



Incorporation of monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) in mesoporous silica: An alternative to CO₂ capture



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ABSTRACT

Monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are substances used in the CO₂ capture industrial process. The inconvenience of their use is that these species have low thermal stabilities, are volatile, and in the presence of air undergo oxidation processes to form corrosive products. This work proposed the incorporation of MEA, DEA and MDEA in a mesoporous silica substrate as an alternative for CO₂ adsorption. The mesoporous materials have a high surface area and a large pore size. The high material porosity enabled the incorporation of a large quantity of ethanolamine. The presence of MEA inside the silica pores promoted the acceleration of the decomposition process. The materials prepared using a mixture of mesoporous silica and DEA and MDEA had an optimal CO₂ capture efficiency than the isolated ethanolamines. This increased CO₂ capture efficiency was most significant in the sample prepared using MDEA. The increase of CO₂ efficiency capture by the incorporated material was 30% higher compared with free MDEA. DEA and MDEA incorporated in mesoporous silica had a higher CO₂ capture efficiency in the second and third adsorption cycles than free DEA and MDEA. The study showed that the incorporation of DEA and/or MDEA in mesoporous silica may increase CO₂ capture efficiency.

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1. Introduction

The increase of CO₂ concentration is the principal reason for global climate change. Aiming to reduce the atmospheric CO₂ concentration, some materials capable of CO₂ absorption/adsorption have been developed. Liquid ethanolamine solutions, principally monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA), are utilized to capture CO₂ in industrial processes. The CO₂ capture occurs by passing gaseous fluid through the ethanolamine solution, producing carbamates and/or bicarbonates [1].

While ethanolamines have a high capacity for CO₂ capture, they are volatile substances that are easily oxidized. The oxidation of ethanolamines can produce carboxylic acids, ammonia and other corrosive substances. The regeneration of the solutions involves high energy consumption and there is the inconvenience of the work using liquid substances [1–4].

The presence of oxygen in a gaseous fluid can promote the degradation of ethanolamines, producing ammonia and a mixture of organic compounds such as organic acids and aldehydes, especially acetic acid and formic acid. This is an irreversible process, so it is necessary to replace the starting material [5].

The efficiency of CO₂ capture is inversely related to the thermal stability. Steric impediment inhibits the reaction between the ethanolamine and CO₂. Thus, although MEA is less stable than the other ethanolamines, it has the greater CO₂ capture efficiency. The thermal decomposition of DEA involves an intramolecular reaction

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that produces MEA and ethylene oxide. The presence of the methyl radical increases the thermal stability of MDEA, due to steric impediment [6].

Due to the low thermal stability of ethanolamines, it is necessary to develop solids that are CO₂ adsorbent in order to obtain a stable material that is efficient at CO₂ capture. Porous solid materials can be used as adsorbent surfaces, catalysts, catalytic supports, pharmaceutical excipients, and chromatographic support, among others. These applications are possible because these materials have a large pore size, high surface area and ordered pore distribution. According to the IUPAC definition, porous materials are divided into three classes based on the pore diameter [7–10]: microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm).

The incorporation of ethanolamines in microporous materials has already been studied. The presence of Al in the zeolite structure increases the polarity of the material, then; the interaction between the material structure and water molecules is more intense in this kind of solids. However, because of their highly hydrophilic character, the flue gas needs extensive drying prior to CO₂ capture. The other inconvenient about the incorporation of ethanolamine in microporous materials is the limitation of pore sizes (<2 nm) [1,11].

In addition to low cost, ideally an adsorption medium for CO₂ removal and recovery at ambient temperature and high pressure should combine high CO₂ uptake, complete regeneration under mild condition, high thermal stability, favourable adsorption–desorption kinetics and selective CO₂ adsorption. Current research activity on CO₂ capture processes focused on oxides and mixed oxides, high surface area porous materials such zeolites, carbon, metal organic frameworks (MOFs), organo-silica and surface-modified silica [11–17]. It is however intriguing that despite the significant growth in the area of periodic mesoporous materials since their discovery there are only few studies devoted to CO₂ adsorption on plain mesoporous silica such as SBA-15.

