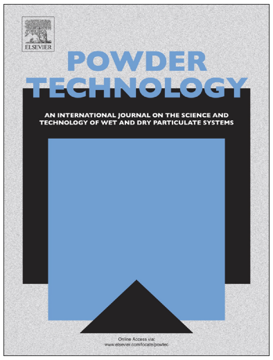

Formulation, adsorption performance, and mechanical integrity of triamine grafted binder-based mesoporous silica pellets for CO2 capture

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Formulation, Adsorption Performance, and Mechanical Integrity of Triamine Grafted Binder-Based Mesoporous Silica Pellets for CO_2 Capture

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ABSTRACT

This work explored formulation of mesoporous silicas pellets using a range of bentonite and colloidal silica (LUDOX), aiming to optimise the binder composition that minimises any deteriorating effects on adsorption performance, while provides an adequate mechanical integrity. Thermogravimetric analysis, scanning electron microscopy, and dynamic mechanical analysis were used to structurally characterise the pellets. Furtherer, CO_2 adsorption isotherms of synthesised pellets, pre and post triamine grafting, were measured. Bentonite was found to be an effective single binder that forms mechanically strong pellets and retains up to 85% of CO_2 capacity of the base adsorbent. At the presence of LUDOX, hardness of the pellets was lower, caused the largest decrease in CO_2 capacity. Formulation with 25% bentonite was found to provide pellets with post triamine functionalisation CO_2 capacity equivalent to powder SBA-15, at an amine efficiency of 0.41 mol CO_2/mol, while minimising pore blockage and maintaining a compressive strength of 1.5 MPa.

Keywords: SBA-15, pellet formation, bentonite binder, amine grafting, carbon capture, adsorption

Abbreviations

AC	Activated carbon
BdB	Broekhoff-de Boer
BJH	Barrett-Joyner-Halenda
EA	Elemental analysis
SEM	Scanning Electron Microscope
DMA	Dynamic Mechanical Analysis
TGA	Thermogravimetric analysis

1 Introduction

Carbon capture using adsorbents has been a promising approach to tackling anthropogenic CO_2 emissions, with their potential to be utilised in swing adsorption processes to reduce energy demands, compared to conventional amine scrubbing [1,2]. Within the subgroup of adsorbents, amine functionalised mesoporous silicas have shown promise, providing enhanced CO_2 capacities with highly selective separations from N_2 and CH_4 containing gas mixtures [3,4]. However, these mesoporous silica adsorbents are often synthesised and functionalised as powders, and cannot be practically employed in conventional fixed bed contactors due to several reasons, including the carryover of fines, high pressure drop, and diffusion mass resistance across the adsorbent bed [5–7]. Hung et al.[8] quantified the difference in pressure drop and showed that the powder form of a MCM-41 material can reach a pressure drop of 7000 mbar/g, while in their formed beads of 1.7 mm sizes, it was almost negligible at equivalent superficial velocities. As the pressure drop across an adsorber increases, the operational and capital costs of the associated compressor increases, and so, it must be kept adequately low.

The preparation of pellets from mesoporous silica is therefore an important part of employing them for commercial separations, with the optimisation of binder formulations a crucial part of minimising the changes in performance. There have been several techniques used within the literature to prepare pellets from mesoporous silica powders. One such method is the formation of micro-sized pellets using presses. The advantage of this technique is the elimination of a heat-treatment step, allowing for the pelletisation of the material post-functionalisation, without the possibility of stripping away the incorporated amine functionalities. Utilising this method, Rezaei et al.[9] carried out a study probing the effect of different pressing pressures on the adsorption performance of functionalised SBA-15. They used pressures of 7 MPa and 34 MPa to prepare pellet sizes of 0.25 and 0.5 mm. They found that the change in performance was highly dependent on the pressing pressure used, with higher pressures of 34 MPa causing a 40% decrease in adsorption capacity of both impregnated and grafted SBA-15 materials, while at lower pressures no considerable change on the adsorption capacity or kinetics was observed. This change in performance is material specific, as Yang et al.[10] recently showed that pressing pressures of 40 MPa to form zeolite beads of 1.1-1.4 mm had no effect on their CO_2 adsorption performance. The negligible effect on adsorption was similarly demonstrated in MOF materials, in the range of 0.25-0.5 mm, by Peterson et al.[11]. In the work by Rezaei et al., the prepared beads were very small, so further investigation on their mechanical integrity is required, and on the issue of pressure drop, or fines carry over. Klinthong et al.[12] introduced a novel method to pelletise MCM-41, using polyallylamine and NaOH solution, with the latter acting as the primary 'binder'. The prepared pellets were 5x2 mm in size, can be prepared after amine functionalisation, and have a mechanical strength of 0.3-0.5 MPa, depending on the concentration of NaOH added. This method produced pellets suitable for packed-bed studies, and showed a small decrease in capacity of only 10% compared to powdered samples, with good cyclability over 10 consecutive cycles. Although with promising results, polyallylamine is an expensive chemical, which makes large scale production economically unfavourable. Additionally, Thermogravimetric (TGA) studies were left to adsorb for 7 hours, and so the kinetic change post pelletisation requires further investigation. Comparatively, Sharma et al.[13] studied the effect of using bentonite as a primary binder to pelletise SBA-15, since bentonite is a cheap, readily available chemical, and has proven uses for a variety of applications, including as an adsorbent and catalyst binder. They primarily studied a binder composition made up of 20% bentonite and 5% activated carbon (AC), and prepared polyethylenimine (PEI) impregnated MCM-41 pellets post-pelletisation. There was no change in the equilibrium adsorption uptake compared to the powdered alternatives. However, the method of preparation involved a high temperature calcination step, and the expansion of the activated carbon significantly affected the internal morphology; the effect this had on the dynamic performance of the pellet material requires further scrutiny. Additionally, since the pellets studied were impregnated with a 50% PEI loading, the efficiency of the formed pellets as materials for amine grafting is unclear, which is important as they offer better cyclic stability than their impregnated counterparts, but whose adsorbent loading is dependent on the available surface silanols for bond formation.

To the best of our knowledge, no study has investigated the change in adsorption performance as the binder concentration changes, specifically in amine grafted mesoporous silicas, which is an important step in translating laboratory scale performance to real-world applications. Accordingly, this study aims to identify the optimal binder composition that minimise changes to the adsorption performance while maximising pellet strength, using bentonite as the primary binder and LUDOX as a co-binder. Bentonite is a low cost material readily used to provide mechanical strength to a variety of materials[14]. LUDOX is a similarly low cost commercial chemical, made up of amorphous silica dispersed in water and commonly used to manufacture binders, catalyst support, and as a silica source for zeolites[15]. We assessed the mechanical integrity and the resulting CO_2 adsorption performance of a variety of binder compositions, to narrow down the interdependency of adsorption capacity and pellet toughness. Additionally, LUDOX was investigated as a co-binder that could provide surface silanols for amine grafting, that replace active sites that may be blocked by bentonite. Finally, the efficiency of grafting triamine on the synthesised pellets was assessed, and the optimal binder make-up was compared with a powdered sample for CO_2 adsorption capacity, adsorption rate, and selectivity.

