



Original Article

Evaluation on the Stability of Amine-Mesoporous Silica Adsorbents used for CO₂ Capture

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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 $\approx 280^{\circ}\text{C}$, while PEI-MPS was thermally decomposed at $\approx 180^{\circ}\text{C}$ only. PEI-MPS was particularly less stable when operating under dry condition; and 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.

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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 retrofitted 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 polyethylenimine 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.

2. Methods

2.1. Materials

Polyethyleneimine, branched (PEI, Mw \approx 600), 3-aminopropyltriethoxysilane (97%, APTES), absolute ethanol, mesoporous silica (MPS), and silica bead were purchased from Sigma Aldrich. MPS has particle size from 75–150 μm , pore volume 1.15 cm^3/g , pore size 11.5 nm, and surface area 300 m^2/g . Silica bead has particle size from 250–500 μm , pore volume 0.75 cm^3/g , pore size 0.6 nm, and surface area

480 m²/g. CO₂ gas (99.9 %) and N₂ (99.99%) were supplied by Gulf Industrial Gases CO. L.L.C.

2.2. 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 °C for 3 h in an oven and stored in containers for later characterization and evaluation.

2.3. 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°C in atmospheric condition at ramping rate of 5°C/min. Samples did not undergo CO₂ adsorption test prior to TGA analysis, however, certain amount of CO₂ could be adsorbed from atmosphere. Fourier Transform Infrared Spectroscopic (FTIR) measurements were conducted on a vertex 80 spectrometer (Bruker).

2.4. 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 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 beads are actually silicagel beads with low CO₂ adsorption capacity [20], which, therefore, will not significantly influence on the results of CO₂ adsorption study. The reactor was made of stainless-steel column with 1.27 cm inner diameter and 20 cm length. The reactor was heated by an electric ring heater and reaction temperature was monitored by a thermocouple inserted on the reactor in the center of the reactor. Feed gas was run through a humidifier (A) (V1 closed while V2 and V3 opened), 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. For a dry condition test, V1 opened, while V2 and V3 closed to by-pass humidifier. In an adsorption stage, the simulated flue gas was fed into the reactor at 30°C for one hour. 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. The CO₂ concentration in the effluent gas was monitored by a CO₂ Transmitter Series GMT220 (Vaisala, Finland). All gas flow rates and CO₂ concentration were recorded and used for the calculation of CO₂ loading. 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°C/120°C for APTES-MPS and 75/110°C for PEI-MPS, respectively. These adsorption and regeneration temperatures were determined based on the results obtained from the investigation on the effect of temperature on the CO₂ adsorption of the adsorbents, which was conducted in pure

CO₂ instead of 15 vol% CO₂ gas. The CO₂ loading was calculated based on regeneration data; it is the amount of CO₂ desorbed in regeneration step per mass of adsorbent.

3. 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 (A) after impregnated with PEI (B) and APTES (C) 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 are expected to have high CO₂ capture capacity.

The TGA profiles of the as-synthesized adsorbents were shown in Figure 3. All materials show mass loss from room temperature to 150°C 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. In the temperature range of 150-800°C, 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°C 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°C. This is likely because of 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.

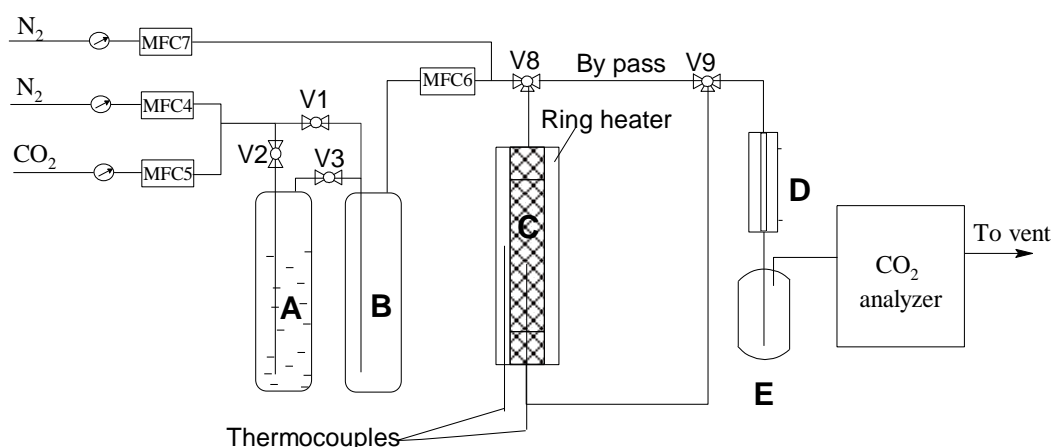


Figure 1. A schematic illustration of a fixed bed reactor for CO₂ adsorption/regeneration tests.

