



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Novel amine-impregnated mesostructured silica materials for CO₂ capture

Manuel Ojeda^a, Matjaz Mazaj^b, Susana Garcia^{a,*}, Jin Xuan^a, M. Mercedes Maroto-Valer^a,
Natasa Zabukovec Logar^{b,c}

^aCentre for Innovation in Carbon Capture and Storage (CICCS), School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

^bNational Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

^cUniversity of Nova Gorica, Vipavska 13, 5000 Nova Gorica Slovenia

Abstract

In this work, mesostructured KIL-2 silica materials were synthesized and functionalized by impregnation with two different amino sources, polyethylenimine (PEI) and Tetraethylenepentamine (TEPA), for their application to low temperature CO₂ capture. Infrared spectroscopy verified that amino groups were successfully incorporated on the surface of the silica support and within its interparticle porosity. N₂ sorption analysis of the synthesized silica materials showed a decrease in surface area and total pore volume as a result of the impregnation with the amine groups. The CO₂ capture capacity of prepared sorbents was evaluated by CO₂ adsorption/desorption isotherms at 25°C and 90°C. The highest sorption capacity was achieved at 90°C for KIL-2-TEPA material (4.35 mmol/g ads), which is significantly higher than values previously reported in the literature for similar type of disordered mesopore structure materials under similar conditions.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: adsorbents; KIL-2; carbon dioxide capture; wormhole silica; amine-impregnated.

* Corresponding author. Tel.: +44-(0)-131-451-8083.
E-mail address: S.Garcia@hw.ac.uk

1. Introduction

One of the major concerns of most industrialised countries is climate change and global warming. As a result, new goals in order to reduce greenhouse emissions were established in the United Climate Change Conference, which was held in Paris in December 2015, pursuing efforts to limit the Earth's temperature increase to below 2°C. Anthropogenic generated CO₂ is considered one of the major greenhouse gasses responsible for global warming, primarily due to the combustion of fossil fuels for energy production, accounting for more than 65% of global CO₂ emissions.[1, 2] Hence, new technologies to produce clean energy as well as to reduce emissions from current energy production systems, mostly based in fossil fuels, need to be successfully developed and implemented. Therefore, significant efforts are underway to advance CO₂ capture and storage technologies (CCS) for the reduction of CO₂ into the atmosphere.[3-5] Chemical absorption processes such as those based on aqueous amines have been used in large scale industries since the 1930s for CO₂ capture.[6] However, due to their high corrosion issues as well as the elevated regeneration costs, the utilisation of solid CO₂ adsorbents is considered a promising alternative for capturing CO₂. [7, 8]

Solid adsorbents show attractive properties such as their potential utilisation at different temperatures, low energetic requirements for regeneration and large adsorption capacity.[9] Different porous materials have been widely described in literature for CO₂ capture (e.g. silica materials, carbonaceous materials, metal organic frameworks, amongst others).[10-14] Amongst them, mesoporous silica materials feature high surface area, thermal stability as well as large pore volume, which allow for amines group immobilisation, enhancing their CO₂ adsorption capacity at low temperatures.[15, 16] However, the pore volume decreases significantly after amine loadings ca. 50 wt% due to pore blockage which hinders CO₂ diffusion through the material, and therefore, limits the CO₂ interaction with inner amine groups, reducing the overall amine efficiency. In this regard, Son et al.[17] studied the behaviour of different mesoporous silica materials with different average pore size in the range of 2.8-6.5 nm after their amine functionalisation (polyethylenimine, -PEI- 50 wt%). The results showed that materials with higher pore size were more efficient in CO₂ adsorption. Moreover, the capture efficiency was reported to be higher in materials with a connected pores network which could facilitate the diffusion and contact between CO₂ and the impregnated amine. Accordingly, mesoporous materials with connected wormhole framework and large pore volume are gaining a great deal of attention in the recent years.[18-21]

