Evaluation of the CO_2 capture capacity of polyethylenimine (PEI) functionalized SBA-15 sorbents in a fixed bed reactor

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Highlights

- PEI-functionalized SBA-15 samples have been synthesized for CO_2 capture.
- Reaction conditions have been established for repetitive and cyclic CO_2 capture and desorption.
- The 50 wt.% PEI sample presents the highest CO_2 capture capacity of 6.8% of its weight.

1. Introduction

Global warming, caused by the accumulation of greenhouse gases in the atmosphere, presents a major negative impact on ecosystems and settlements. Therefore, efforts in research and development of technologies mitigating its causes, such as integrated CO_2 capture and utilization (ICCU), are of paramount importance. This consists in capturing CO_2 from the atmosphere or industrial exhausts for its use as raw material. Currently, wet scrubbing is a well-established technology for CO_2 capture, while recently amine-functionalized solid sorbents have received considerable attention as a promising alternative technology. The use of mesoporous silica SBA-15 [1] as a support for functionalized CO_2 sorbents has generated interest due to its uniform structure and large specific surface area and pore volume [2]. On the other hand, polyethylenimine (PEI) is a suitable CO_2 capture agent due to its high amine content and stability [2]. Thus, the objective of the present work is to determine the reaction conditions that guarantee a repetitive and stable CO_2 capture and desorption cyclic operation. Different sorbents are prepared with different PEI loading and their CO_2 capture capacity and desorption temperature are determined.

2. Methods

SBA-15 was synthetized following the method described by Wang et al. [3] using pluronic P123 as structure directing agent and tetraethyl orthosilicate (TEOS) as silica source. SBA-15 was functionalized with 30, 40 and 50 % of PEI by wet impregnation method using the Büchi rotavapor R-114 (30 °C; 3 mmHg). All samples were characterized by X-ray diffraction (XRD), N_2 physisorption and thermogravimetric analysis (TGA). On the one hand, TGA was used to estimate the PEI loading in the sorbents by calcination up to 750 °C (5 °C/min, 30 minutes). On the other hand, PEI stability was studied in cyclic thermal experiments by increasing temperature from 50 °C to maximum temperatures of 80, 100, 120 and 140 °C (5 °C/min). The CO_2 sorption capacity of the samples was measured in both TGA and fixed bed reactor (FBR). Sorption in TGA was carried out by exposing the samples to four cycles of CO_2 capture (1% CO_2/Ar at 40 °C) and desorption (He at 80 °C). Experimentation on FBR reactor was performed in a Micrometrics AutoChem II unit; during the experiment samples were saturated with CO_2 (2.5% CO_2/He at 40 °C) and desorption was promoted at 80 °C in helium, while CO_2 concentration was continuously monitored at the reactor outlet with a calibrated TCD detector.

3. Results and discussion

The XRD patterns show the usual diffraction pattern of SBA-15 (peaks around 1°, 1.5° and 1.7° 2θ), which confirms the correct synthesis of the solid with a well-defined two-dimensional mesoporous structure [1]. Physico-chemical properties of prepared samples and the CO_2 capture capacities in FBR and TGA are shown in Table 1. Both surface area and volume decrease with the addition of PEI, due to progressive blocking of the pore structure. The amount of PEI loaded in the sample was determined

by measuring the weight loss after a high temperature calcination protocol (up to 750 ºC), where the measured amount of PEI resulted similar to nominal values. Thermal cyclic experiments showed that the maximum allowed temperature was 80 °C to guarantee a stable operation, due to PEI degradation above this temperature, i.e. a progressive mass loss of the sample was recorded in each cycle. The maximum CO_2 capture capacity of the samples when running the operation in FBR reactor and TGA are shown in last two columns (Table 1, where an increase in CO_2 capture capacity with PEI content can be observed, achieving the maximum capture capacity with the PEI50/SBA sample (≈6.8%).

Table 1. Physico-chemical properties of the samples and the CO_2 capture capacity in FBR reactor and TGA.

Sample	BET (m^2/g)	Pore vol. (cm^3/g)	% PEI	$\frac{m_{CO_2}}{m_{total}}$ FBR (%)	$\frac{m_{CO_2}}{m_{total}}$ TGA (%)
SBA-15	721.6	0.95	-	0.45	0.20
PEI30/SBA	159.9	0.34	30.4	5.96	4.85
PEI40/SBA	99.5	0.20	41.1	6.34	5.97
PEI50/SBA	8.9	0.02	50.2	6.75	6.84

Figure 1 depicts the evolution of the volume percentage of CO_2 at the fixed bed reactor outlet together with the evolution of the sample temperature with time (the inner graph is an enlargement of CO_2 percentage vs. time). A gas stream containing 2.5% CO_2 was fed to the reactor from minute 5 to 65. The CO_2 breakthrough is delayed for the PEI functionalized samples with respect to the bare SBA-15 support, revealing a high affinity of CO_2 to be captured onto impregnated PEI. After 60 minutes, samples are saturated with CO_2 and desorption is promoted by increasing temperature up to 80 ºC with a temperature ramp of 5 ºC/min under inert helium gas. Progressively, CO_2 concentration increases and peaks around 0.8% when temperature approaches 80 ºC. Afterwards, the CO_2 concentration is progressively reduced back to zero, while temperature is maintained at 80 ºC, which reveals complete CO_2 desorption from the solid sorbent. The integration of the area under the CO_2 concentration curve during the desorption phase is used to calculate the maximum CO_2 capture capacity, shown in Table 1. The stable and cyclic CO_2 capture and desorption operation was also confirmed by TGA experiments.

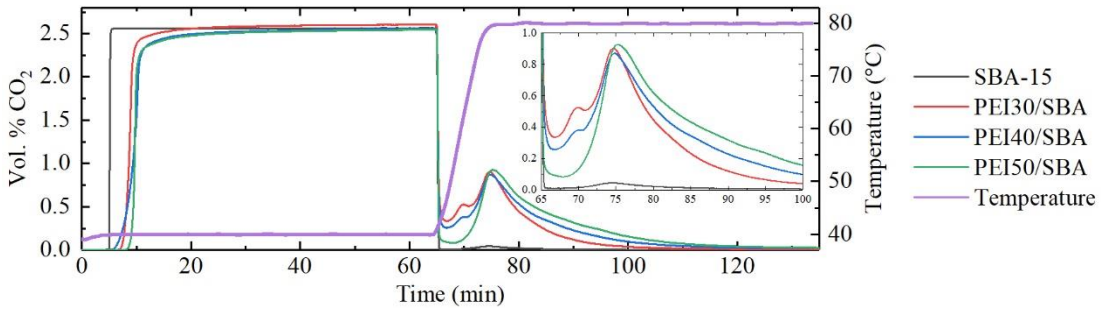

Figure 1. Volume percentage of CO_2 in the outlet of the fixed bed reactor and temperature in the bed.

4. Conclusions

PEI-functionalized SBA-15 has proven to be suitable for industrial application in the ICCU technology, with great CO_2 sorption capacity and easy operability. Stable and cyclic CO_2 capture and desorption operation has been achieved running the capture step at 40 ºC and promoting desorption at 80 ºC. Under these conditions, the sample PEI50/SBA provides the best results, demonstrating a CO_2 capturing capacity of 6.8% with respect to the mass of the sorbent.

References

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Keywords
ICCU; CO_2 capture; SBA-15; Polyethylenimine; Fixed bed reactor.