2 Materials and methods

2.1 Materials

SBA-15 adsorbent was supplied by XFNANO. The chemicals 3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (triamine), toluene (99.8%), methanol (HPLC grade), LUDOX®, . (4,000 cP at 2%), bentonite, and poly(vinyl alcohol) (Mw 13,000-23,000) were purchased from Sigma-Aldrich, UK. The gases nitrogen and carbon dioxide were purchased from BOC, UK and were of a purity above 99.99%.

2.2 Pellet Synthesis

The synthesis of the SBA-15 pellets followed a modified version of a procedure previously described by Sharma et al.[13]. Bentonite or a mixture of bentonite and LUDOX were used as the permanent binder, while methyl cellulose and PVA acted as temporary binders. First, 3 g of SBA-15 was mixed with a given quantity of bentonite, and methyl cellulose, as per **Table 1**. The produced powder mixture was then placed in a rotary mixer for 2 hours. For some samples, the quantity of LUDOX as per Table 1 was added. Further, 5% PVA, acting as a temporary binder, was dissolved into water, and used to make a paste which was then extruded into thin cylindrical shapes. Finally, the extrusions were left to dry in air for 24 hours and then placed in an oven at a heating rate of 2.5°C/min up to 550°C and then was kept for 10 hours to calcine. The synthesised pellets had an equivalent diameter of ~2 mm with lengths of 5-10 mm. The pelletised samples were denoted as (x)BE(y)LU, were x is the fraction of bentonite and y the fraction of LUDOX added. This procedure was repeated to produce two batches, to ensure consistency in the synthesised samples.

2.3 Amine grafting

SBA-15 powder and selected synthesised pellets were grafted with triamine under an inert reflux procedure, described in details by Wadi et al. [16]. In short, 4 mmol/g of triamine was added to 1 g of SBA-15 and refluxed for 4 hours at 90°C in toluene solvent. The grafted pellets were washed with plenty of toluene and methanol, and then filtered under vacuum suction and left to air dry under a fume hood for 24 hours.

2.4 Characterisation methods

2.4.1 Determination of amine loading

Thermogravimetric analysis (TGA 8000, PerkinElmer) was used to estimate the quantity of amine grafted on each pelletised sample. 10-15mg of sample was subjected to a nitrogen flow of 80ml/min and heated up to 800°C at 20°C /min. A 10-minute hold was carried out at 120°C and a 5-minute hold under air flow at 800°C.

2.4.2 Surface morphology

Each material's internal pore structure was determined from nitrogen adsorption at -196°C using a 3P Meso 222 volumetric sorption unit (3P instruments). A sample weight of 0.3g was used for each run and outgassed for 2 hours under vacuum at 90°C. The surface area (S_{BET}) was estimated using the Brunauer-Emmett-Teller (BET) in the pressure range of $0.05 < p/p^o > 0.3$. The pore volume was evaluated by the Barrett-Joyner-Halenda (BJH) method at $p/p^o=0.95$. The pore size distribution (PSD) was determined by the BJH method using the Broekhoff-de Boer (BdB) [17].

Scanning electron microscopy (SEM) was used to capture the surface topography of the materials, using TESCAN S8000G. The samples were held onto an aluminium SEM stub and coated with a 10nm of gold in a Quorum sputter coater, and then imaged at magnification and conditions shown in the presented image.

2.4.3 Pellet mechanical strength

The compressive strength of the formed pellets was measured using an electro-mechanical driven universal testing machine Instron® 5965 5kN test system equipped with a 50N cell. The pellets were mounted between compression plates and the test conducted at a crosshead speed of 0.5 mm/min. The displacement and force, from which the stress-strain curve was derived, was recorded once the total force exceeded 0.1 N. This procedure was repeated at least 3 times for each pellet composition.

2.4.4 Adsorption measurements

CO_2, N_2, and CH_4 adsorption isotherms were measured using the same 3p meso unit used above, with each material (0.25-0.3g) undergoing the same outgassing procedure described in section 2.4.2. The temperature was held at 25°C using an anti-freeze bath (3P instruments).

Dynamic adsorption by TGA was conducted for kinetic and stability data of selected materials. A 10 mg sample weight was loaded into the unit and degassed at 105°C for 30 minutes under nitrogen. Then, the sample temperature was reduced and held at 25°C for 25 mins and the gas switched to CO_2 at 60 ml/min. For desorption, the temperature was increased at a rate of 10°C/min to 90°C and held for 15 minutes to regenerate the adsorbent under nitrogen flow at 60 ml/min. The temperature was then decreased to 25°C, stabilised, and the adsorption-desorption repeated for 5 total cycles.

3 Results and Discussion

3.1 structural morphology

Figure 1 and **Table 1** present the compositional and structural characteristics of the synthesised SBA-15 pellets. The nitrogen adsorption isotherms of the pelletised samples are of type IV, in line with the SBA-15 powder and signify that the internal pore structure was unaltered by the addition of bentonite or colloidal silica. The type H1 hysteresis is another indication that the uniform mesopores in SBA-15 remain intact.

Referring to **Figure 2**, at least 20% bentonite is needed for a solid enough post calcination pellet to be formed. The addition of 20% bentonite decreased S_{BET} by 20% from 490 to 395 m^2/g and V_p by 15% from 1.2 to 1.01 cm^3/g. However, any additional increase in bentonite did not decrease the effective surface area any further. At fractions of 25% and 30% bentonite, the pore volume decreased by 22% and 23%, respectively. It seems that a considerable effect on porosity occurs from the initial binder addition, which becomes less pronounced as binder composition increases.

No pellet was formed when using only LUDOX at a concentration of 20%. Consequently, it was added in 5% quantities to contribute to pellet strength and investigate if any benefit can be achieved. As seen by the addition of bentonite, no additional change in the surface area was observed when a 5% quantity of LUDOX was added to 20-25% bentonite binders, and a negligible change in specific surface area from 394 to 385 m^2/g at 10% LUDOX.

From a morphology aspect, bentonite has a smaller effect on the adsorbent's porosity compared to LUDOX. This is further confirmed by comparing the PSD of the pellets prepared, with 20BE10LU demonstrating the largest volume of blocked pores below 8 nm (**Figure 3**). The temporary binders used here consist of PVA and methylcellulose, which during the calcination step turn into combustion gases, affecting the internal porosity of the adsorbent by creating pores or expanding them. This has been previously observed using pore forming agents such as biomass waste (ash), activated carbon, and even plastic/rubber waste[13,18,19]. Their use may have contributed to the observed PSD and BET, leading to the similar internal morphology in all samples, but their extent of influence is unclear.

The SEM images presented in **Figure 4** compare powdered SBA-15 with 20BE0LU and 20BE10L, and confirm that LUDOX does not alter the structural morphology in a different manner compared to bentonite, and therefore the larger effect on PSD is a result of its migration into the pores rather than agglomeration along the adsorbent's surface.

