



# Reuse and recycling of amine-functionalized silica materials for CO<sub>2</sub> adsorption

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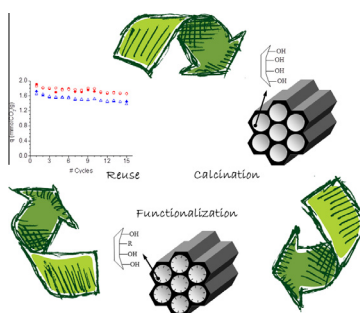
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## HIGHLIGHTS

- CO<sub>2</sub> desorption conditions are optimized for energy-saving purposes.
- Up to 15 reuse cycles are performed in selected “mild” desorption conditions.
- Amine-silica CO<sub>2</sub> adsorbents are recycled by calcination and re-functionalization.
- Recycled PEI samples show no changes in silica structure or amine efficiency.
- Grafted adsorbents display significant changes in both properties.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 22 July 2016

Received in revised form 21 September 2016

Accepted 22 September 2016

Available online 26 September 2016

### Keywords:

CO<sub>2</sub> Capture

Amine-SBA-15

Desorption conditions

Material recycling

## ABSTRACT

The reuse and recycling of amine-silica materials as CO<sub>2</sub> adsorbents were investigated for understanding their industrial viability. CO<sub>2</sub> adsorbents were obtained by grafting of diethylenetriamine (DT) or impregnation of polyethylenimine (PEI) onto SBA-15 silica. CO<sub>2</sub> desorption conditions were evaluated, optimizing the time and temperature to reduce energy costs. In all cases, conditions as mild as 90 °C and 90 min were enough to completely remove all CO<sub>2</sub> adsorbed. After that, a number of adsorption-desorption cycles at 110 °C for DT (60 min) and PEI (75 min) samples were carried out in order to study their cyclability.

The recycling of CO<sub>2</sub> adsorbents after their lifespan was studied by analysing the physicochemical properties and CO<sub>2</sub> uptake of recycled samples obtained by calcination and subsequent re-functionalization with DT or PEI. Materials obtained after grafting the calcined samples exhibited progressively thicker silica walls and lower silanol surface concentration, yielding a smaller amine efficiency during CO<sub>2</sub> capture. On the contrary, materials obtained after impregnating the calcined samples maintained their CO<sub>2</sub> adsorption properties even after 6 cycles, without significant changes in their silica structure or amine efficiency for CO<sub>2</sub> adsorption.

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## 1. Introduction

The dependence on fossil fuels as a source of energy has led to a gradual increase of the atmospheric concentration of carbon diox-

ide in the last decades [1]. The Intergovernmental Panel on Climate Change (IPCC) pointed to anthropogenic CO<sub>2</sub> as a major contributor of global warming and climate change [2], which is now considered a global problem. Thus, the challenge of reducing CO<sub>2</sub> emissions has become a crucial issue for the 21<sup>st</sup> century, leading to the expansion of renewable technologies, energy saving and carbon capture and sequestration (CCS) [3,4].

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Among CCS technologies, those based on absorption with aqueous amine solutions (such as methyldiethanolamine, monoethanolamine and diethanolamine) are currently used on large-scale facilities such as thermal power plants [5,6]. Amines are known to have a considerable reactivity and selectivity towards CO<sub>2</sub> under ambient conditions [7,8], although they entail some problems, such as corrosivity and high energy consumption during regeneration [9,10].

In an attempt to replace liquid absorbents to capture CO<sub>2</sub>, solid porous adsorbents were proposed [11,12] for physisorption, e.g. zeolites [13], activated carbon [14], metal oxides [15–17], and metal–organic frameworks [18]. However, industrial post-combustion conditions (low pressure and high temperature) are the opposite of the optimum conditions for physical adsorption (high pressure and low temperature).

Mesoporous silicas have been largely studied for CO<sub>2</sub> capture. Although the physisorption capacity can be slightly modified by varying the textural parameters [19], competitive values have not been achieved and thus, the immobilization of amines on porous materials has been approached [20–23]. These supports present large surface areas to tether amines, which bind carbon dioxide selectively. Other advantages of amine-containing solid sorbents versus liquid absorbents are (i) the lower energy penalty associated to sorbent regeneration (ii) the lower equipment corrosion, (iii) the higher CO<sub>2</sub> adsorption-desorption rates, and (iv) the lower toxicity of amines anchored to solid supports [24–28].

With the aim of loading supports with active amines, two methods are commonly used: grafting and impregnation. The grafting of amino-silanes in solid supports is based on the reaction between organosilane precursors (namely methoxy and ethoxy ending groups) and surface silanol groups [29]. Diethylene-triamine organosilane (DT) is one of the typically used molecules due to its high amine content (three groups per molecule). On the contrary, wet impregnation, which is not based in chemical reactions, allows the use of any organic molecule regardless its chemical structure. Furthermore, there is no loading limitation related with the availability of silanol groups, so the whole pore volume can be filled up with organic molecules during impregnation. Polyethyleneimine (PEI) is the most common impregnating agent due to its high content of active amino sites and lower volatility compared to other amines [30], leading to a higher thermal stability.

