

# ALUMINA-SUPPORTED [EMIM][GLY] IONIC LIQUID FOR CO<sub>2</sub> CAPTURE FROM MODEL FLUE-GAS

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## Abstract

In this paper, we report on CO<sub>2</sub> capture results under model flue-gas conditions for a commercial γ-Al<sub>2</sub>O<sub>3</sub> functionalized with [Emim][Gly] ionic liquid (IL) at 5 and 9% wt. loadings. N<sub>2</sub> pore size analysis for the selected sorbents demonstrated that the adopted impregnation protocol was effective in producing a uniform distribution of the IL into the substrate pores. CO<sub>2</sub> dynamic adsorption runs at 303 and 353 K revealed that an increase in the operating temperature determines longer breakpoint times and slower saturation kinetics for the functionalized sorbents. Both functionalized sorbents displayed an enhanced CO<sub>2</sub> capture capacity with respect to the parent sorbent, mainly at 353 K and at larger IL loading (up to a threefold increase in the best case), likely for a greater availability of reactive centers deriving from a reduction of the active phase viscosity at higher temperature.

## Introduction

The reduction of CO<sub>2</sub> emissions, mainly deriving from the power sector, is nowadays considered as mandatory to mitigate global warming [1]. Post-combustion purification systems for CO<sub>2</sub> removal from flue-gas have the greatest near-term potential to mitigate CO<sub>2</sub> environmental impacts, as they can be retrofitted to existing power stations [2]. The use of ionic liquids (IL) as alternative solvents for post-combustion CO<sub>2</sub> capture has potential advantages over the benchmark technology based on carbon dioxide chemical scrubbing in aqueous monoethanolamine solutions, thanks to the high thermo-chemical stability and easy-to-tune chemico-physical properties of IL [3]. Recent works are developing adsorbent materials for CO<sub>2</sub> capture based on IL supported onto porous substrates (supported IL phase, SILP), to overcome the main limits in the IL practical use represented by a high market cost and generally high viscosities [4–7]. Despite the great potentiality of SILP sorbents for the development of high-efficiency CO<sub>2</sub> separation processes, there is still limited knowledge about the effect of dispersing

IL into porous solids on their CO<sub>2</sub> capture performances, under typical flue-gas conditions. This work investigates the CO<sub>2</sub> adsorption properties of a commercial alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) functionalized with 1-ethyl-3-methylimidazolium glycine [Emim][Gly] IL, at two different active phase loadings. Continuous CO<sub>2</sub> adsorption tests on model flue-gas streams were performed at 303 and 353 K in a fixed-bed adsorber.

## Experimental

*Preparation and characterization of [Emim][Gly]-impregnated alumina.* Commercial mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supplied by Sasol (1 mm diameter spheres, sample termed A-raw) was adopted as substrate for the functionalization with [Emim][Gly] IL (Sigma Aldrich). The impregnation of the adsorbent was performed as follows: A-raw was contacted in a batch stirred system with the IL in ethanol solution (liquid to solid ratio=7.2 L kg<sup>-1</sup>) at two different active phase initial concentrations ( $C^0=1.08\times10^{-2}$  and  $2.01\times10^{-2}$  kg L<sup>-1</sup>) for 24 h. Afterward, the liquid solution was separated from the solid in a rotary evaporator (Heidolph Rotary Evaporator, Laborota 4000), at 343 K and for 30 min. Residual solvent evaporation was achieved in an oven under vacuum at 323 K for 24 h. The functionalized sorbents were labelled according to the IL loading onto the support as A-[Emim][Gly]5% and A-[Emim][Gly]9% for IL weight percentages equal to 5 and 9%, respectively (as obtained from thermogravimetric analysis). Thermogravimetric (TG) measurements allowed the determination of the specific amount of IL loaded on alumina at each impregnation condition, post-processing sorbent mass loss data. TG tests were performed using a Perkin Elmer STA 6000 instrument operated in the temperature range 298–1143 K under N<sub>2</sub> atmosphere (gas flow rate= $3.3\times10^{-4}$  L s<sup>-1</sup>) at  $1.67\times10^{-1}$  K s<sup>-1</sup> scan rate. The N<sub>2</sub>-based pore size analysis for both raw and IL-impregnated alumina was carried out at 77 K in a Sorptomatic 1990 apparatus.