Compressive strength

Figure 5 presents the mean compressive strength of the prepared pellets. The detailed measured parameters, including the compressive displacement, is provided in **Table S1** in the **Supplementary Information**. The measured values showed a variation that is represented by the standard deviation values in **Table S1**. The large deviation is caused by the small pellet sizes as well as differences in the extruded shapes prepared. From a comparison of the mean compressive strength, LUDOX provides a much lower contribution to mechanical strength compared to bentonite. This is specifically seen in 25BE5LU, and 20BE10LU, which withstood 1.15 and 0.86 MPa compared to 1.5 and 2 MPa for 25BE0LU and 30BE0LU, respectively.

3.2 Amine grafting of SBA-15 pellets

Triamine was grafted on selected materials to study the effect of the binder material on the efficiency of amine grafting, and the measured loading of amine is presented in **Figure 6** and **Table 2**. One of the principal factors of amine grafting is the availability of accessible surface silanol hydroxyl groups, and the effect of the binder must be shown to have a minimal effect on this [20–22]. The organic content of amine was measured by the weight change after 200°C, as any vaporisation below that temperature is attributed to water or toluene solvent. The change in weight with the temperature of 20BE0LU and 20BE5LU showed a profile identical to triamine grafted SBA-15 powder. 25BE0LU and 20BE10LU both showed a slightly different profile, with a commencement of triamine vaporisation at ~300°C instead of 400°C. The reason for the faster removal of triamine in these samples is unclear, but since the triamine reagent used has a boiling point of 118°C, it is likely caused by the degradation of triamines bonded to the surface of the pellets rather than the internal pores. Since 25BE0LU demonstrates a higher grafted amine loading than 20BE5LU and 20BE10LU, it can be concluded that colloidal silica does not offer any added benefits, such as additional surface sites, but rather hinders the organosilane reagent's interaction with surface silanols.

3.3 CO_2 adsorption performance

The CO_2 adsorption isotherms of the unfunctionalised powder and pelletised SBA-15 is presented in **Figure 7** and **Table 3.** 20BE0LU had the lowest decrease in adsorption uptake from powdered SBA-15, a 16% drop down to 0.38 mmol/g. The second set of materials using 25% total binder fractions are 25BE0LU and 20BE5L, and a larger decrease in capacity of 28% is seen in 25BE0LU compared to 23% in the latter. At these lower quantities of binder composition, LUDOX does not affect pore access in the same manner that is seen binder compositions above 25%. For instance, 25BE5LU shows the largest drop in uptake at 100 kPa, decreasing from 0.45 mmol/g to 0.30 mmol/g in powder SBA-15. A similar decrease in performance has been demonstrated in bentonite containing zeolites, and can be attributed to the decrease in surface area in the formed pellets [23].

Compared to bentonite, the addition of LUDOX at quantities above 25% of a binder formulation causes a greater decrease in the adsorption capacity, and referring to **Figure 5**, creates mechanically weaker pellets. Additionally, the brittleness resulting from high LUDOX compositions can be clearly seen by the particle fractures in the 20BE10LU sample, presented in **Figure 2**. The highest addition of bentonite at 30% resulted in only a slight decrease in capacity compared to 25BE0LU, but the highest compressive strength of 2.15 MPa. Out of the studied compositions, the pellets of 20BE0LU, 20BE5LU, and 25BE0LU had the highest uptake, pore volume, and reasonable mechanical strength, and were chosen to be functionalised by triamine. Additionally, the 20BE10LU sample was functionalised to clarify the effect of LUDOX incorporation on the adsorption of CO_2 post grafting.

Figure 8 presents the CO_2 adsorption isotherms of the pelletised and powdered SBA-15 post functionalisation, while the recorded capacities and amine efficiency at 100 kPa are listed in **Table 2**. Amine efficiency is an effective method of comparing the different samples while accounting for any variations in total amine loading, it is defined as the moles of CO_2 adsorbed per gram of amine grafted. 20BE0LU and 20BE5LU samples showed a negligible difference in amine efficiency compared to the SBA-15 powder, adsorbing ~0.41 mmol CO_2/mmol amine. It seems that in these two samples, the employed binder had no effect on the accessibility of amine moieties by CO_2 compared to the powder.

25BE0LU and 20BE10LU both demonstrated a slightly lower efficiency, ~0.39 mmol CO_2 /mmol N. However, the variation is small and allows us to conclude that at the grafted loadings, all the binder formulations have a minimal effect on the amine promoted adsorption of CO_2. Even more, the addition of 10% LUDOX did not provide any discernible benefit, and may be considered to hinder adsorption rather than provide additional sites for adsorbate-adsorbent interactions. Out of all the pellets, 20BE0LU sample showed the highest uptake of CO_2 at an amine efficiency equal to the powder but was mechanically weakest. Considering pellet strength and adsorption capacity, 25BE0LU pellets would be the ideal pellet formulation to further assess the effect of the binder on the CO_2 adsorption rate, and selectivity in flue-gas or biogas like mixtures.

The N_2 and CH_4 adsorption isotherms are presented in **Figure 9.**, and the respective CO_2 ideal selectivity is illustrated in **Figure 10**. There is no observed change to the N_2 adsorption after pelletisation, and only a small difference for CH_4. This translates to a very similar CO_2:N_2 and CO_2:CH_4 selectivity between the powder and pellet material, with a deviation that grows bigger as CO_2 pressure increases. It can be inferred that the binder does not block the mesoporousity of the SBA-15 powder up to 100 kPa, providing structural integrity while maintaining macro-level accessibility to the internal active-sites for CO_2, CH_4, and N_2 adsorption.

TGA adsorption studies were carried out to compare the adsorption rate of 25BE0LU-TA post-pelletisation, **Figure 11.** The presence of the binder had no effect on the kinetics at 100 kPa, with the powder and pellet materials both demonstrating an almost equivalent adsorption rate. As previously mentioned, most of the internal pores are not blocked, and CO_2-amine interactions readily take place. However, the binder may affect adsorption performance more significantly at higher pressures, altering the selectivity as well, since the overall pore volume and surface area decreases post-pelletisation, and consequently the diffusivity and saturation loading of all adsorbates. This will be the subject of later studies, in which 20BE5LU pellets would be used for fixed-bed breakthrough studies at elevated pressure.

It is well established that amine grafting on mesoporous silicas provides enhanced stability compared to impregnation[24–27]. The chosen triamine functionalised pellets were subject to several adsorption-desorption cycles to confirm that pelletisation does not affect this quality, **Figure S.1**. An initial drop following the first cycle is observed, but the adsorption capacity is maintained at 4% weight gain after this step. This is likely a result of the mild desorption conditions used rather than leaching of amines, which employed a temperature of 90°C for 15 minutes to regenerate the adsorbent in between cycles. Overall, 20BE0LU-TA shows good cycle stability comparable to typical amine grafted powder SBA-15, and better than amine impregnated pellet and powder SBA-15[13,25,28].

