the mass change can be seen as soon as N2 passes over the adsorbent and temperature starts ramping. Whereas, the chemically adsorbed water usually forms chemical bonds with –OH groups on substrate. Chemically adsorbed water can only be eliminated at high temperature, however, its content may not be significant. The lower mass loss of MPS in comparison with that of other adsorbents at this low temperature range is mainly due to its low content of physically adsorbed water. Meanwhile, the adsorbents contain amines that may have higher moisture together with the CO2 adsorbed from atmosphere causing higher mass loss in TGA profiles. Adsorbents containing different amines have CO2 adsorption capabilities varying with adsorption temperatures; the optimal adsorption temperature of APTES-MPS and PEI-MPS are 100 oC and 75 oC, respectively [16]. Lower adsorption temperature allows PEI-MPS adsorb more CO2 at lower temperature and as a result more mass loss due to the release of CO2 and moisture can be observed on TGA profile. This explained the reason why the more mass loss was observed on PEI-MPS in comparison with the others. In the temperature range of 150–800oC, the mass loss of MPS occurred at very slow rate due to the elimination of chemical water; however, it occurred vigorously on amine-impregnated MPS. The mass of PEI-MPS decreased rapidly at temperatures from 150 to 400 oC due to the vaporization and thermal degradation of PEI impregnated in MPS structure. APTES-MPS posed to be more thermally stable with the mass loss observed from 280 to about 600 oC. This is because APTES formed chemical bonds with silica substrate which is more stable than the physical interactions of PEI with silica substrate [16]. This result indicated that APTES-MPS is more thermally stable than PEI-MPS adsorbent.

The TGA analysis indicated that APTES-MPS has higher stability compared to PEI-MPS thanks to the formation of chemical bonds to avoid the leaching and vaporization of amines. To evaluate the influence of the adsorbent’s stability on their CO2 adsorption/regeneration cyclability, both APTES-MPS and PEI-MPS were tested on the packed bed reactor at optimum adsorption/regeneration temperatures; 100 oC/120 oC for APTES-MPS and 75/110 oC for PEI-MPS, respectively. The evaluation made after 10 adsorption/regeneration cycles was presented in **Figure 4**. As shown in this figure, the stability of both adsorbents was obviously differentiated after 10 adsorption/regeneration cycles in dry condition. The CO2 adsorption of APTES-MPS was constant, while that of PEI-MPS (dry?) began reducing at the third cycle and decreased by 22.1% after 10 cycles. Several studies revealed that PEI-MPS had better stability when tested with flue gas in a packed bed reactor. This is probably due to the effect of moisture in adsorbent and in flue gas since the actual flue gas always contains significant amount of moisture. To elucidate this assumption, another study was conducted to investigate the effect of moisture on the CO2 adsorption stability of PEI-MPS. Results as exhibited in **Figure 4** suggested that the PEI-MPS became stable after 10 CO2 adsorption/regeneration cycles. This indicated that the physical bonds between PEI and MPS were relatively week in dry condition due to less hydrogen bonds. When moisture increased, more hydrogen bonds were created which prevent the PEI from vaporization at regeneration temperature. It is evident that moisture in adsorbed gas plays a very important role in the CO2 adsorption stability and the durability of amine-impregnated adsorbent. This study showed that APTES-MPS is the best adsorbent regarding to the stability thanks to the chemical bonds formed between amino groups and MPS. APTES-MPS can work well in both dry and humid conditions, whereas, PEI-MPS can be stable in humid condition only.

|  |  |
| --- | --- |
| **Figure 3**. TGA profiles of different adsorbents |  **Figure 4.** The stability of CO2 adsorbent over multiple adsorption/regeneration cycles with the consideration of different humidity.  |

1. **Conclusion**

In this study, two adsorbents have been successfully prepared by the wet impregnation of APTES and PEI onto MPS following with the evaluation on their stability and CO2 adsorption performance. Both adsorbents can maintain their porous structure allowing good CO2 adsorption capacities; however, APTES-MPS possesses a better thermal stability thanks to the formation of chemical bond between APTES and MPS substrate. PEI-MPS decomposed at relatively low temperatures (180–380oC), while APTES-MPS decomposed at higher temperatures (280–600 oC). CO2 adsorption on APTES-MPS was constant after 10 adsorption/regeneration cycles in dry condition, while PEI-MPS loss 22.1% in CO2 adsorption capacity, which, however, can be improved by adding moisture into the adsorbed gases. This suggested that APTES-MPS can operate at higher adsorption/regeneration temperatures (100 oC/120 oC) in both humid and dry condition, while PEI-MPS can operate at low temperature (75 oC/110 oC) but only in humid condition.

**Acknowledgement**

This work was supported by The Phenikaa University Foundation for Science and Technology Development

**References**

[1] NOAA, Atmospheric CO2 at Mauna Loa Observatory cited on 07/8/2019, in, 2018.

