



# CO<sub>2</sub> capture by functionalized alumina sorbents: DiEthanolAmine on $\gamma$ -alumina



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## ABSTRACT

Alumina-based mesoporous solid sorbents have been successfully prepared in high amount, directly from commercial pellets functionalized with diethanolamine (DEA). The effectiveness of the deposition procedure is confirmed by the detection of diagnostic IR bands characterizing the DEA organic molecule, whose intensity is increasing almost linearly at increasing DEA contents. These materials have shown interesting results in CO<sub>2</sub> adsorption both in dry and humid conditions (from 12 to 28 mg<sub>CO<sub>2</sub>ads</sub>/g), very good resistance to water vapour in the feed and a remarkable regeneration capacity in very mild conditions. Increasing the DEA loading from 15% to 36 wt% resulted in superior capture capacity and useful adsorption time, although the correlation found between DEA content and adsorbed CO<sub>2</sub> is less than linear, likely due to a strong interaction between the DEA and the support. Mechanistic spectroscopic IR studies in static conditions point out that CO<sub>2</sub> chemisorbs on the amine sites, mainly in form of carbamate species, whose formation should be favoured by the high degree of the surface hydroxylation. On the other side, urea formation is also likely, mainly over samples having the highest DEA content.

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## 1. Introduction

Currently, separation and removal of CO<sub>2</sub> from gas streams is achieved by techniques based on physical and chemical processes such as absorption by liquid solution systems, adsorption onto solid systems, cryogenic separation, and permeation through membranes [1–3]. Among various CO<sub>2</sub> separation techniques, amine solution-based CO<sub>2</sub> absorption/desorption systems are one of the most suitable for capturing CO<sub>2</sub> from high volumetric flow rate gas streams. Commonly used solvents in such systems are aqueous solutions of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA). Certain sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP), can also be used as absorbents. Among these, MEA is most widely used because of its low cost and high CO<sub>2</sub> absorption rate, which allows to use shorter absorption columns. However, these systems present major drawbacks, including the large amount of heat required to regenerate the solvent and operational problems caused by the presence of particulate, corrosion (due to acidic CO<sub>2</sub> dissolution) and chemical degradation of amine sorbent (i.e. polymerization, oxidation,

interaction with other contaminants such as SO<sub>x</sub> and NO<sub>x</sub>). Moreover, secondary and hindered amines (e.g. DEA, DIPA, AMP) provide more moderate CO<sub>2</sub> absorption rates than MEA.

The CO<sub>2</sub> can also be captured by adsorption on solid sorbents. Solids such as silica gel, alumina, zeolites are typically used as a physical adsorbent for separation of CO<sub>2</sub> [1,4]. Activated carbons are also interesting materials for this application, due to their very high surface area, large distribution of pore size, low cost, resistance to water and no need for the activation before adsorption [1]. However, the adsorption capacities of these adsorbents decline rapidly with increasing temperature.

As these considerations show, there is a need for an improved CO<sub>2</sub> sorption system which should be efficient, economical, readily available and regenerative, and should provide a high removal capacity at relatively high temperature. The gas–solid chemisorption is considered to be one of the most promising technologies for capturing CO<sub>2</sub> from flue gases because it could allow an energy consumption reduction; as a matter of fact, both heat capacity and regeneration temperature of the solid sorbent would be lower in comparison to amine-solution absorption. Further, because the amine is anchored on the surface material and not dissolved into the water, absence of corrosion phenomena is expected.

A possible solution, recently proposed and evaluated, is the functionalization with amines of solid supports, mainly porous

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oxides such as high-area alumina or silica, to improve some characteristics of gas sorbents in the solid phase [5–7]. Metal organic framework compounds (MOFs) and active carbons have also been tested for this application. These materials can be obtained by grafting or impregnation processes and show interesting CO<sub>2</sub> adsorption capacity [7–9]. However, the grafting procedure can result complex, expensive, owing to reagents cost, and with very low yield and presents difficulties due to the grafted amines thermal stability.

Considering the above reported considerations, the objective of this work has been to develop a sorbent based on solid substrate supporting amines to employ for the post-combustion CO<sub>2</sub> capture, where the treatment of high flow rates at atmospheric pressure and with low CO<sub>2</sub> concentration is required.

We prepared, through low cost and simple methodologies, relatively large amounts of sorbents with suitable properties for a TSA application in fixed bed. For this purpose, diethanolamine (DEA) has been deposited by impregnation at increased loadings on an alumina commercial support in pellets shape, with high specific surface area and porosity. The samples obtained have been thoroughly characterized and tested to determine CO<sub>2</sub> adsorption capacity and regeneration ability.

## 2. Experimental

### 2.1. Adsorbents preparation

Commercial alumina support SA6176 (SA in the following) was provided by Saint Gobain NorPro (Ohio, USA). It consists of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in shape of cylindrical pellets, 3 × 3 mm dimensions, 9.8 nm average pore diameter, 234 m<sup>2</sup>/g surface area.