*CO<sub>2</sub> adsorption experiments.* Adsorption tests on either raw or [Emim][Gly]-functionalized alumina were carried out in a fixed-bed column (length=12 cm; inner diameter=1.4 cm) integrated in a lab-scale plant [6]. The fixed-bed temperature was controlled by means of a heating system, arranged coaxially with the adsorber column: it consists of three 500 W cylindrical shell band heaters (Watlow), enveloped in a thermal insulating layer of ceramic fibres. Two mass flow controllers (series El Flow Bronkhorst 201-CV) were used to control the feed gas composition (N<sub>2</sub>+CO<sub>2</sub>). CO<sub>2</sub> concentration was monitored by a continuous NDIR gas analyser (AO2020 Uras 26 model provided by ABB). Experimental runs were performed by feeding the column, charged with 14 g of either sorbent, with a 15% vol. CO<sub>2</sub> (balance N<sub>2</sub>) gas stream (total flow rate equal to  $8.33\times10^{-3}$  L s<sup>-1</sup>). CO<sub>2</sub> adsorption tests were carried out at 303 and 353 K (1 atm total gas pressure). CO<sub>2</sub> dynamic capture data were processed to evaluate the saturation adsorption capacity of each solid ( $\omega^s$ , mol kg<sup>-1</sup>), via a material balance on CO<sub>2</sub> over the fixed-

bed unit.

### Results and discussion

*Adsorbents properties.* Table 1 lists the main textural parameters derived from N<sub>2</sub> adsorption tests at 77 K carried out on all the adsorbents, and expressed in terms of specific surface area ( $S_{BET}$ ), total pore volume ( $V_p$ ) and mean pore diameter ( $d_p$ ). The values of IL specific molar amount loaded on the support at each impregnation condition (mmol<sub>IL</sub> g<sup>-1</sup>) as computed through TG analysis are reported as well.

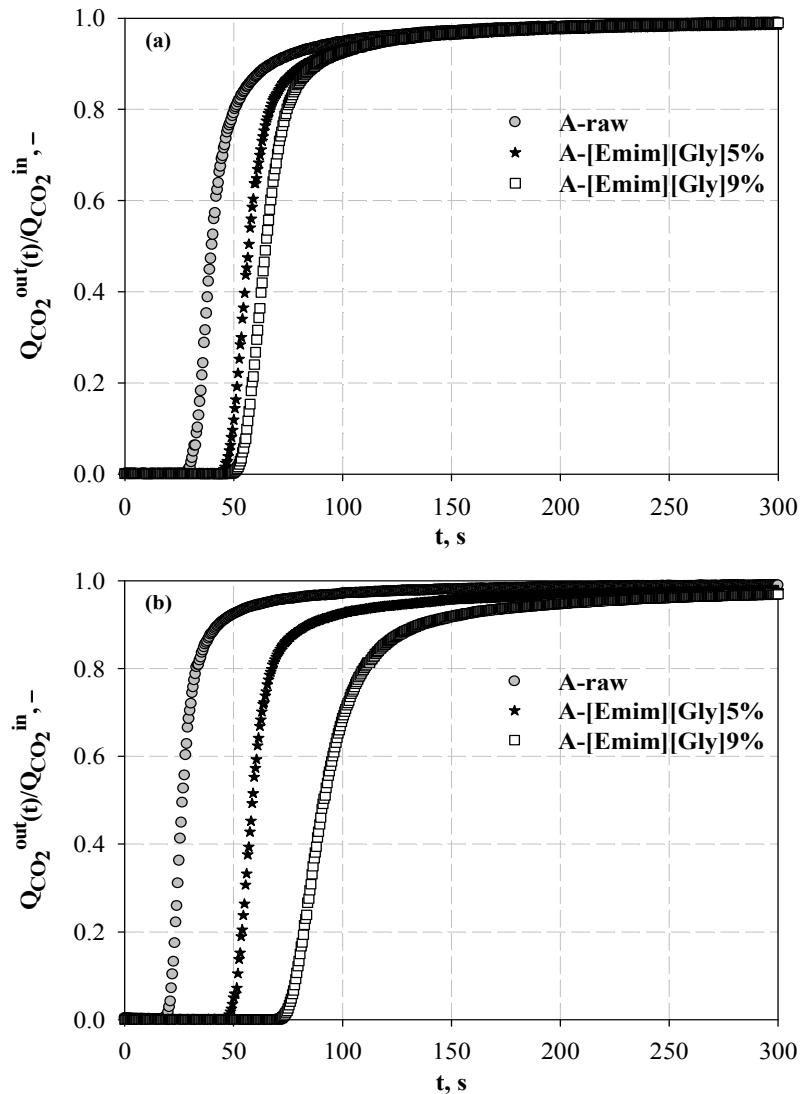
**Table 1.** Main parameters derived from N<sub>2</sub> pore size and TG analyses.