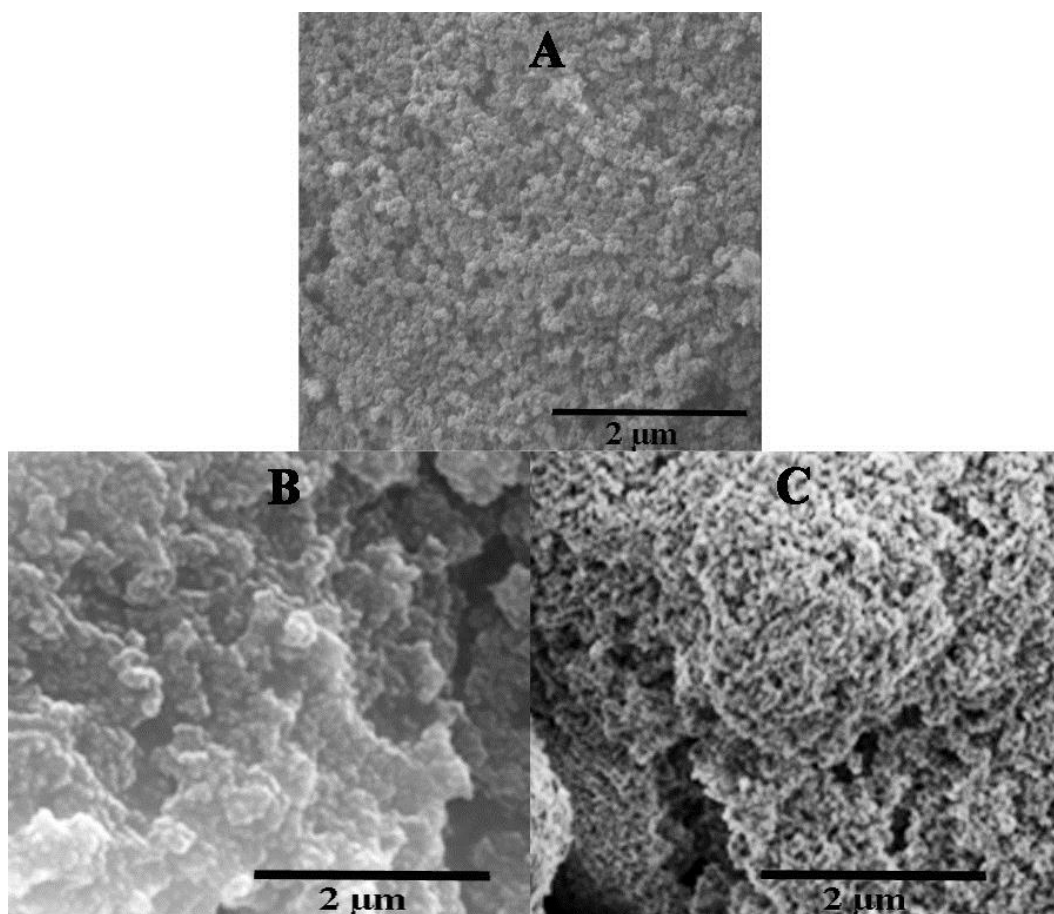
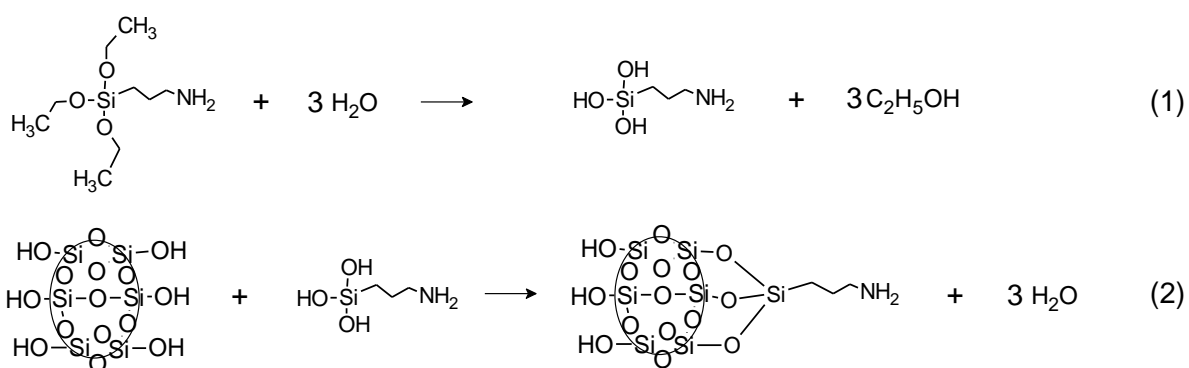


Figure 2. SEM images of MPS (A) and adsorbents synthesized by wet impregnation of PEI (B) and APTES (C).



Scheme 1. The hydrolysis and condensation of APTES and MPS.

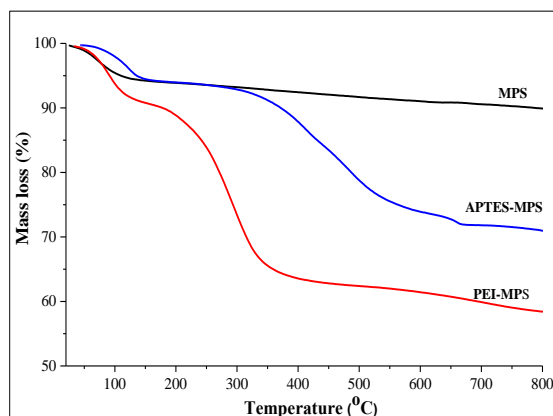


Figure 3. TGA profiles of different adsorbents.