In the last 10 years, numerous research works have been published focusing on the study of amine-modified materials as CO<sub>2</sub> scrubbers, with PEI being the main amine-containing compound used [11,12,31–34]. Firstly, the synthesis of new adsorbents and the maximization of CO<sub>2</sub> uptake were the main goals [11,12] with numerous mesoporous silicas such as MCM-41 [22], MCM-48 [35], HMS [36], MSU [26], SBA-15, and pore-expanded silicas [37–39] being considered. These materials generally exhibit high pore volume, large pore sizes (up to 30 nm) and thick walls (up to 9 nm), with the latter being very important for increasing the stability of the structure [40,41]. Once the important synthesis work was approached, other variables were studied. Some interesting studies were related to amine stability with temperature [42–44], CO<sub>2</sub> adsorption and desorption kinetics [23,37,45], solid state CO<sub>2</sub>-NH reactivity [46,47], and desorption conditions to avoid re-dilution of captured CO<sub>2</sub> [48,49].

For an adsorbent to be widely employed in the industry, it is crucial to consider the reuse and recycling processes. The reutilization of amine-containing CO<sub>2</sub> adsorbents has been studied by performing continuous adsorption-desorption cycles [50,51]. Thus, the lifespan of a given adsorbent is determined by the number of adsorption-desorption cycles that it can work without substantial losses in the CO<sub>2</sub> uptake. However, to the best of our knowledge there are no studies addressing the recycling of spent sorbents. In this study, calcination and re-functionalization of adsorbents is

proposed as a recycling technique for exhaust adsorbents. SBA-15-based adsorbents obtained by grafting with diethylenetriamine (DT) and by impregnation with polyethyleneimine (PEI) were considered, evaluating the reuse and recycling possibilities. In order to simulate an end-of-life treatment, functionalized samples were calcined and functionalized again with DT and PEI, repeating this calcination-functionalization cycle up to 6 times. Physicochemical properties of the silica support as well as CO<sub>2</sub> uptake and amine efficiency of the adsorbents obtained after each calcination-functionalization cycle were studied. Moreover, the desorption process was studied by analysing the influence of the desorption time and temperature on the CO<sub>2</sub> desorption step.

## 2. Materials and methods

### 2.1. SBA-15 synthesis

SBA-15 was synthesized by the hydrothermal method proposed by Zhao et al. [52]. Pluronic P123 (PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub>, M ≈ 5800, Sigma-Aldrich) was used as a structure directing agent and TEOS (tetraethyl orthosilicate, 98%, Sigma-Aldrich) as a silica source. Pluronic P123 was dissolved in a 1.9 M hydrochloric acid solution and the mixture was stirred until complete dissolution. After this step, TEOS was added to the acid mixture and maintained at 40 °C for 20 h. The formation of SBA-15 siliceous structure was completed in a 24 h ageing step at 110 °C. The obtained solid was filtered and then calcined in air at 550 °C to remove the surfactant from the porous structure. This sample was named 1-SBA.

### 2.2. SBA-15 functionalization

1-SBA was functionalized by two different methods: grafting and impregnation. Grafted adsorbents were obtained by subjecting 1-SBA to a reflux process. Firstly, 1 g 1-SBA was dispersed in 250 mL of toluene. After that, 6.88 mmol N-(3-trimethoxysilylpropyl) diethylenetriamine, abbreviated as DT (technical grade, Sigma-Aldrich) was dissolved in the previous mixture and kept under reflux for 24 h.

Mesoporous SBA-15 impregnation was carried out using an organic polymer, polyethyleneimine (PEI, M<sub>w</sub> 800 Da., Sigma-Aldrich). An organic amount of 50 wt.% was achieved in the final material by dissolving 1 g PEI in 8 g methanol firstly. After its complete dissolution, 1 g of 1-SBA was added. The mixture was stirred for 30 min and afterwards the solvent was removed by drying at room temperature.

Chemical structures of PEI and DT are presented in Scheme 1. The ratio of primary, secondary and tertiary amines in 800 M<sub>w</sub> PEI are of 1:1.1:0.7,<sup>1</sup> with approximated percentages being of 36%, 39%, and 25%.

### 2.3. Recycling procedure

Both grafted and impregnated samples were calcined to remove DT and PEI respectively and then re-functionalized to check the reusability of the materials. Up to six calcination-functionalization cycles were performed. A temperature of 550 °C with a heating rate of 1.8 °C/min was used to calcine the materials. Calcined silicas were denoted as N-SBA<sub>g</sub> and N-SBA<sub>i</sub>, while functionalized samples were named N-SBA<sub>g</sub>-DT and N-SBA<sub>i</sub>-PEI. In all cases, N represents the number of calcination cycles applied to a given material (from 1 to 7). Thus, samples 1-SBA<sub>g</sub>-DT and 1-SBA<sub>i</sub>-PEI are both fresh silica functionalized for the first time.

<sup>1</sup> Value provided by Sigma-Aldrich.

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