

EXPLORING THE PERFORMANCE IN CO₂ UPTAKE OF LOW COST CARBON-BASED MATERIALS

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There is a growing interest in adsorption processes by solid sorbents as a promising technique to reduce the anthropogenic greenhouse gas emissions [1]. Solid sorbents offer remarkable advantages in post-combustion CO₂ capture strategy such as reduced energy for regeneration, great capacity, selectivity, ease of handling. Solid sorbents are conventionally classified on the basis of the kind of interaction that takes place between CO₂ and the material: physical interaction (physisorption) and chemical interaction (chemisorption). Typical physisorbents are porous carbonaceous materials, zeolites, alumina, silica gels, and metal organic framework (MOF). Chemisorbents are usually porous surface-modified materials incorporating basic sites (alkaline carbonates and amino groups) capable of strongly interact with acidic CO₂. Supported ionic liquids phase (SILP) materials are recently emerging as very promising sorbents bearing basic sites [2]. These systems combine the unique properties of the IL (non volatility, high solvent capacity, negligible vapor pressures, high thermal stabilities and tunable properties) and those of the support materials. Recent studies strongly encourage also the use of low-cost metal oxide as sorbents [3, 4]. The tendency of metal oxide nanoparticles to agglomerate, lowering the CO₂ sorption capacity, was recently overcome with the intercalation of carbonaceous material (graphite nanoplatelets, nanotubes) in the metal-oxide network [5].

Aim of this work is to explore the role of the surface features of the substrate in the designing of competitive sorbents for CCS strategies. The CO₂ adsorption behavior of different materials prepared starting from a low-cost commercial carbon black (CB) was investigated. Three kind of CB surface modifications were proposed, namely oxidation and functionalization with ammino-groups, coating with magnetic iron oxides (magnetite Fe₃O₄) and impregnation with ionic liquid (IL). The ability of such materials to act as CO₂ sorbents was evaluated on the basis of the breakthrough curves obtained in a lab-scale fixed bed set-up at atmospheric pressure and room temperature. The use of fixed bed set-up is a convenient way to perform a rapid screening of the performances of different solid sorbents synthesized in small amounts [6], achieving more realistic fluid-dynamic conditions compared to thermogravimetric analysis.

Experimental section

The investigated materials were labeled according to Table 1. The materials can be gathered in three groups: *Group 1*) CB, CBox and CBox-NH₂ produced by chemical modification of the raw CB; *Group 2*) CB-FM and CBox-FM produced exploiting the co-precipitation with magnetite (FM); *Group 3*) CB-IL, CBox-IL in which the carbonaceous material is used as supporting matrix for a IL.

The first group includes three carbonaceous materials with different surface functionalization: hydrophilic CBox is obtained by wet oxidation of the raw hydrophobic CB. CBox was further surface-modified with aminogroups by grafting with diethyltriamine (DETA). The second group includes carbon-based magnetite composites. The role of hydrophobic (CB) and hydrophilic (CBox) carbonaceous part was investigated in order to evaluate their possible use as low-cost carbonaceous component in substitution of more expensive nanotubes and graphene nanoplatelets to enhance the CO₂ uptake capacity and to prevent the magnetite agglomeration [5]. The third group investigates SILP produced by using hydrophobic CB and hydrophilic CBox as supporting material. The different carbonaceous surfaces allow evaluating the role of polar functional groups on the surface of the supporting material and possible interactions with IL. The selected IL was trihexyl(tetradecyl)phosphonium triazole ([P66614][Triz]) because of its high thermal stability (>300 °C), remarkable absorption capacity (0.95 mole CO₂ per mole IL) and good absorption enthalpy (ca. 56 kJmol⁻¹) [7].