	$S_{BET}$ , m <sup>2</sup> g <sup>-1</sup>	$V_p$ , cm <sup>3</sup> g <sup>-1</sup>	$d_p$ , nm	mmol <sub>IL</sub> g <sup>-1</sup> (TG)
A-raw	166	0.47	10.0	—
A-[Emim][Gly]5%	140	0.40	10.5	0.28
A-[Emim][Gly]9%	104	0.33	11.5	0.50

Data highlight that both pore volume and surface area of the raw alumina decrease with the IL content on the sample ( $V_p$  diminishes almost linearly), due to a partial pore clogging. On the other hand, the functionalization treatment does not significantly modify the pore size distribution of the parent substrate, as confirmed by very similar figures of the mean pore diameter obtained for the different adsorbents. A slight increase in  $d_p$  observed, in particular, for A-[Emim][Gly]9% with respect to A-raw can be ascribed to a greater occlusion of smaller-size pores induced by the active phase. Finally, pore size results testify the effectiveness of the adopted impregnation protocol in determining a homogeneous distribution of the ionic liquid onto the pore surface of the substrate.

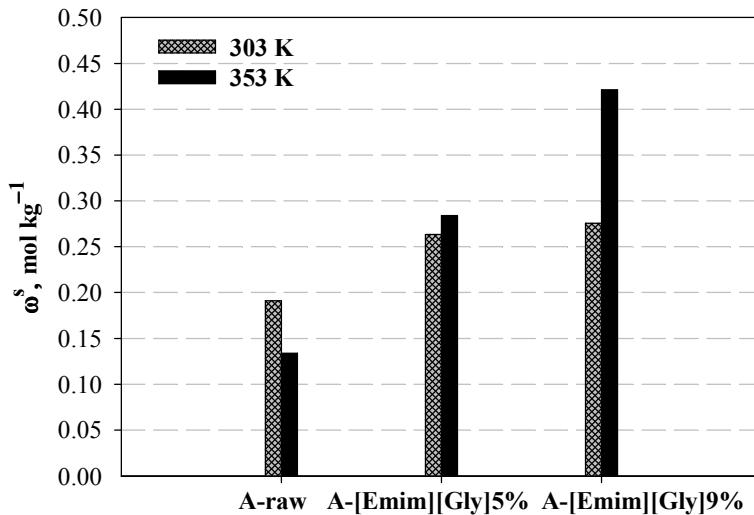
*Adsorbents CO<sub>2</sub> capture performances.* Figure 1 shows the breakthrough curves obtained for the selected adsorbents tested at  $T=303$  and 353 K, and for a 15/85% vol. CO<sub>2</sub>/N<sub>2</sub> gas mixture fed to the adsorption column. The CO<sub>2</sub> dynamic adsorption patterns are expressed in terms of the ratio of the volumetric flow rate of CO<sub>2</sub> at the bed outlet relative to that in the feed,  $Q_{CO_2}^{out}(t)/Q_{CO_2}^{in}$ . Results derived for A-raw testify a significantly shorter breakpoint time  $t_b$  (time for which  $Q_{CO_2}^{out}(t)/Q_{CO_2}^{in}=0.05$ ) and a faster sorbent saturation when the process temperature increases, likely imputable to an enhanced intraparticle diffusion rate [8]. Moreover, both [Emim][Gly]-impregnated sorbents display greater  $t_b$  values when compared to the raw substrate at each tested  $T$ -level. An opposite influence of the operating temperature on the CO<sub>2</sub> capture kinetics for the functionalized sorbents can be inferred. In fact, both  $t_b$  and the saturation time  $t^*$  (for which the CO<sub>2</sub> concentration at the fixed-bed outlet reaches its inlet value) increase with temperature, and the effect is more marked at larger IL loading. As an example, for