Different mesostructured materials, such as titanium oxide,[22] γ -alumina,[23] as well as organic polymers[24] have shown notable uptake capacity. Jiao et al.[25] investigated the effect of the ordered hexagonal framework structure of SBA-15, and disordered 3D wormhole structure of MSU-J on CO₂ capture capacity. The results indicated that MSU-J showed better performance in CO₂ uptake than SBA-15, which could be due to the higher pore volume and surface area at the same amine loading. In the light of these recent developments, a new family of mesostructured silica materials, namely KIL-2, has been identified as potential candidate for CO₂ capture due to their wormhole pore structure as well as their large pore volume.[26] This material showed outstanding results in heterogeneous catalysis after its functionalisation with different metal nanoparticles.[27-29] However, to the best of the authors' knowledge the utilisation of KIL-2 as CO₂ adsorbent has not been reported before. Accordingly, in this work, low temperature adsorbents based on silica material KIL-2 with interparticle mesoporosity and high thermal stability were functionalised with two different amine sources by the impregnation method. Materials performance for CO₂ capture was then evaluated at different temperatures.

2. Materials and methods

2.1. KIL-2 synthesis

Synthesis of mesostructured silica KIL-2 was carried out according to a two-step protocol, as previously reported.[26] Tetraethyl Orthosilicate (TEOS), triethanolamine (TEA) and tetraethylammonium hydroxide (20% TEOH) were acquired from Sigma-Aldrich and used as received. A molar ratio of TEOS: 1, TEA: 0.5, TEOH: 0.1 and H₂O: 11 was used in the synthesis. Thus, the required mass of TEOS was mixed with TEA and stirred

during 30 min to obtain a homogeneous solution. H₂O and TEAOH were then added to the mixture and stirred to obtain the homogeneous gel. Subsequently, the gel was dried in an oven at 50 °C overnight. In a second step, the dried gel was solvothermally treated in ethanol at 150 °C using a Teflon-lined stainless-steel autoclave during 48 h. The product was cooled down to room temperature and then filtered and washed with ethanol several times. The obtained yellowish powder was finally calcined at 600 °C for 10 h for template removal.

2.2. Amino-impregnation of synthesized KIL-2 materials

Amino-functionalisation of as-synthesized KIL-2 materials was carried out by a typical wetness impregnation method described elsewhere.[15] Two different amines were used: Polyethylenimine (PEI Mw=800, Sigma) and Tetraethylenepentamine (TEPA, Sigma). The amine source was mixed with methanol and stirred during 30 min. Then, KIL-2 was added to the solution in a theoretical weight ratio of 1:1 Amine/KIL-2 and stirred during 1 h. The mixture was then dried in an oven at 50 °C overnight to obtain the final amino-functionalised KIL-2 material. The synthesized materials were denoted as KIL-2-PEI and KIL-2-TEPA, indicating impregnation with PEI or TEPA, respectively.

2.3. Materials characterization and evaluation of CO₂ capture capacity

Nitrogen isotherms were carried out using an automated gas adsorption analyser ASAP 2020 (Micromeritics, Instrument Co) at 77 K. Prior to the analysis, samples were degassed at 110 °C during 2 h. BET surface area was obtained from the adsorption branch in the relative pressure range between 0.05 and 0.3. Pore size distribution was calculated by BJH method. Infrared analysis was performed using an ATR Smart DuraSampIIR equipment, and measured over the range 4000-400 cm⁻¹. To determine the CO₂ capture capacity of amino-KIL-2 materials, CO₂ adsorption-desorption isotherms were carried out at different temperatures (25 °C and 90 °C) and up to a bar with an IMI-HTP manometric sorption analyzer (Hiden Isochema, Inc.). The samples were outgassed at 110 °C overnight prior the measurements.

3. Results and discussion

Mesoporous silica materials KIL-2 with interparticle mesoporosity were synthesized by a two-step method, and subsequently impregnated using two different amine sources (PEI and TEPA) in a weight ratio of 1:1 amine:support. The textural parameters calculated from Nitrogen adsorption-desorption isotherms for KIL-2 materials are shown in Table 1.

Table 1. Textural properties of KIL-2 materials.

