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Post-combustion CO₂ capture: On the potentiality of amino acid ionic liquid as modifying agent of mesoporous solids



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ABSTRACT

In this paper, mesoporous γ -Al₂O₃ was impregnated with [Emim][Gly] ionic liquid (IL) at different loadings (5, 9 and 16% wt). The obtained sorbents were tested for CO₂ capture under typical conditions of combustion flue-gas at temperatures varying in the range 303–373 K. N₂ porosimetric analysis on the samples, coupled with kinetic tests of CO₂ adsorption, revealed that a lower pore volume occurring at the highest IL loading ended up in a slower saturation process. The enhancement of CO₂ capture capacity of the raw sorbent was monotonic with the IL loading and the best results were achieved at 303 K. The chemisorption nature of the adsorption process for IL-containing sorbents was assessed by means of FT-IR analysis. Finally, preliminary tests of cyclic adsorption/desorption showed that nearly 80% of the original CO₂ capture capacity of sorbent was restored by steam desorption at 388 K.

1. Introduction

The development of high-efficiency and cost-effective purification processes for the removal of CO₂ from flue-gas deriving from fossil-fueled power plants represents one of the most stimulating scientific and technological challenges of the third millennium to face the global climate change [1,2]. Different post-combustion technologies for the selective CO₂ capture – including chemical absorption into aqueous amines/ammonia/K₂CO₃ solutions, membrane separation, cryogenic distillation, microalgae biofixation and adsorption – have been investigated in literature, as they can be easily retrofitted to depuration trains already existing for the emissions control of other pollutants (such as particulate matter, Hg, NO_x and SO_x) [3–7]. Adsorption offers different potential advantages over other depuration methods such as high efficiency and versatility, generally low maintenance costs and easy handling [8–10]. CO₂ adsorption from flue-gas can be achieved by means of both physisorbents (e.g. activated carbons, zeolites, metal organic frameworks and ordered mesoporous silicas) and chemically reactive solids (f.i. metal oxides, alkali metal carbonates and amine-functionalised sorbents) [7,11–14]. In particular, the use of monomeric or polymeric amines either impregnated or covalently tethered onto a

porous support has been widely proposed for CO₂ removal at temperatures generally lower than 373 K, because these functionalised sorbents potentially allow reducing the high energy duty associated with the regeneration step of aqueous amine solutions and to prevent equipment corrosion problems [2,5,7,9]. On the other hand, while amine-impregnated sorbents have shown to suffer from thermal degradation during regeneration and leaching under humid conditions, amine-grafted materials exhibit higher thermal/mechanical stability but the amine loading is limited by the number of functional groups on substrate surface required to anchor the amine-containing compound [8,9,12]. In this framework, the use of reactive ionic liquids (ILs) (such as amino-, amino acid-, azolate- and phenolate-based ILs), also supported onto porous solids, is a promising option for post-combustion CO₂ capture to circumvent the cited drawbacks of conventional amine-based sorbents [15–22]. In fact, ILs reactivity towards CO₂ can be finely tuned by incorporating active chemisorption sites in the anion and/or cation structures and ILs are characterised by excellent thermal stability [15,23,24]. Moreover, the IL confinement within a porous matrix can provide additional benefits for their application, including a more effective exploitation of their CO₂ capture capacity due to reduced diffusion limitations when compared to their unsupported counterpart,

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often characterised by high viscosity [21,25]. In turn, this allows reducing the high utilisation costs of ionic liquids.

Generally, few studies are retrievable in the pertinent literature concerning CO₂ adsorption on supported ionic liquid phase (SILP) materials under low CO₂ concentrations (typically lower than 15% vol. as in flue-gas streams) and on the effect of the operating temperature on sorbent capture performance [16,19,25]. Recently, this research group investigated the application of the amino acid IL 1-ethyl-3-methylimidazolium glycinate [Emim][Gly] supported onto highly microporous activated carbons for CO₂ adsorption under conditions mimicking a combustion flue-gas [16]. Data highlighted a worsening of the capture capacity at 303 K with respect to the raw sorbents related to pore blocking upon IL impregnation. On contrary, [Emim][Gly] was effective in ameliorating the CO₂ adsorption performances of raw carbons at 353 K, due to a prevailing contribution of CO₂ chemisorption offered by IL over support physisorption. Following the path drawn by the authors in the previously published article, this work aims at providing a deeper understanding of the effect of confining [Emim][Gly] IL into a porous support – i.e. mesoporous alumina – on CO₂ capture performances under typical conditions of combustion flue-gas (e.g. CO₂ concentration equal to 15% vol.). On the basis of our previous observations, this mesoporous substrate was selected to reduce pore clogging effects induced by the IL insertion in the porous matrix. More specifically, a ready-to-use commercial γ -Al₂O₃ was chosen as it is characterised by a good compromise between a satisfying value of surface area to disperse the IL and an adequate width of pores, so to avoid undesired pore occlusions and, simultaneously, diffusion limitations during the CO₂ capture process. The relationships among IL loading, sorbent textural properties, role of IL in the CO₂ capture process and dynamic capture performances were assessed by coupling N₂ porosimetry, thermogravimetric analysis, infrared spectroscopy and adsorption tests performed at different temperatures (in the range 303–373 K) in a fixed-bed column. Preliminary tests of cyclic capture adopting steam as CO₂ desorbing agent were carried out. To the best of our knowledge, the use of steam for the regeneration of SILP sorbents has not been reported so far: this represents a more realistic operating mode for the recovery of CO₂ in concentrated form for geological storage or chemical utilisation purposes.