Mesoporous silicas grafted by amines incur additional costs compared to benchmark adsorbents such as Zeolite 13x or typical activated carbons, with both being sold at around £900-2600 per ton, and showing CO_2 adsorption capacities >1.45 mmol/g[29–33]. Mesoporous silica itself can be expensive, selling for £50,000 per ton, but the cost of amino silanes for grafting is not very significant, and at a laboratory scale can range between £43-80 per kg of mesoporous silica to functionalise, and at industrial scale £700-800 per ton of mesoporous silica to functionalise. Although with down-sides, the advantage of amine functionalisation of silicas is the superior selectivity to CO_2, high capacity at low CO_2 partial pressures, and performance that is unaffected by the presence of moisture[16,34–37]. When these parameters need to be prioritised, this class of sorbent becomes effective, and its pelletisation for real-world use becomes essential. The method presented here would incur very little additional cost, since bentonite's market price can be as low as £100 per ton, while methylcellulose and PVA would add minimal costs of £60-70 per ton sorbent synthesised. Nevertheless, further work should concentrate on the use of cheap silica powder, at lower market prices of £500-2200 per ton, to be pelletised, to elucidate whether the binder formed macropores following the pelletisation step can aid for effective amine functionalisation and performance, while maintaining an extremely competitive price for large-scale deployment.

4 Conclusion

Within a laboratory environment, the adsorption performance of adsorbents is often studied in powder form, but resulting data is often non-representative of industrial applications. This is because these processes require the minimisation of the pressure drop across the bed, and the limitation of the carryover of fines; they therefore often utilise beads or extruded pellets. In this work, pellets using different binder formulations of SBA-15 have been prepared and grafted by triamine, to investigate the ideal binder composition that can maximise mechanical strength, while minimising any deteriorating effect on the adsorption performance. This formulation can then be used for fixed-bed adsorption studies, and produce more representative results of the adsorption behaviour of amine grafted silicas for CO_2 adsorption in commercial applications. The formation of SBA-15 pellets using a minimum of 20% bentonite binder showed good structural strength but decreased CO_2 adsorption by up to 30% compared to powder SBA-15. However, the triamine grafted pellets showed no change in the adsorption behaviour, with amine efficiency remaining almost equivalent to the powder sample. LUDOX was tested as a co-binder that provides pellet strength, and as a source of replacement silanol/hydroxyls for amine grafting. However, there was no enhancement in adsorption performance, or in the quantity of grafted amine compared to non-LUDOX containing pellets. Out of all the compositions, 25BE0LU showed high mechanical strength combined with no change in the amine's efficiency to capture CO_2 after triamine functionalisation, achieving equivalent selectivity and adsorption rates to its powder counterpart. However, an optimisation of the quantity of bentonite can be made without much effect on the total CO_2 adsorbed, and so, bentonite at a quantity of 25-30% of SBA-15 would be an acceptable binder composition for pellet formulations for further fixed bed breakthrough studies. This is an important step for two reasons; (1) the lower porosity of the pellets compared to the powder will likely affect the high-pressure performance and saturation adsorption of the adsorbent, and (2) different pellet shapes and sizes require further screening, to ensure consistent mechanical strength, and a minimal pressure drop across the bed while maximising pellet strength and dynamic performance. Suggestions for future work include a detailed investigation on the molecular interactions and extent of influence temporary binders and pore forming agents, such as PVA, and methyl cellulose, have on pelletisation of mesoporous mediums, or exploring very small additions of activated carbon to minimise pore deformation while maximising pore accessibility for surface interactions. Understanding these dependencies can allow for the optimisation of a powdered adsorbent even after synthesis, while being applicable for industrial scale uses, at minimal costs. This work confirmed the successful grafting of triamine on SBA-15, but other amine reagents such as primary and diamine silanes should be investigated, to understand the effect of amine type on grafting efficiency, capacity, selectivity, and adsorption kinetics. Finally, the high cost of mesoporous silica is a major roadblock in widespread use of these materials, and the possibility of optimising alternative cheaper supports, such as silica oxide powder, through pelletisation and then functionalisation should be studied.

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Credit author statement

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Q. Zhu, Developments on CO_2-utilization technologies, Clean Energy. 3 (2019)

85–100. https://doi.org/10.1093/ce/zkz008.

[2] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO_2 capture technology—The U.S. Department of Energy's Carbon Sequestration Program, Int. J. Greenh. Gas Control. 2 (2008) 9–20. https://doi.org/https://doi.org/10.1016/S1750-5836(07)00094-1.

[3] Y. Belmabkhout, A. Sayari, Adsorption of CO_2 from dry gases on MCM-41 silica at ambient temperature and high pressure. 2: Adsorption of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 binary mixtures, Chem. Eng. Sci. 64 (2009) 3729–3735. https://doi.org/10.1016/j.ces.2009.05.039.

[4] L. Mafra, T. Čendak, S. Schneider, P. V. Wiper, J. Pires, J.R.B. Gomes, M.L. Pinto, Amine functionalized porous silica for CO_2 /CH_4 separation by adsorption: Which amine and why, Chem. Eng. J. (2018) 612–621. https://doi.org/10.1016/j.cej.2017.12.061.

[5] R.W. Rousseau, 12.7 Process Design Considerations, Handb. Sep. Process Technol. (1987) 670–672. https://app.knovel.com/hotlink/khtml/id:kt003IO9M2/handbook-separation-process/process-design-considerations.

[6] G.A. Gabriel, G.R. Inamdar, An experimental investigation of fines migration in porous media, in: SPE Annu. Tech. Conf. Exhib., Society of Petroleum Engineers, 1983.

[7] C. Gruesbeck, R.E. Collins, Entrainment and deposition of fine particles in porous media, Soc. Pet. Eng. J. 22 (1982) 847–856.

[8] C. Hung, H. Bai, M. Karthik, Ordered mesoporous silica particles and Si-MCM-41 for the adsorption of acetone: A comparative study, Sep. Purif. Technol. 64 (2009) 265–272. https://doi.org/https://doi.org/10.1016/j.seppur.2008.10.020.

[9] F. Rezaei, M.A. Sakwa-Novak, S. Bali, D.M. Duncanson, C.W. Jones, Shaping amine-based solid CO_2 adsorbents: Effects of pelletization pressure on the

physical and chemical properties, Microporous Mesoporous Mater. 204 (2015) 34–42. https://doi.org/10.1016/j.micromeso.2014.10.047.

[10] J. Yang, H. Bai, H. Shang, J. Wang, J. Li, S. Deng, Experimental and simulation study on efficient CH_4/N_2 separation by pressure swing adsorption on silicalite-1 pellets, Chem. Eng. J. 388 (2020) 124222. https://doi.org/https://doi.org/10.1016/j.cej.2020.124222.

[11] G.W. Peterson, J.B. DeCoste, T.G. Glover, Y. Huang, H. Jasuja, K.S. Walton, Effects of pelletization pressure on the physical and chemical properties of the metal–organic frameworks Cu3(BTC)2 and UiO-66, Microporous Mesoporous Mater. 179 (2013) 48–53. https://doi.org/https://doi.org/10.1016/j.micromeso.2013.02.025.

[12] W. Klinthong, C.-H. Huang, C.-S. Tan, Polyallylamine and NaOH as a novel binder to pelletize amine-functionalized mesoporous silicas for CO_2 capture, Microporous Mesoporous Mater. 197 (2014) 278–287. https://doi.org/https://doi.org/10.1016/j.micromeso.2014.06.030.