Surface grafting method makes the interaction between supported materials and functional groups much stronger and stable so that the adsorbents can be operated at relatively high temperature. A series of mesoporous materials grafted with aminosilanes were prepared to enhance CO₂ adsorption performance [18]. The synthesis of grafting materials is more sophisticated and involve high cost. The amine impregnated in mesoporous materials can be a more interesting alternative because it is not necessary the amine functionalization in the silica structure. The large pore sizes of the mesoporous material allow the incorporation of a large quantity of ethanolamine. Moreover, the encapsulation of these substances inside the silica pores can increase their thermal and chemical stability.

The incorporation of MEA, DEA and/or MDEA in mesoporous materials may provide an interesting and new alternative to CO₂ capture, as demonstrated in this work. The pore size, pore volume and surface area of supported materials were observed to play an important role in the CO₂ capture process. Due to the high pore volume and the large pore size, it is possible to incorporate a large quantity of ethanolamine in the solid materials, which may in turn increase the thermal stability of ethanolamines.

This study proposed the incorporation of MEA, DEA and MDEA in a SBA-15 silica, which has a 2D configuration and a hexagonal pore structure that is synthesized using the triblock copolymer Pluronic® P123 as a template [19]. SBA-15 presents a unique structure with its hexagonally ordered mesoporous structure connected by irregular micropores [20]. A thermal analytic study of the materials produced by the incorporation of ethanolamine in the SBA-15 silica was conducted and the efficiency of these materials for the CO₂ capture process was tested.

2. Materials and methods

2.1. Adsorbent synthesis

2.1.1. SBA-15 synthesis

SBA-15 silica was prepared based on established techniques [19] with a minor modification; it was synthesized with triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (EO₂₀–PO₇₀–EO₂₀, Pluronic P123; BASF) copolymer as a structure directing agent (template) and tetraethyl orthosilicate (TEOS; Aldrich, USA) as a silica source. TEOS was added dropwise into the homogeneous solution. The mixture was maintained in a Teflon bottle and it was subjected to hydrothermal treatment at 100 °C for 48 h. The solid product (SBA-15) was filtered, washed with distilled water and air-dried at room temperature. SBA-15 was heated in a tube furnace under air by slowly increasing the temperature at 1 °C min⁻¹ from room temperature to a target temperature of 550 °C under a nitrogen atmosphere and calcined at the target temperature for 6 h under an air atmosphere. The template, Pluronic P123, has surfactant properties. The following stoichiometric molar ratios for the SBA-15 synthesis were used: 1.0 TEOS: 0.0167 Pluronic P123: 5.82 HCl: 190 H₂O.

Two major routes for the formation of silica-based ordered mesoporous materials have been described in the literature. According to the first route, the surfactant molecules organize independently of the inorganic species into a liquid crystal phase; the silicate ions condense and polymerize around the pre-formed structure. The second one is the cooperative templating mechanism and, in this case, the building blocks are the micelles; so the cooperative templating mechanism occurs at low surfactant concentrations. In such a mechanism, the interactions between the surfactant and the inorganic precursor are responsible for the mesoporous materials formation. The synthesis can be achieved through either an electrostatic pathway, based on a supramolecular assembly of charged surfactants with charged inorganic precursors or a neutral pathway (S⁰ H⁺ – X⁻ I⁺), in which hydrogen bonding is responsible for the cohesiveness between the surfactant and the inorganic precursor [21–23]. Therefore, the interaction between Pluronic P123 and the acid specie are important during the mesoporous silica formation. The ionic force of the solution influences the mesoporous structure, so the acid concentration and the anionic species are important to form the material structure [24].

2.1.2. Ethanolamine incorporation in SBA-15 silica

The MEA and DEA studied samples were donated by Oxiteno S. A., and the MDEA sample was donated by Dow of Brazil S.A. Mixtures of SBA-15/MEA, SBA-15/DEA and SBA-15/MDEA were prepared with different mass ratios, starting at a 1:1 mass proportion until the addition of a large amount of ethanolamine was possible while conserving the material in a solid state. Mixtures made using MEA were made between 1:1 and 1:3 mass proportions; mixtures made using DEA were made between 1:1 and 1:4 mass proportions; mixtures with MDEA were made only at 1:1 and 1:2 mass proportions. The ethanolamine incorporation was performed by adding MEA, DEA or MDEA to a SBA-15 and acetone suspension. The amount of acetone used was sufficient to dissolve the ethanolamine. The mixture was prepared by magnetic stirring until the formation of a pasty material, and then dried in a desiccator under reduced pressure.

2.2. Characterization

The morphology of the samples was studied with a scanning electron microscope (SEM) (Quanta 600 FEI) and the pore

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