Samples Preparation

CB N110 type (furnace CB) was obtained by Phillips Petroleum Co. Its density at 25 °C is 1.8 g/mL, and the SA is 143 m²/g. *CBox*. CB was oxidized with nitric acid (67 wt.%) at 100 °C under stirring for 24 hours. *CBox-NH₂*. Amminogroups were introduced on the CBox surface sonicating for 4 h at 40 °C a CBox dispersion in DETA. *FM*. FeCl₃•6H₂O (1.35 g) and FeSO₄•7H₂O (0.70 g) were dissolved in water and kept at 30 °C for 15 minutes. After that a 28% ammonia solution was added to reach a pH 10 and the mixture was rapidly stirred for 1 h at 90 °C and cooled to room temperature. The solid was recovered and purified by dialysis against water. *CB-FM and CBox-FM*. CB-FM and CBox-FM composites were produced adapting the strategy reported for the graphite oxide by Luo [8]. CB and CBox were suspended in water and an aqueous solution of FeCl₃•6H₂O (1.35 g) and FeSO₄•7H₂O (0.70 g) was added. The mixtures were kept at 30 °C and a 28% ammonia solution was added to adjust the pH at 10. The mixture was stirred for 1 h at 90 °C. *IL*. The IL was prepared according to the procedure reported in [7]. *CB-IL and CBox-IL*. The CB-IL and CBox-IL materials were produced by grounding in a mortar the IL and the carbonaceous support (CB and CBox, respectively) in order to obtain a homogeneous material. The amount of the loaded IL is 25 wt.%.

Methods

The C, N, H content was measured by a Perkin–Elmer 2400 CHNSO Elemental Analyzer. The oxygen amount was evaluated by difference. The thermal stability of the samples was evaluated on a Perkin–Elmer Pyris 1 Thermogravimetric

Analyzer in oxidative environment (air) heating the samples from 30 °C to 750 °C at a rate of 10 °C min⁻¹. The BET specific surface areas (SA) of the samples were measured by N₂ adsorption at 77 K using a Quantachrome Autosorb 1-C. CO₂ adsorption experiments were performed in a laboratory scale experimental apparatus equipped with a fixed bed Pyrex micro-reactor (ID=1 cm, length=60 cm). The CO₂ concentration in the inlet and outlet gas streams has been measured by an online continuous ABB infrared gas analyzer (AO2020). All adsorption tests have been carried out at atmospheric pressure and room temperature. In a typical experiment, the sorbent (0.35 g, particle size: 180-400 μm) is loaded in the reactor. Then, a CO₂/N₂ gas mixture (15 Nl/h) at a fixed CO₂ concentration (3% vol.) is fed through the bed from the top of the reactor. CO₂ concentration profiles have been obtained as a function of time *t*, which has been counted from the time the gas mixture takes to flow from the fixed bed to the analyzer. This transit time has been previously measured for each gas flow rate by flowing the gas mixture through the empty bed (about 50 s).

Results and discussion

Surface (BET) areas, pore size distribution and CO₂ adsorption characteristics are reported in Table 1 together with the thermal stability in oxidant environment (air).

Table 1. Samples characteristics and pore size distribution.

<i>Sample name</i>	<i>Sample description</i>	<i>Bulk oxidation °C</i>	<i>SA (m²/g)</i>	<i>m_{ads} (mgCO₂/g)</i>	<i>t* (s)</i>
CB	carbon black	690	143.0	3.9	2
CBox	Oxidized CB	670	263.0	6.6	0
CBox-NH ₂	CBox functionalized with amino-groups	670	29.5	12.8	1
FM	Magnetite	-	154.3	10.8	1
CB-FM	CB-Magnetite composite	540*	160.0	11.6	2
CBox-FM	CBox-Magnetite composite	540*	150.5	6.8	1
CB-IL	Ionic liquid (IL) supported on CB	680	35.6	27.3	18
CBox-IL	IL supported on CBox	680	40.2	9.9	6