[13] P. Sharma, J.-K. Seong, Y.-H. Jung, S.-H. Choi, S.-D. Park, Y.I.I. Yoon, I.-H. Baek, Amine modified and pelletized mesoporous materials: Synthesis, textural–mechanical characterization and application in adsorptive separation of carbondioxide, Powder Technol. 219 (2012) 86–98.

[14] L. Xinbing, Discussion on Performance Index of Bentonite Used for Metallurgical Pelletizing, Sinter. Pelletizing. (2010) 4.

[15] Grace, LUDOX® Colloidal Silica in Catalyst Applications, (2015). https://grace.com/catalysts-and-fuels/en-us/Documents/LUDOX Brochure_Catalysts_HR_5-12-15.pdf.

[16] B. Wadi, A. Golmakani, V. Manovic, A. Nabavi, Effect of combined primary and secondary amine densities on the adsorption mechanism of CO_2 and CH_4, Chem. Eng. J. (2021). Manuscript Under Review.

[17] Lukens Wayne W., P. Schmidt-Winkel, D. Zhao, J. Feng, G.D. Stucky, Evaluating Pore Sizes in Mesoporous Materials: A Simplified Standard Adsorption Method and a Simplified Broekhoff−de Boer Method, Langmuir. 15 (1999) 5403–5409. https://doi.org/10.1021/la990209u.

[18] F.N. Ridha, Y. Wu, V. Manovic, A. Macchi, E.J. Anthony, Enhanced CO_2 capture by biomass-templated Ca(OH)2-based pellets, Chem. Eng. J. 274 (2015) 69–75. https://doi.org/https://doi.org/10.1016/j.cej.2015.03.041.

[19] J. Sun, Y. Sun, Y. Yang, X. Tong, W. Liu, Plastic/rubber waste-templated carbide slag pellets for regenerable CO_2 capture at elevated temperature, Appl. Energy. 242 (2019) 919–930. https://doi.org/https://doi.org/10.1016/j.apenergy.2019.03.165.

[20] K.C. Vrancken, P. Van Der Voort, K. Possemiers, E.F. Vansant, Surface and Structural Properties of Silica Gel in the Modification with γ-Aminopropyltriethoxysilane, J. Colloid Interface Sci. 174 (1995) 86–91. https://doi.org/https://doi.org/10.1006/jcis.1995.1367.

[21] K.C. Vrancken, P. Van der Voort, I. Gillis-d'Hamers, E.F. Vansant, Influence of Water in the reaction of γ-Aminopropyltriethoxysilane with Silica Gel, J. Chem. Soc. Faraday Trans. 88 (1992) 3197–3200. https://doi.org/10.1039/FT9928803197.

[22] P. Van Der Voort, I. Gillis-D'Hamers, K.C. Vrancken, E.F. Vansant, Effect of porosity on the distribution and reactivity of hydroxyl groups on the surface of silica gel, J. Chem. Soc. Faraday Trans. 87 (1991) 3899–3905.

[23] A. Ojuva, F. Akhtar, A.P. Tomsia, L. Bergström, Laminated Adsorbents with Very Rapid CO_2 Uptake by Freeze-Casting of Zeolites, ACS Appl. Mater. Interfaces. 5 (2013) 2669–2676. https://doi.org/10.1021/am400122r.

[24] N. Hiyoshi, K. Yogo, T. Yashima, Adsorption characteristics of carbon dioxide on organically functionalized SBA-15, Microporous Mesoporous Mater. 84 (2005)

357–365. https://doi.org/10.1016/j.micromeso.2005.06.010.

[25] N. Rao, M. Wang, Z. Shang, Y. Hou, G. Fan, J. Li, CO_2 Adsorption by Amine-Functionalized MCM-41: A Comparison between Impregnation and Grafting Modification Methods, Energy & Fuels. 32 (2018) 670–677. https://doi.org/10.1021/acs.energyfuels.7b02906.

[26] Y. Belmabkhout, A. Sayari, Isothermal versus non-isothermal adsorption-desorption cycling of triamine-grafted pore-expanded MCM-41 mesoporous silica for CO_2 capture from flue gas, Energy and Fuels. 24 (2010) 5273–5280. https://doi.org/10.1021/ef100679e.

[27] E.S. Sanz-Pérez, T.C.M. Dantas, A. Arencibia, G. Calleja, A.P.M.A. Guedes, A.S. Araujo, R. Sanz, Reuse and recycling of amine-functionalized silica materials for CO_2 adsorption, Chem. Eng. J. 308 (2017) 1021–1033. https://doi.org/10.1016/j.cej.2016.09.109.

[28] A. Zhao, A. Samanta, P. Sarkar, R. Gupta, Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study, Ind. Eng. Chem. Res. 52 (2013) 6480–6491. https://doi.org/10.1021/ie3030533.

[29] M. V Gil, N. Álvarez-Gutiérrez, M. Martínez, F. Rubiera, C. Pevida, A. Morán, Carbon adsorbents for CO_2 capture from bio-hydrogen and biogas streams: Breakthrough adsorption study, Chem. Eng. J. 269 (2015) 148–158. https://doi.org/https://doi.org/10.1016/j.cej.2015.01.100.

[30] I. Durán, N. Álvarez-Gutiérrez, F. Rubiera, C. Pevida, Biogas purification by means of adsorption on pine sawdust-based activated carbon: Impact of water vapor, Chem. Eng. J. 353 (2018) 197–207. https://doi.org/10.1016/j.cej.2018.07.100.

[31] J.F. Vivo-Vilches, A.F. Pérez-Cadenas, F.J. Maldonado-Hódar, F. Carrasco-Marín, R.P. V Faria, A.M. Ribeiro, A.F.P. Ferreira, A.E. Rodrigues, Biogas upgrading by selective adsorption onto CO_2 activated carbon from wood pellets,

J. Environ. Chem. Eng. 5 (2017) 1386–1393. https://doi.org/https://doi.org/10.1016/j.jece.2017.02.015.

[32] S. Cavenati, C.A. Grande, A.E. Rodrigues, Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures, J. Chem. Eng. Data. 49 (2004) 1095–1101. https://doi.org/10.1021/je0498917.

[33] Z. Bacsik, O. Cheung, P. Vasiliev, N. Hedin, Selective separation of CO_2 and CH_4 for biogas upgrading on zeolite NaKA and SAPO-56, Appl. Energy. 162 (2016) 613–621. https://doi.org/https://doi.org/10.1016/j.apenergy.2015.10.109.

[34] E.S. Sanz-Pérez, M. Olivares-Marín, A. Arencibia, R. Sanz, G. Calleja, M.M. Maroto-Valer, CO_2 adsorption performance of amino-functionalized SBA-15 under post-combustion conditions, Int. J. Greenh. Gas Control. 17 (2013) 366–375. https://doi.org/https://doi.org/10.1016/j.ijggc.2013.05.011.