Sample	BET Surface area (m ² /g)	Total pore volume V _{BJH} (cm ³ /g)	Average pore size (nm)
KIL-2	702	1.61	9.55
KIL-2-PEI	127	0.35	9.10
KIL-2-TEPA	177	0.46	8.47

The surface area of the material decreased after the amine impregnation as well as the pore volume (Table 1). Likewise, the average pore size in the amine-functionalized materials is lower when compared with the non-functionalized support. This is due to the incorporation of amine groups into the pore structure, which is in good agreement with previously reported data in literature.[15, 25]

The amino impregnation of KIL-2 material was confirmed by infrared spectroscopy (ATR). Figure 1 shows the acquired spectra of KIL-2-PEI and KIL-2-TEPA along with that of the initial mesoporous support. Different IR bands in the amino-impregnated materials at 3295 and 1597 cm^{-1} (NH stretching and bending vibrations), as well as at 2985, 2949 and 1479 cm^{-1} (CH stretching and bending vibrations from aliphatic carbon) indicate that KIL-2 has been successfully impregnated with the amino source.

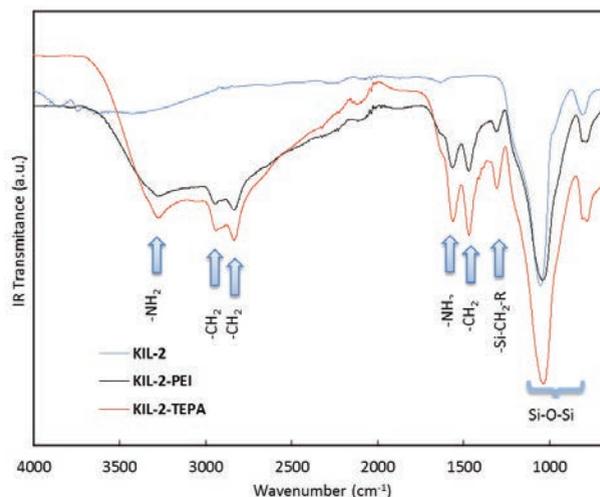


Fig. 1. Infrared spectra of KIL-2 materials.

To determine the CO_2 capture capacity of amino-KIL-2 materials, CO_2 adsorption-desorption isotherms were carried out at 25°C and 90°C (Figure 2) and up to 1 bar of pressure. Table 2 shows the CO_2 sorption capacities of amine-impregnated silica materials at 1 bar. Pristine KIL-2 material shows negligible CO_2 uptake regardless of the temperature of adsorption. On the other hand, the amino-modified silica matrices show significant enhancement of the CO_2 capture capacity at the two studied temperatures. At 25°C both modified samples show a very steep uptake at low pressures (up to 50 mbar) and reach almost full saturation at 1 bar, showing a capacity of 2.19 mmol CO_2/g adsorbent and 3.37 mmol CO_2/g for KIL-2-PEI and KIL-2-TEPA, respectively.

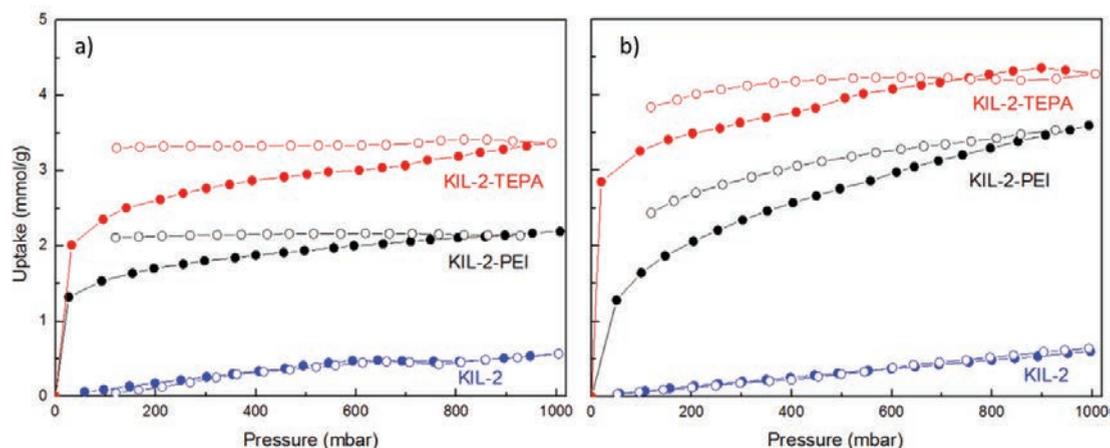


Fig. 2. CO_2 isotherms of KIL-2 materials: a) at 25°C; b) 90°C.