[2] J.R. Petit, J. Jouzel, D. Raynaud, N.I. Barkov, J.M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V.M. Kotlyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. PÉpin, C. Ritz, E. Saltzman, M. Stievenard, Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399 (1999) 429-436.

[3] M. Ranjan, H.J. Herzog, Feasibility of air capture, Energy Procedia, 4 (2011) 2869-2876.

[4] M. Bui, C.S. Adjiman, A. Bardow, E.J. Anthony, A. Boston, S. Brown, P.S. Fennell, S. Fuss, A. Galindo, L.A. Hackett, J.P. Hallett, H.J. Herzog, G. Jackson, J. Kemper, S. Krevor, G.C. Maitland, M. Matuszewski, I.S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D.M. Reiner, E.S. Rubin, S.A. Scott, N. Shah, B. Smit, J.P.M. Trusler, P. Webley, J. Wilcox, N. Mac Dowell, Carbon capture and storage (CCS): the way forward, Energy & Environmental Science, 11 (2018) 1062-1176.

[5] E. Adu, Y. Zhang, D. Liu, Current situation of carbon dioxide capture, storage, and enhanced oil recovery in the oil and gas industry, The Canadian Journal of Chemical Engineering, 97 (2019) 1048-1076.

[6] D.W. Keith, Why Capture CO2 from the Atmosphere?, Science, 325 (2009) 1654-1655.

[7] M.R.M. Abu-Zahra, L.H.J. Schneiders, J.P.M. Niederer, P.H.M. Feron, G.F. Versteeg, CO2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine, International Journal of Greenhouse Gas Control, 1 (2007) 37-46.

[8] N. El Hadri, D.V. Quang, E.L.V. Goetheer, M.R.M. Abu Zahra, Aqueous amine solution characterization for post-combustion CO2 capture process, Applied Energy, 185 (2017) 1433-1449.

[9] S. Zhang, C. Chen, W.-S. Ahn, Recent progress on CO2 capture using amine-functionalized silica, Current Opinion in Green and Sustainable Chemistry, (2018).

[10] D.V. Quang, A.V. Rabindran, N. El Hadri, M.R. Abu-Zahra, Reduction in the regeneration energy of CO2 capture process by impregnating amine solvent onto precipitated silica, European Scientific Journal, 9 (2013).

[11] D.V. Quang, M. Soukri, J. Tanthana, P. Sharma, T.O. Nelson, M. Lail, L.J. Coleman, M.R. Abu-Zahra, Investigation of CO2 adsorption performance and fluidization behavior of mesoporous silica supported polyethyleneimine, Powder Technology, 301 (2016) 449-462.

[12] C. Chen, S.-T. Yang, W.-S. Ahn, R. Ryoo, Amine-impregnated silica monolith with a hierarchical pore structure: enhancement of CO2 capture capacity, Chemical Communications, (2009) 3627-3629.

[13] A. Zhao, A. Samanta, P. Sarkar, R. Gupta, Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study, Industrial & Engineering Chemistry Research, 52 (2013) 6480-6491.

[14] T.O. Nelson, L.J.I. Coleman, A. Kataria, M. Lail, M. Soukri, D.V. Quang, M.R.M.A. Zahra, Advanced Solid Sorbent-Based CO2 Capture Process, Energy Procedia, 63 (2014) 2216-2229.

[15] M. Czaun, A. Goeppert, R.B. May, D. Peltier, H. Zhang, G.K.S. Prakash, G.A. Olah, Organoamines-grafted on nano-sized silica for carbon dioxide capture, Journal of CO2 Utilization, 1 (2013) 1-7.

[16] D.V. Quang, T.A. Hatton, M.R.M. Abu-Zahra, Thermally Stable Amine-Grafted Adsorbent Prepared by Impregnating 3-Aminopropyltriethoxysilane on Mesoporous Silica for CO2 Capture, Industrial & Engineering Chemistry Research, 55 (2016) 7842-7852.

[17] R.B. Vieira, P.A.S. Moura, E. Vilarrasa-García, D.C.S. Azevedo, H.O. Pastore, Polyamine-Grafted Magadiite: High CO2 Selectivity at Capture from CO2/N2 and CO2/CH4 Mixtures, Journal of CO2 Utilization, 23 (2018) 29-41.

[18] Y. Kong, G. Jiang, Y. Wu, S. Cui, X. Shen, Amine hybrid aerogel for high-efficiency CO2 capture: Effect of amine loading and CO2 concentration, Chemical Engineering Journal, 306 (2016) 362-368.

[19] K. Min, W. Choi, C. Kim, M. Choi, Oxidation-stable amine-containing adsorbents for carbon dioxide capture, Nature Communications, 9 (2018) 726.