Sorbents with the following amine loadings were prepared: 15, 25 and 36 wt%, named in the following as 15DEA-SA, 25DEA-SA and 36DEA-SA. The typical preparation procedure for these sorbents is as follows. 120 g of as received alumina support pellets was contacted with 250 ml of methyl alcohol within a 1 l round bottom flask, in order to remove any residual impurities on the surface before the amine impregnation. This mixture was stirred for about 30 min. The excess methanol from the previous step was decanted and about 200 ml of methanol was added to the wetted support. The mixture was further stirred for 30 min and then again decanted. The wet SA pellets were thoroughly dried within a rotating vacuum flask evaporator which was partially submerged in a water bath maintained at 90 °C.

A support coating solution was prepared by adding 56, 40 or 23 g, respectively for the samples with 36, 25 or 15% of diethanolamine (DEA in the following), of as received DEA (Aldrich, purity ≥99.0%) and 10 g of distilled water to 200 ml of methanol. The above prepared solution was added to 100–130 g of the dried SA support, as indicated in Table S1 (Supplementary data). This mixture was stirred within a rotating flask at about 50 °C for 1 h. The mixture was dried within the constant temperature water bath maintained at 50 °C and with the rotating flask evaporator at vacuum until the bulk of the methanol was removed. The temperature of the bath was then raised to 90 °C while maintaining a vacuum within the rotating flask evaporator. The elevated temperature facilitates the removal of methanol and water from the coated support while contributing to the bonding of the diethanolamine coating to the support.

### 2.2. Physicochemical characterization

FT IR studies of the fresh (as prepared) samples have been performed following two experimental procedures.

- (a) Skeletal FT IR studies: the samples have been finely ground and diluted (1% w/w) in KBr matrix, then pressed in self supporting disks in order to record the skeletal IR spectrum in air.
- (b) Pure powders FT IR studies and static adsorption experiments (transmission technique): the pure powders have been pressed in self supporting disks (average weight 20 mg) and placed in the IR cell connected to a gas manipulation apparatus. The powders have been outgassed (10<sup>-2</sup> Torr) at room temperature and at 80 °C, in order to desorb water and weakly held contaminants before any adsorption experiments. CO<sub>2</sub> adsorption has been carried out at room temperature at decreasing CO<sub>2</sub> partial pressure (15 Torr and 1 Torr) and after outgassing. All the spectra have been recorded using a Thermoquest Nexus 750 FT IR instrument, operating with OMNIC™ acquisition software (100 scans, DTGS detector, KBr beamsplitter).

Surface areas were calculated applying the multipoint BET method and pore volume and pore diameters were calculated by the BJH method. The samples have been outgassed prior to these measurements at 343 K overnight.

Scanning electron microscopy (SEM) and EDS analysis were also used to obtain magnified images and elemental chemical analysis of 36DEA sample (Zeiss, Supra 40).

### 2.3. Adsorption tests

The CO<sub>2</sub> adsorption capacity of the three prepared samples was studied by means of repeated alternated adsorption/desorption cycles, up to 4 cycles, in alternated dry and humid conditions.

The absorption/desorption cycles were carried out in a fixed-bed stainless steel tubular unit (length 400 mm, I.D. 60 mm) operating in continuous flow mode and equipped with a porous metallic disk supporting the sorbent bed. The unit was uniformly heated by a water jacket connected to a circulating bath with temperature control. The reactor was loaded with 135 g of sorbent. The adsorbent bed temperature was measured with a type K thermocouple placed in the middle of the sorbent bed.

During the adsorption phase the reactor was fed with 60 NI/h of a mixture with the following composition: 10% v/v CO<sub>2</sub>, 3% O<sub>2</sub>, 10% H<sub>2</sub>O, N<sub>2</sub> at balance (wet conditions). Adsorption tests were performed also in dry conditions, maintaining the same gas composition except for the absence of water and the increase of nitrogen content (at balance). The desired temperature and pressure values were 40 °C and 1 atm, respectively. The gas stream was humidified using a thermostated saturator. The inlet and the outlet unit gas composition was measured by continuous analyzers specifically designed for CO<sub>2</sub>, NO (Siemens, ULTRAMAT 5E) and SO<sub>2</sub> (ABB, Optima Advance Uras 14). The adsorption step was stopped when the CO<sub>2</sub> concentration at the outlet of the reactor raises above a threshold  $\alpha$ . Tests parameters (temperature, sorbent particle dimensions, CO<sub>2</sub> concentration, flow rate) were chosen as the most representative of the real process conditions.

To restore the adsorption capacity after each adsorption cycle, the sorbent was submitted to a regeneration cycle. Regeneration was performed by stripping the reactor with 60 NI/h of N<sub>2</sub> while increasing the temperature up to 85 °C and 1 atm. The cycle was stopped when the CO<sub>2</sub> concentration released by the sorbent and measured at the outlet of the reactor goes approximately to zero. CO<sub>2</sub> stripping in N<sub>2</sub> flow allowed us to follow by continuous analyser the overall CO<sub>2</sub> desorption process to verify the sorbent complete regenerability and to compare the total amount of CO<sub>2</sub> evolved with the CO<sub>2</sub> adsorbed in the lab-scale tests.

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