The higher sorption capacity of KIL-2-TEPA sample can be related to the difference in the nitrogen content in the amino molecule utilized, which is higher in TEPA than in PEI.[30] Besides, PEI, which is bulkier than TEPA, can occupy more of the accessible pore volume, leading to lower specific surface area and lower CO₂ capture capacity.[31] At 90°C, sorption capacity is largely improved in both cases, with values at 1 bar of 3.59 and 4.35 mmol CO₂/g ads for KIL-2-PEI and KIL-2-TEPA, respectively. Moreover, these values are significantly higher than those previously reported in literature for disordered mesopore structure materials in similar conditions (Table 2).

Table 2. CO₂ sorption capacities of amine-impregnated silica materials at 1 bar.

Sample	Temperature (°C)	Amine content (wt.%)	Sorption capacity (mmol CO ₂ /g ads)	Reference
MSU-J-TEPA-50	25	50	3.73	[32]
	85		1.29	
MSU-J-PEI-50	30	50	2.04	[33]
	100		2.95	
HMS-PEI-50	30	50	2.27	
	100		2.72	
45-PEI/HMS	50	45	2.70	[34]
	90		2.91	
MSU-TEPA	75	50	3.80	[35]
KIL-2-PEI	25	50	2.19	This work
	90		3.60	
KIL-2-TEPA	25	50	3.37	
	90		4.35	

Improved sorption capacities of KIL-2-TEPA and KIL-2-PEI at higher temperature may be assigned to higher diffusion rate of CO₂ through the pore structure of the sorbent. KIL-2-TEPA shows a better adsorption capacity, which could be due to the lower viscosity of TEPA compared to PEI.[31] This fact along with a higher pore volume after impregnation (0.46 cm³/g) could facilitate the diffusion and contact between CO₂ and the amine groups localized in the pore structure.[17]

4. Conclusions

A mesoporous silica matrix material, KIL-2, was modified with polyethylenimine (PEI) and tetraethylenepentamine (TEPA) and it was evaluated for capturing CO₂ at low temperatures (up to 90°C). The successful impregnation of both poly-functional amino-precursors was confirmed by N₂ sorption analysis and FT-IR spectroscopy. Both amino-modified samples showed significant improvement of CO₂ sorption capacity at 25°C when compared with the non-modified silica support, with strong binding of CO₂ with NH₂ groups. The CO₂ capture capacity, which seems to be strongly dependent on the size of the amino-precursors, can be further enhanced at higher temperatures. An uptake of 4.35 mmol of CO₂ per gram of adsorbent at 1 bar and 90°C for the KIL-2-TEPA sample indicates that the modification of foam-like silica matrix with poly-functional amines leads to the design of very efficient adsorbents for CO₂ capture.

Acknowledgements

Manuel Ojeda gratefully acknowledges the Royal Society of Edinburgh for the concession of an International Exchange Programme Award. The financial support of the Centre for Innovation in Carbon Capture and Storage (CICCS) at Heriot-Watt University and Research program P1-0021 Nanoporous materials from Slovenian Research Agency is also gratefully acknowledged.