[35] A. Kumar, D.G. Madden, M. Lusi, K.J. Chen, E.A. Daniels, T. Curtin, J.J. Perry, M.J. Zaworotko, Direct Air Capture of CO_2 by Physisorbent Materials, Angew. Chemie - Int. Ed. 54 (2015) 14372–14377. https://doi.org/10.1002/anie.201506952.

[36] Y. Belmabkhout, G. De Weireld, A. Sayari, Amine-Bearing Mesoporous Silica for CO_2 and H2S Removal from Natural Gas and Biogas, Langmuir. 25 (2009) 13275–13278. https://doi.org/10.1021/la903238y.

[37] A. Sayari, Y. Belmabkhout, Stabilization of amine-containing CO_2 adsorbents: dramatic effect of water vapor., J. Am. Chem. Soc. 132 (2010) 6312–6314. https://doi.org/10.1021/ja1013773.

Figure 1. N_2 adsorption isotherms of the different pelletised materials at -196°C.

Figure 2. Categorisation of the pellets formed by the quantity of bentonite and LUDOX added per SBA-15.

Figure 3. PSD calculated from nitrogen adsorption isotherms of pelletised SBA-15 as a function of (a) increasing LUDOX quantity at 20% bentonite, (b) increasing LUDOX quantity at 25% bentonite, (c) increasing bentonite quantity at 0% LUDOX.

Figure 4. SEM image of raw SBA-15 (a), 20BE0LU (b), and 20BE10LU (c) materials. All scale bars are 2 μm.

Figure 5. Mean compressive strength of the prepared pellets.

Figure 6. The weight change of grafted triamine on SBA-15 powder and pellets with increasing temperature.

Figure 7. CO_2 adsorption isotherms of the unfunctionalised powder and pelletised materials.

Figure 8. Experimental CO_2 adsorption isotherms of triamine functionalised powder and pelletised materials.

Figure 9. N_2 and CH_4 adsorption isotherms at 25°C and 100 kPa. (◆) SBA-P-TA-N_2, (○)25BE0LU-TA-N_2, (▲) SBA-P-TA-CH_4, (●)25BE0LU-TA-CH_4

Figure 10. CO_2:N_2 and CO_2:CH_4 ideal selectivity of triamine functionalised powder SBA-15 and selected pelletised material.

Figure 11. CO_2 uptake by TGA of triamine functionalised powder SBA-15 and selected pellet.

Table 1. Structural characteristics compositional make-up of the pelletised materials compared to powder SBA-15 (SBA-P). S_{BET} is BET surface area, V_p is pore volume, and D_p is pore diameter,

				Fraction Added	
Sample	S_{BET}(m^2/g)	V_p(cm^3/g)	D_p(nm)	Bentonite (%)	LUDOX (%)
SBA-P	490	1.200	7.8	-	-
20BE0LU	395	1.017	7.1	20	0
20BE5LU	398	0.984	7.6	20	5
25BE0LU	391	0.938	7.5	25	0
25BE5LU	395	0.907	7.5	25	5
30BE0LU	391	0.919	7.8	30	0
20BE10LU	384	0.888	8.0	20	10

Table 2. Amine loading of triamine grafted pellets

Sample	N mmol/g	Uptake (mmol/g)	%Diff*	Amine efficiency (CO_2 mmol/mmol amine)
SBA-P-TA	3.32	1.46		0.43
20BE0LU-TA	3.05	1.25	-14.3	0.41
20BE5LU-TA	2.76	1.15	-21.2	0.41
25BE0LU-TA	2.94	1.15	-20.8	0.39
20BE10LU-TA	2.83	1.09	-25.1	0.38

*The percent difference of each material compared to the powder SBA-15

Table 3. CO_2 adsorption of pelletised SBA-15 compared to the powder SBA-15.

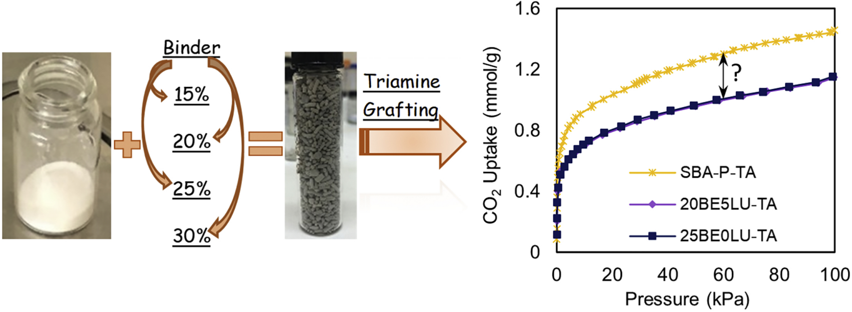
	CO_2 loading (mmol/g)	%Diff*
SBA-P	0.45	-
20BE0LU	0.38	-16

20BE5LU	0.35	-23
25BE0LU	0.33	-28
25BE5LU	0.30	-34
30BE0LU	0.32	-30

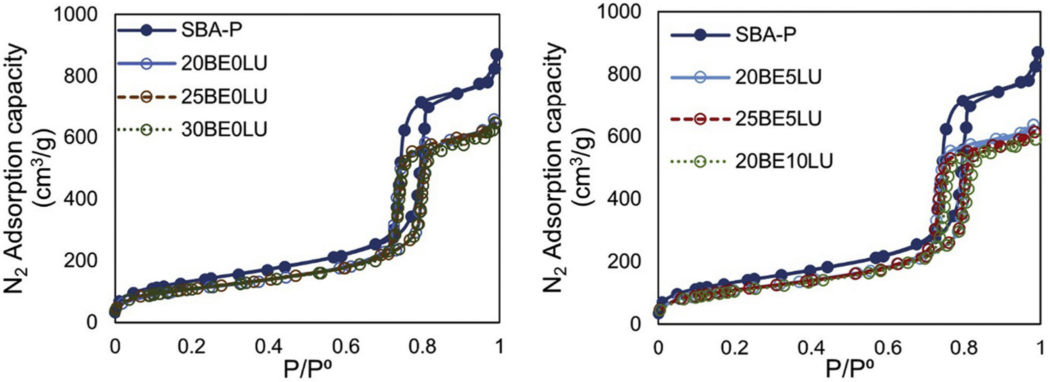
*The percent difference of each material compared to the powder SBA-15 functionalised by triamine

Highlights

- Pelletised SBA-15 with a range of binder compositions using bentonite and LUDOX
- Investigated efficiency of amine grafting and CO_2 adsorption of binder-based pellet
- LUDOX as a co-binder resulted in mechanically weaker pellets
- Bentonite was found to be an effective single binder to make pellets



Graphics Abstract



1000
800
600
400
200
0
N$_2$ Adsorption capacity (cm^3/g)
0
0.2
0.4
0.6
0.8
1
P/P°
SBA-P
20BE0LU
25BE0LU
30BE0LU
1000
800
600
400
200
0
N$_2$ Adsorption capacity (cm^3/g)
0
0.2
0.4
0.6
0.8
1
P/P°
SBA-P
20BE5LU
25BE5LU
20BE10LU