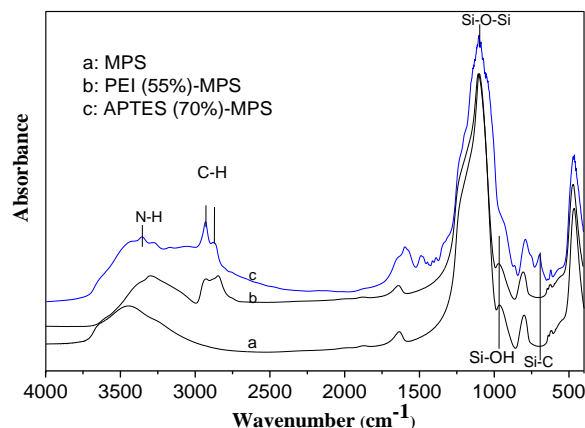


Figure 4. FTIR spectra of MPS and APTES-MPS.

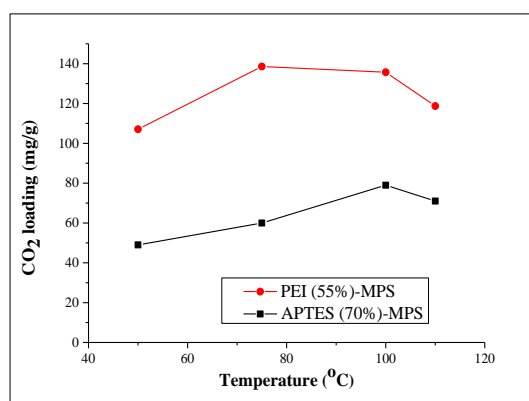
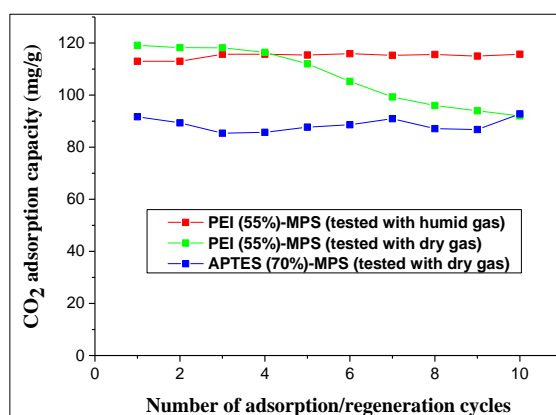


Figure 5. Adsorption capacity of adsorbents at different temperature.

Figure 6. The stability of CO₂ adsorbent over multiple adsorption/regeneration cycles.

To elucidate the state of bonds formed between impregnated amines and MPS, FTIR spectra were collected and are shown in Figure 4. As seen in the FTIR spectra, vibrational band for silanol group at about 965 cm^{-1} was observed on both MPS substrate and PEI-MPS adsorbent, however, disappeared on the spectrum of APTES-MPS. On the other hand, a new peak assigned to Si-C bond emerged at 695 cm^{-1} on the spectrum of APTES-MPS. These results suggested that PEI was impregnated and bound to MPS via physical interactions, which do not alter the surface of MPS, whereas, APTES formed chemical bonds with MPS through hydrolysis and condensation (Scheme 1). The

condensation among silanol groups of hydrolyzed APTES and MPS caused the depletion of silanol groups and as the result caused the disappearance of vibrational band at 965 cm^{-1} . This consolidates the confirmation that the more thermal stability observed on APTES-MPS is due to the formation of chemical bonds between APTES and MPS that help the resulting adsorbent avoid leaching and vaporization of amines.

The variation in the CO₂ adsorption capacity of the prepared adsorbents as a function of temperature is exhibited in Figure 5. PEI-MPS had maximum adsorption capacity at 75°C , while that for APTES-MPS was observed at

100°C. These results allow us to determine the effective working temperature of the adsorbent. Accordingly, the adsorption/regeneration temperatures for PEI-MPS and APTES-MPS were fixed at 75°C/110°C and 100°C/120°C, respectively.

To evaluate the stability of adsorbent after multiple cycles, 10 adsorption/regeneration cycles were conducted and results are presented in Figure 6. 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 began reducing at the third cycle and decreased by 22.1% after 10 cycles. This indicated that APTES-MPS is high stability; but PEI-MPS is not stable in the dry condition. 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 6 suggested that the PEI-MPS became more stable after 10 CO₂ adsorption/regeneration cycles in humid condition. It is likely that the physical bonds between PEI and MPS were relatively weak in dry condition due to less hydrogen bond. 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 more stable adsorbent thanks to the chemical bonds formed between amino groups and MPS. PEI-MPS is less stable due to physical bond; however, it can be improved in humid condition.

3. 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 (180–380°C), while APTES-MPS decomposed at higher temperatures (280–600°C). 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°C/120°C) in both humid and dry condition, while PEI-MPS can operate at low temperature (75°C/110°C) but only in humid condition.

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