References

- [1] M. Mikkelsen, M. Jorgensen, F.C. Krebs, The teraton challenge. A review of fixation and transformation of carbon dioxide, *Energy Environ. Sci.*, 3 (2010) 43-81.
- [2] IPCC, *Climate Change 2014: Mitigation of Climate Change*, Cambridge University Press, Cambridge, UK and New York, NY, USA, 2015.
- [3] M.M. Maroto-Valer, Z. Tang, Y. Zhang, CO₂ capture by activated and impregnated anthracites, *Fuel Process. Technol.*, 86 (2005) 1487-1502.
- [4] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, *Renew. Sust. Energ. Rev.*, 39 (2014) 426-443.
- [5] A. Sanna, M.M. Maroto-Valer, CO₂ Capture at High Temperature Using Fly Ash-Derived Sodium Silicates, *Ind. Eng. Chem. Res.*, 55 (2016) 4080-4088.
- [6] G.T. Rochelle, Amine Scrubbing for CO₂ Capture, *Science*, 325 (2009) 1652-1654.
- [7] M.G. Plaza, S. García, F. Rubiera, J.J. Pis, C. Pevida, Post-combustion CO₂ capture with a commercial activated carbon: Comparison of different regeneration strategies, *Chem. Eng. J.*, 163 (2010) 41-47.
- [8] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-Combustion CO₂ Capture Using Solid Sorbents: A Review, *Ind. Eng. Chem. Res.*, 51 (2012) 1438-1463.
- [9] J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare, Z. Zhong, Recent advances in solid sorbents for CO₂ capture and new development trends, *Energy Environ. Sci.*, 7 (2014) 3478-3518.
- [10] J.C. Fisher, M. Gray, Cyclic Stability Testing of Aminated-Silica Solid Sorbent for Post-Combustion CO₂ Capture, *ChemSusChem*, 8 (2015) 452-455.
- [11] W.M. Verdegaal, K. Wang, J.P. Sculley, M. Wriedt, H.-C. Zhou, Evaluation of Metal-Organic Frameworks and Porous Polymer Networks for CO₂-Capture Applications, *ChemSusChem*, 9 (2016) 636-643.
- [12] T.H. Nguyen, S. Kim, M. Yoon, T.-H. Bae, Hierarchical Zeolites with Amine-Functionalized Mesoporous Domains for Carbon Dioxide Capture, *ChemSusChem*, 9 (2016) 455-461.
- [13] H.M. Coromina, D.A. Walsh, R. Mokaya, Biomass-derived activated carbon with simultaneously enhanced CO₂ uptake for both pre and post combustion capture applications, *J. Mater. Chem. A*, 4 (2016) 280-289.
- [14] J. Gale, C. Hendriks, W. Turkenberg, C.F. Martín, S. García, J.J. Pis, F. Rubiera, C. Pevida, 10th International Conference on Greenhouse Gas Control Technologies Doped phenol-formaldehyde resins as precursors for precombustion CO₂ capture adsorbents, *Energy Procedia*, 4 (2011) 1222-1227.
- [15] E.S. Sanz-Pérez, A. Arencibia, R. Sanz, G. Calleja, New developments on carbon dioxide capture using amine-impregnated silicas, *Adsorption*, 22 (2015) 609-619.
- [16] H. Lee, C.T. Yavuz, Increasing mesoporosity by a silica hard template in a covalent organic polymer for enhanced amine loading and CO₂ capture capacity, *Micropor. Mesopor. Mater.*, 229 (2016) 44-50.
- [17] W.-J. Son, J.-S. Choi, W.-S. Ahn, Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials, *Micropor. Mesopor. Mater.*, 113 (2008) 31-40.
- [18] H. Yang, Y. Yuan, S.C.E. Tsang, Nitrogen-enriched carbonaceous materials with hierarchical micro-mesopore structures for efficient CO₂ capture, *Chem. Eng. J.*, 185-186 (2012) 374-379.
- [19] C. Chen, W.-S. Ahn, CO₂ capture using mesoporous alumina prepared by a sol-gel process, *Chem. Eng. J.*, 166 (2011) 646-651.
- [20] L. Ma, R. Bai, G. Hu, R. Chen, X. Hu, W. Dai, H.F.M. Dacosta, M. Fan, Capturing CO₂ with Amine-Impregnated Titanium Oxides, *Energy Fuels*, 27 (2013) 5433-5439.
- [21] K. Huang, F. Liu, S. Dai, Solvothermal synthesis of hierarchically nanoporous organic polymers with tunable nitrogen functionality for highly selective capture of CO₂, *J. Mater. Chem. A*, (2016).
- [22] X. Feng, G. Hu, X. Hu, G. Xie, Y. Xie, J. Lu, M. Luo, Tetraethylenepentamine-Modified Siliceous Mesocellular Foam (MCF) for CO₂ Capture, *Ind. Eng. Chem. Res.*, 52 (2013) 4221-4228.
- [23] W. Chaikittisilp, H.-J. Kim, C.W. Jones, Mesoporous Alumina-Supported Amines as Potential Steam-Stable Adsorbents for Capturing CO₂ from Simulated Flue Gas and Ambient Air, *Energy Fuels*, 25 (2011) 5528-5537.
- [24] S. Makhseed, J. Samuel, Microporous organic polymers incorporating dicarboximide units for H₂ storage and remarkable CO₂ capture, *J. Mater. Chem. A* 1(2013) 13004-13010.
- [25] J. Jiao, J. Cao, Y. Xia, L. Zhao, Improvement of adsorbent materials for CO₂ capture by amine functionalized mesoporous silica with worm-hole framework structure, *Chem. Eng. J.*, 306 (2016) 9-16.
- [26] N.N. Tušar, A. Ristić, G. Mali, M. Mazaj, I. Arčon, D. Arčon, V. Kaučič, N.Z. Logar, MnOx Nanoparticles Supported on a New Mesostructured Silicate with Textural Porosity, *Chem. Eur. J.*, 16 (2010) 5783-5793.
- [27] N.N. Tušar, D. Maučec, M. Rangus, I. Arčon, M. Mazaj, M. Cotman, A. Pintar, V. Kaučič, Manganese Functionalized Silicate Nanoparticles as a Fenton-Type Catalyst for Water Purification by Advanced Oxidation Processes (AOP), *Adv. Funct. Mater.*, 22 (2012) 820-826.
- [28] M. Tasbihi, U. Lavrenčič Štancar, U. Černigoj, J. Jirkovsky, S. Bakardjieva, N. Novak Tušar, Photocatalytic oxidation of gaseous toluene on titania/mesoporous silica powders in a fluidized-bed reactor, *Catal. Today*, 161 (2011) 181-188.