A-[Emim][Gly]9% sorbent  $t_b=54.0$  and 76.5 s at 303 and 353 K respectively, while the saturation time rises by a factor 1.8 ( $t^*$  is 516 and 909 s at 303 and 353 K, respectively; data out of Figure 1 range). The discussed experimental evidences clearly witness a greater availability of the IL amine reactive centers for  $\text{CO}_2$  molecules at 353 K with respect to 303 K (*vide infra*), thus producing a shift of the breakthrough curves towards longer times as the temperature rises, with an associated slower sorbent saturation.



**Figure 1.**  $\text{CO}_2$  breakthrough curves on alumina raw and functionalized with [Emim][Gly] IL at (a) 303 K and (b) 353 K.

Figure 2 reports  $\omega^s$ -values (obtained at  $t^*$ ) for the sorbents tested at 303 and 353 K, as obtained by processing the breakthrough curves in Figure 1.



**Figure 2.** CO<sub>2</sub> saturation adsorption capacity for A-raw, A-[Emim][Gly]5% and A-[Emim][Gly]9% sorbents at 303 and 353 K.

For A-raw, the adsorption results show a reduction of  $\omega^s$  with  $T$ , as expected for a purely physisorption process. In addition, results demonstrate the effectiveness of the functionalization treatment with [Emim][Gly] IL in determining an increase of the parent sorbent CO<sub>2</sub> capture performances, mainly at 353 K. The adsorption capacity of the impregnated sorbents monotonically increases with the IL loading when compared to A-raw at a fixed operating temperature. More specifically, A-[Emim][Gly]5% and A-[Emim][Gly]9% exhibit an  $\omega^s$  value slightly larger than the one attained for A-raw at 303 K ( $\omega^s=0.191$ , 0.264 and 0.276 mol kg<sup>-1</sup> for the bare support and the sorbents with IL loading equal to 5 and 9% wt., respectively). At 353 K, the effect of the IL loading on the improvement of the capture capacity becomes more evident:  $\omega^s$  for A-[Emim][Gly]5% and A-[Emim][Gly]9% is about 2- and 3-times the figure obtained for A-raw, respectively. It should be highlighted that the increase in the CO<sub>2</sub> capture capacity with the temperature observed for the functionalized sorbents is unexpected on the basis of the exothermic nature of the CO<sub>2</sub> conversion process with [Emim][Gly] (to form carbamate or carbamic acid) [9,10]. The following arguments could be invoked to explain the observed adsorption trends: i) at low temperature (303 K), a larger IL loading produces an increase in the number of reactive adsorption sites counterbalanced by a higher mass transfer resistance of CO<sub>2</sub> in the IL (also related to a pore volume reduction, Table 1); ii) at 353 K, the increasing availability of reactive sites at larger IL content is a prevailing factor in producing a greater adsorption capacity, possibly

due to a reduction of the IL viscosity with temperature allowing an easier accessibility of CO<sub>2</sub> molecules in the substrate pore network.

### Conclusions

CO<sub>2</sub> adsorption tests onto a mesoporous alumina impregnated with [Emim][Gly] IL at different loadings (i.e. 5 and 9% wt.) were performed at 303 and 353 K under mimicking flue-gas conditions in a fixed-bed column. Results demonstrated the effectiveness of the functionalization treatment with the IL in improving the substrate CO<sub>2</sub> capture capacity mainly at 353 K, likely due to a reduction of the active phase viscosity with increasing temperature, allowing an easier accessibility of adsorbate molecules in the substrate pore network. The obtained results are particularly encouraging in the light of a practical application of the tested sorbents for the treatment of moderately high-temperature flue-gases, thus potentially determining significant economic benefits for the CO<sub>2</sub> capture process.

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