Figure 1

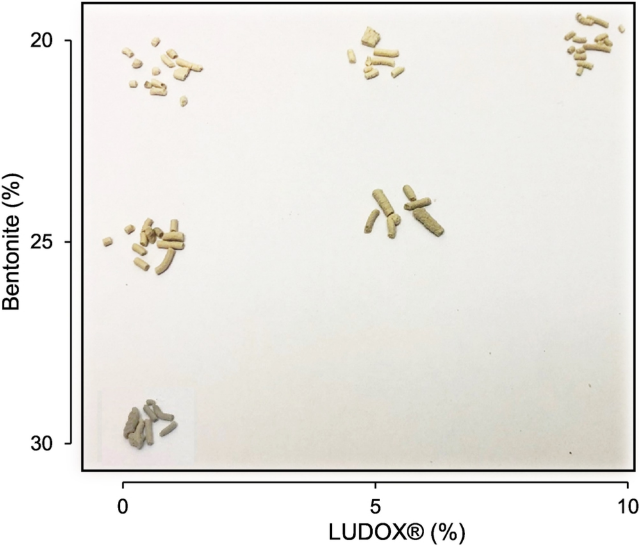


Figure 2

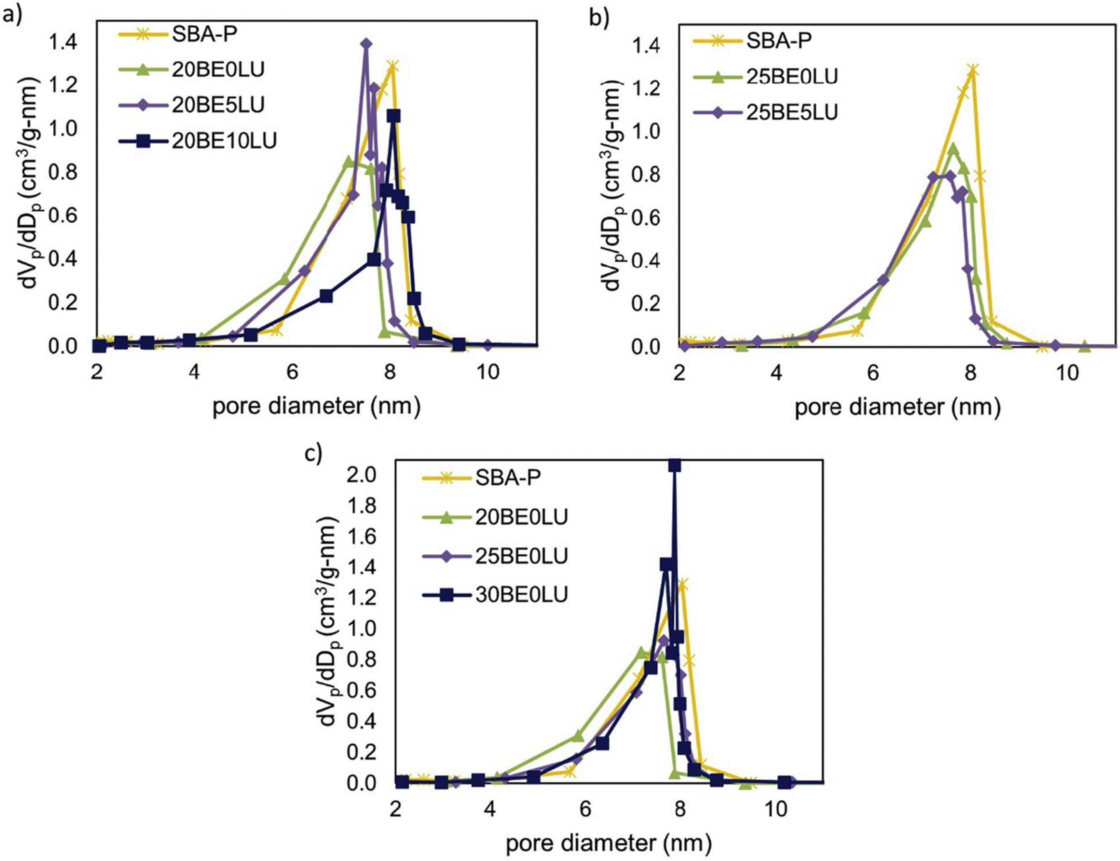

a)
SBA-P
20BE0LU
20BE5LU
20BE10LU
dV$_p$/dD$_p$ (cm^3/g-nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
2
4
6
8
10
pore diameter (nm)
b)
SBA-P
25BE0LU
25BE5LU
dV$_p$/dD$_p$ (cm^3/g-nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
2
4
6
8
10
pore diameter (nm)
c)
SBA-P
20BE0LU
25BE0LU
30BE0LU
dV$_p$/dD$_p$ (cm^3/g-nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2
4
6
8
10
pore diameter (nm)

Figure 3

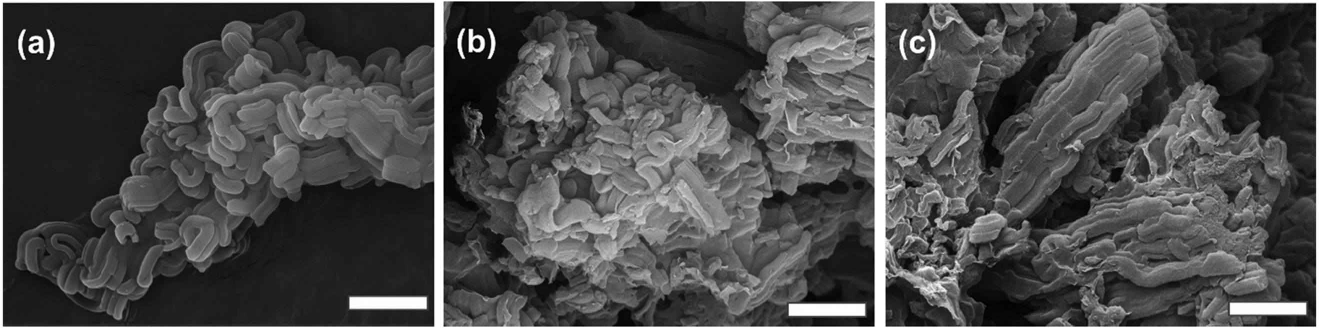


Figure 4

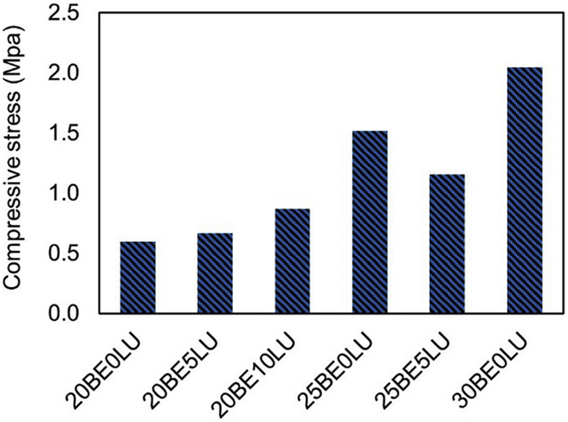

Compressive stress (Mpa)
2.5
2.0
1.5
1.0
0.5
0.0
20BE0LU
20BE5LU
20BE10LU
25BE0LU
25BE5LU
30BE0LU