SA, surface area; * referred to the burn off of the carbonaceous part

The chemical surface modifications introduce many changes to the raw CB in terms of composition, functional groups and textural properties. The oxidation process introduces many oxygenated functional groups (mainly as carbonyl and carboxylic groups) as testified by the increased oxygen content that grows from 0.59 wt.% (raw CB) to 31.8 wt.% (CBox) and by infrared analyses (data not shown). Amino-functionalization of CBox changes both the composition and surface properties of the raw CB. The CBox-NH₂ oxygen content decreases to 23 wt.% (indicative of amide formation) while an increase was detected for both the

hydrogen (from 0.84 to 1.5 wt.%, attributable to the aliphatic chains of the amine groups) and nitrogen contents (from 0.38 to 7.5 wt.%). The bulk oxidation occurs at 670 °C for both CBox and CBox-NH₂, at a slightly lower temperature than the raw CB (690 °C), indicating that the graphitic core remains substantially unchanged upon the wet chemical treatments. SEM images (not shown) indicated that all the wet chemical treatments do not alter the morphology of the carbonaceous grains. CB is a mesoporous solid with a negligible degree of microporosity while CBox exhibits a higher degree of microporosity, consistent with a higher SA (Table 1). The amino-functionalization caused a dramatic decrease of the SA (from 263 to 29.5 m²/g) probably due to the pores blockage operated by the aliphatic sidechains on the carbonaceous surface.

The co-precipitation strategy, exploited for the preparation of the *group 2* samples (CBox-FM and CB-FM), allows the homogeneous incorporation of carbonaceous material into the composites as testified by the TG analyses, SEM imaging and elemental mapping of C, O and Fe estimated by energy dispersive X-ray (EDX) (not shown). The weight loss of 15% in the 520-540 °C region for both the composites, ascribable to the oxidation of the carbonaceous part (CB and CBox), confirms the carbon/iron ratio used in the preparation (14 wt. %). It is noteworthy that iron catalyses the oxidation of the carbonaceous component causing a shift to a lower temperature with respect to CB and CBox, confirming a good mixing between the inorganic and organic components. FM presents a SA comparable to the CB one, but mostly distributed in mesopores of 20-50 Å (Table 2). The CBox-FM and CB-FM composites retain the porosity distribution of FM indicating a coating of the carbonaceous part with a progressive blocking of CB and CBox micropores and mesopores.

As concerns the samples belonging to *group 3*, the immobilisation IL on the CB and CBox surface does not alter the functionalization of the supporting material, as confirmed by the infrared spectra (not shown). The IL supported on CB and CBox is stable up to 230°C in oxidant environment indicating that, differently from activated carbons, silica TiO₂-based SILP materials [2], the stability of the supported IL is not influenced by the nature of the supporting material. The temperatures of CB-IL and CBox-IL bulk oxidation are comparable to those estimated for the raw supporting materials. The IL coating causes a blockage of both the micro and mesopores of the supporting materials; this datum is discernible by the SA drop (Table 1) in both cases.

Figure 1 reports the breakthrough curves (i.e. C/C_0 versus time, C and C_0 are the CO₂ concentration in the effluent and feed stream, respectively) obtained for all the materials. The curves have been worked out to evaluate: i) the mass of CO₂ adsorbed per unit mass of adsorbent, m_{ads} , calculated by integrating the breakthrough curves; ii) the time, t^* , defined as the time interval in which the CO₂ outlet concentration remains constant at the beginning of the test (i.e. the time at which the derivative of the CO₂ concentration profile becomes larger than 0.5). m_{ads} and t^* are reported in Table 1.