2. Experimental

2.1. Sorbents preparation and characterisation

Mesoporous γ -Al₂O₃ supplied by Sasol (1 mm diameter spheres, sample termed Al-raw) was used as substrate for the functionalisation with [Emim][Gly] IL (Sigma Aldrich) whose molecular structure is reported in Fig. 1. The impregnation of the substrate was carried out by contacting the raw alumina with IL in ethanol solution (liquid to solid ratio = 10 L kg⁻¹) at different initial concentrations of IL ($C^0 = 0.042, 0.077$ and 0.135 mol L⁻¹) in a batch stirred system for 24 h. After IL deposition onto the substrate, the liquid solution was separated from the solid in a rotary evaporator (Heidolph Rotary Evaporator, Laborota 4000) at 363 K for 4 h. The residual solvent removal was attained in two steps: a preliminary treatment in oven under vacuum at 333 K for 24 h and, finally, by fluxing N₂ at 353 K for 30 min in a fixed-bed column loaded with sorbent particles.

Thermogravimetric (TG) measurements on bulk [Emim][Gly], raw and functionalised sorbents were performed using a Perkin Elmer STA 6000 instrument operated in the temperature range 298–1143 K under N₂ flux (gas flow rate = 3.3×10^{-4} L s⁻¹) at 0.167 K s⁻¹ scan rate. A

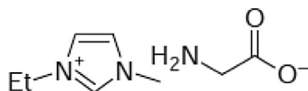


Fig. 1. Molecular structure of [Emim][Gly] ionic liquid.

comparison of mass losses for each impregnated sorbent with respect to the bare alumina for $T > 443$ K – corresponding to the onset of thermal decomposition of [Emim][Gly], as determined from the thermogram of the pure IL – allowed a quantitative estimation of the IL loading effectively dispersed onto the support, according to the following expression:

$$\gamma_{IL} = \frac{(\Delta wt\%_{impr} - \Delta wt\%_{raw})}{100 MW_{IL}} \quad (1)$$

in which γ_{IL} [mol kg⁻¹] is the specific molar amount of IL dispersed on the support at each concentration of active phase, $\Delta wt\%_{impr}$ and $\Delta wt\%_{raw}$ [–] represent the mass percentage losses at $T > 443$ K of the impregnated and raw materials, respectively. Finally MW_{IL} [kg mol⁻¹] is the [Emim][Gly] molecular weight (0.185 kg mol⁻¹). The functionalised sorbents were labelled – according to the IL load onto the support – as Al-[Emim][Gly]5%, Al-[Emim][Gly]9% and Al-[Emim][Gly]16% for IL weight percentages equal to 5, 9 and 16%, respectively (as derived from TG analysis).

The sorbents textural properties were determined by N₂ adsorption/desorption at 77 K with a Sorptomatic 1990 apparatus. In particular, the BET method was adopted for the evaluation of the specific surface area while the pore size distribution (PSD) was obtained via BJH desorption method [26]. Fourier transform infrared analysis (FT-IR) was carried out to provide a deeper insight on the role of the IL in the CO₂ capture process. FT-IR spectra for Al-[Emim][Gly]16% raw and saturated with a 15% vol. CO₂ (in N₂) stream at initial adsorption temperature of 303 K were measured using a FT-IR 430 Jasco spectrometer by KBr pellet method. The FT-IR analysis of the pure ionic liquid was obtained with a FT-IR Nicolet Avatar 360 instrument by forming a thin IL film between two KBr plates. Both FT-IR apparatuses were operated in the 500–4000 cm⁻¹ wavenumber range.

2.2. Adsorption/regeneration tests of CO₂ in fixed-bed

A complete description of the lab-scale apparatus used for adsorption tests was previously reported in Balsamo et al. [27]. Briefly, it consists of a fixed-bed column fed with CO₂ in a N₂ gas mixture obtained by dosing each gas component via mass flow controllers (series El Flow Bronkhorst 201-CV). Dynamic measurements of CO₂ concentration were carried out by an infrared gas analyser (ABB NDIR AO2020 Uras 26). The temperature in the fixed-bed was controlled by electrical heaters coupled with PID controllers (Watlow). The plant was purposely integrated with a steam generation section for the execution of regeneration runs. Steam was produced by feeding liquid water, whose flow rate was adjusted with a peristaltic pump Gilson Minipuls 3, to a thermostatically-controlled hollow cylinder made of stainless steel. The heating system of the vaporisation chamber was composed of a 500 W rope heater thermally insulated with stone wool, and connected to a PID controller (Omega Engineering) equipped with a J-type thermocouple. Prior to CO₂ concentration measurements during desorption, water was removed at the fixed-bed column outlet by means of a trap filled with P₂O₅ (Sicapent, supplied by Merck).

Adsorption tests were performed by feeding the column, loaded with 3.5 g of sorbent, with a 15% vol. CO₂ in N₂ stream representative of a model combustion flue-gas (total flow rate equal to 8.33×10^{-3} NL s⁻¹). CO₂ capture runs were carried out at atmospheric pressure and initial temperatures $T^0 = 303, 323, 353$ and 373 K. It is here underlined that the indication of initial adsorption temperature is related to thermal effects (i.e. temperature rise) observed during the capture process with functionalised sorbents.

A material balance on CO₂ over the fixed-bed column allowed obtaining the specific adsorption capacity for sorbent at saturation ω^{sat} [mol kg⁻¹]:

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