Figure 5

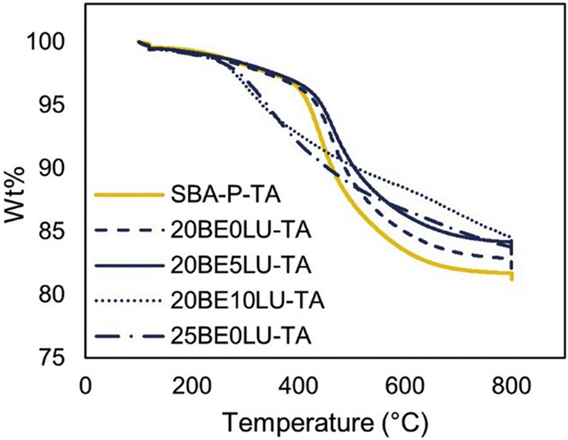
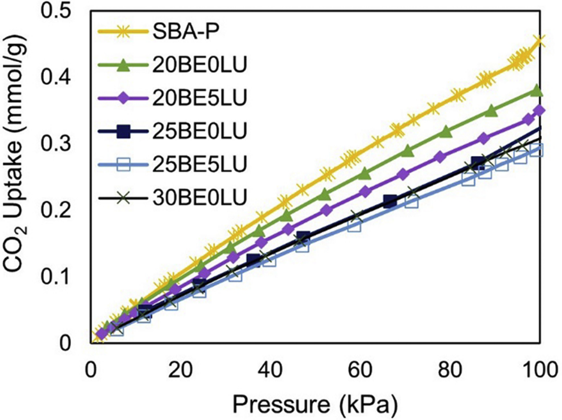

Wt%
100
95
90
85
80
75
0
200
400
600
800
Temperature (°C)
SBA-P-TA
20BE0LU-TA
20BE5LU-TA
20BE10LU-TA
25BE0LU-TA

Figure 6



SBA-P
20BE0LU
20BE5LU
25BE0LU
25BE5LU
30BE0LU
CO2 Uptake (mmol/g)
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
Pressure (kPa)

Figure 7

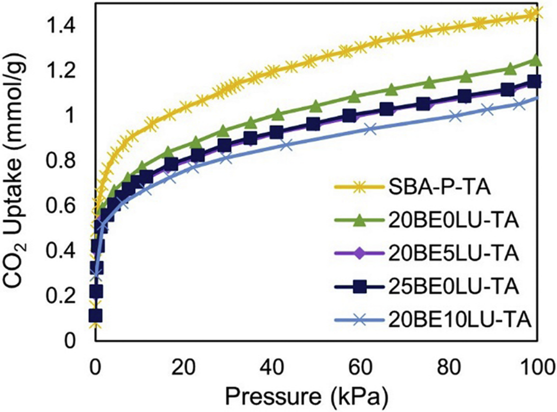

1.4
1.2
1
0.8
0.6
0.4
0.2
0
CO$_2$ Uptake (mmol/g)
0
20
40
60
80
100
Pressure (kPa)
SBA-P-TA
20BE0LU-TA
20BE5LU-TA
25BE0LU-TA
20BE10LU-TA

Figure 8

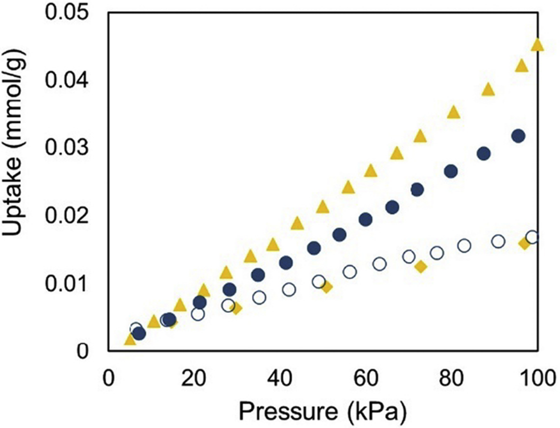

Uptake (mmol/g)
0.05
0.04
0.03
0.02
0.01
0
Pressure (kPa)
0
20
40
60
80
100

Figure 9

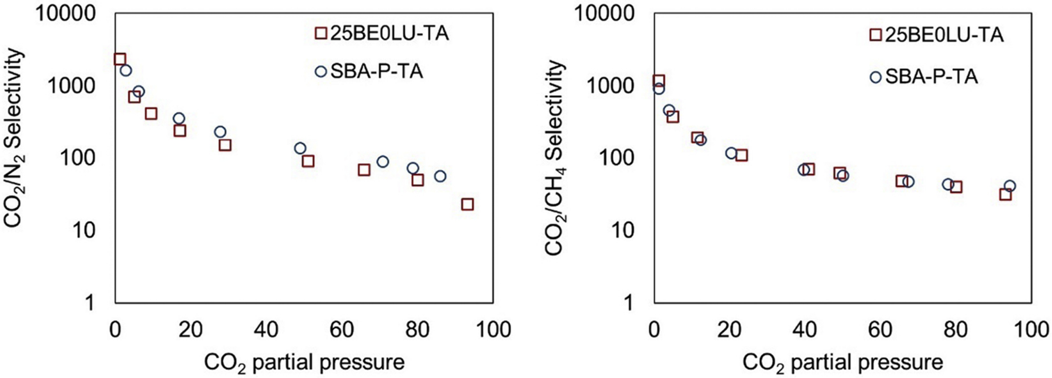

10000
1000
100
10
1
CO_2/N_2 Selectivity
□ 25BE0LU-TA
○ SBA-P-TA
0
20
40
60
80
100
CO_2 partial pressure
10000
1000
100
10
1
CO_2/CH_4 Selectivity
□ 25BE0LU-TA
○ SBA-P-TA
0
20
40
60
80
100
CO_2 partial pressure

Figure 10

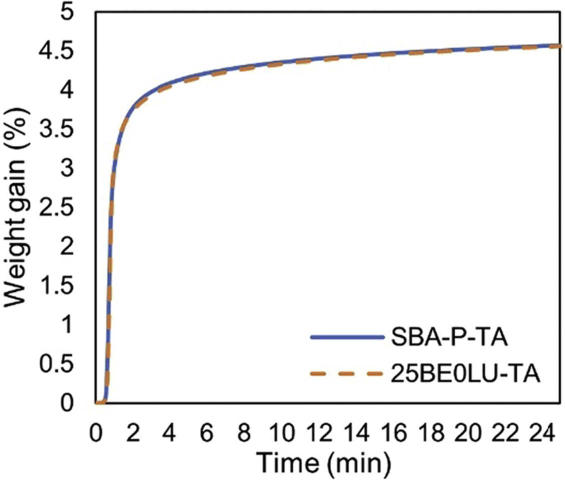

5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Weight gain (%)
0 2 4 6 8 10 12 14 16 18 20 22 24
Time (min)
SBA-P-TA
25BE0LU-TA

Figure 11