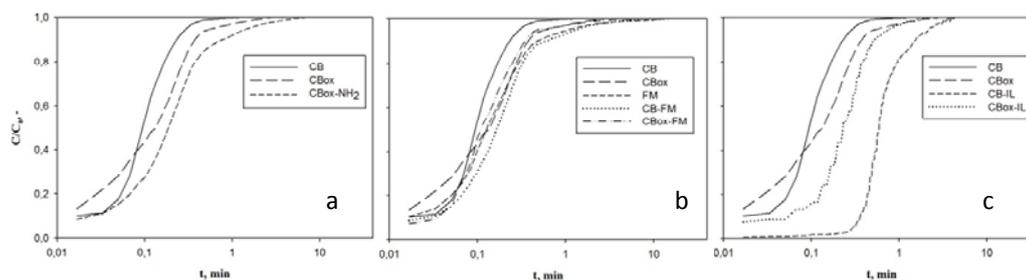


Figure 1. Breakthrough curves of the investigated adsorbents.

As clearly shown in Figure 1a and Table 1, CB presents the lowest adsorption capacity ($3.9 \text{ mgCO}_2/\text{g}$). The oxidizing treatment remarkably increases the adsorption performance of more than 70% ($6.6 \text{ mgCO}_2/\text{g}$) attributable both to the increase of the surface area (Table 1), available for CO_2 physisorption phenomena, and to the effect of the surface polarity. It was reported that the weakly nucleophilic or polar functional groups are able to physisorb CO_2 by means of dipole interactions [9]. The chemisorption phenomena, strongly enhanced by amine-functionalization (CBox- NH_2), further increase the CO_2 uptake (93% more, with respect to CBox). The sorbents FM, CB-FM and CBox-FM are very similar for morphology, thermal stability, porosity surface area and CO_2 uptake capacity (Table 1). CB-FM adsorbs rather the same CO_2 than pure FM even if it contains a lower amount of pure FM (85 %) indicating a strong role of the available surface. The interaction of CO_2 with FM and FM composites (CB-FM and CBox-FM) is based on the formation of bicarbonates and carbonates linkages between the OH groups of the magnetite particles and CO_2 molecules [4]. It is also noteworthy that the CB-FM CO_2 capture performance is higher than CBox-FM probably because the blockage of FM into CBox micropores decreases the availability of FM to interact with CO_2 . The SILP solids represent the most promising materials for CO_2 capture investigated inside this work (Figure 1c). CB-IL is by far the best ones, m_{ads} being 7 times the one obtained with raw CB whereas CBox-IL adsorption performance is comparable to the other adsorbents. The CB-IL and CBox-IL interaction with CO_2 molecules proceeds through the formation of a carbamate involving the triazole units inside the IL [7]. As in the case of the above described magnetite composite, physical adsorption phenomena are negligible due to the low surface area exhibit by both the samples (Table 1). The lowest value found for CBox-IL can be related to the non-easy accessibility of IL inside the CBox micropores, in the exploited experimental conditions, lowering the number of binding sites for CO_2 .

A 13X zeolite has been also tested in the same operating conditions in order to make a comparison with a highly tested adsorbent material [10]. In particular, the amount of CO_2 adsorbed ($7.3 \text{ mgCO}_2/\text{g}$) is significantly lower than that obtained with all the treated samples (the only exception being CBox-FM whose adsorption

capacity is only slightly lower than that of zeolite 13X). Moreover, the results obtained for the treated samples are also comparable to the performances reported in literature for amine-functionalized activated carbons, carbon nanotubes and zeolites, even though the CO₂ partial pressure is up to about seven times larger than that used in this work [6].

Conclusions

The focus of this study is to explore the role of the surface features of the solid substrate in the designing competitive low-cost sorbents for CCS strategies. Three surface-modification were investigated, namely functionalization with amino-groups, coating with magnetite and impregnation with IL. It was found that the solids bearing basic functionalities (CBox-NH₂, CB-IL and CBox-IL) exhibit the higher capacity to adsorb CO₂ through carbamate formation. It was shown that the use of a microporous supporting material limits the accessibility of CO₂ toward the absorbing material (IL or FM) in the exploited experimental conditions (atmospheric pressure and room temperature), lowering the number of binding sites for CO₂. Regeneration and recycling behavior are currently under study.

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