- [29] M. Popova, A. Szegedi, A. Ristic, N.N. Tusar, Glycerol acetylation on mesoporous KIL-2 supported sulphated zirconia catalysts, *Catal. Sci. Technol.*, 4 (2014) 3993-4000.
- [30] R. Sanz, G. Calleja, A. Arencibia, E.S. Sanz-Pérez, CO₂ adsorption on branched polyethyleneimine-impregnated mesoporous silica SBA-15, *Appl. Surf. Sci.*, 256 (2010) 5323-5328.
- [31] E.S. Sanz-Pérez, M. Olivares-Marín, A. Arencibia, R. Sanz, G. Calleja, M.M. Maroto-Valer, CO₂ adsorption performance of amino-functionalized SBA-15 under post-combustion conditions, *Int. J. Greenh. Gas Con.*, 17 (2013) 366-375.
- [32] J. Jiao, P. Lv, L. Wang, S. Dan, L. Qi, Y. Cui, CO₂ capture of amino functionalized three-dimensional worm-hole mesostructured MSU-J silica, *J. Porous Mater.*, 21 (2014) 775-781.
- [33] D. Wang, X. Wang, X. Ma, E. Fillerup, C. Song, Three-dimensional molecular basket sorbents for CO₂ capture: Effects of pore structure of supports and loading level of polyethylenimine, *Catal. Today*, 233 (2014) 100-107.
- [34] C. Chen, W.-J. Son, K.-S. You, J.-W. Ahn, W.-S. Ahn, Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity, *Chem. Eng. J.*, 161 (2010) 46-52.
- [35] X. Wang, H. Li, H. Liu, X. Hou, AS-synthesized mesoporous silica MSU-1 modified with tetraethylenepentamine for CO₂ adsorption, *Micropor. Mesopor. Mater.*, 142 (2011) 564-569.