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CO_2 sorption on surface-modified carbonaceous support: Probing the influence of the carbon black microporosity and surface polarity

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ABSTRACT

The use of solid sorbents is a convenient option in post-combustion CO_2 capture strategies. Sorbents selection is a key point because the materials are required to be both low-cost and versatile in typical post-combustion conditions in order to guarantee an economically advantageous overall process. This work compares strategies to tailor the chemico-physical features of carbon black (CB) by surface-modification and/or coating with a CO_2-sorbent phase. The influence of the CB microporosity, enhanced by chemical/thermal treatments, is also taken into account. Three CB surface modifications are performed and compared: (i) oxidation and functionalization with amino-groups, (ii) coating with iron oxides and (iii) impregnation with an ionic liquid (IL). The CO_2 capture performance is evaluated on the basis of the breakthrough curves measured at atmospheric pressure and room temperature in a lab-scale fixed bed micro-reactor. Most of tested solids adsorb a CO_2 amount significantly higher than a 13X zeolite and DARCO FGD (Norit) activated carbon (up to 4 times more in the best case). The sorbents bearing basic functionalities (amino-groups and IL) exhibit the highest CO_2 sorption capacity. The use of a microporous carbonaceous support limits the accessibility of CO_2 toward the adsorbing phase (IL or FM) lowering the number of accessible binding sites for CO_2.

1. Introduction

CO_2 is one of the major greenhouse gases and it is the main responsible for global warming. Its emission control has become an urgent and challenging target for the mankind, inducing a growing interest in developing technologies for efficient capture and sequestration of large quantities of CO_2. Carbon capture and storage (CCS) embodies an array of effective CO_2 emission abatement strategies that can be gathered into three major approaches: post-combustion capture, pre-combustion capture and oxyfuel processes [1,2]. Post-combustion capture offers more advantages for existing combustion technologies over the other two approaches because it can be applied without radical changes on the plants architecture [3].

Up to now a number of separation technologies useful for post-combustion strategies have been proposed: physical absorption, chemical absorption, adsorption, cryogenics separation and membranes [4–6]. Sorption processes by solid sorbents offer remarkable advantages such as reduced energy for regeneration, great capacity, selectivity, and ease of handling. A variety of promising sorbents including activated carbons (AC), microporous/mesoporous silica or zeolites, carbonates, polymeric resins nitrogen-functionalized, metal-organic frameworks (MOF), metal oxides, supported ionic liquids phases (SILP) have been proposed [4,7–10]. A competitive material for CO_2 capture applications should accomplish a number of requirements: (i) it should be economically convenient, (ii) it should be able to selectively interact with CO_2 over the other flue gas components, and (iii) it should be stable to repeated CO_2 sorption and desorption cycles over a wide range of temperatures and pressures [4,11,12]. Materials with a distinctive surface chemistry and morphology find large applications in CCS technologies [12]. Solid sorbents are conventionally classified on the basis of the typology of interaction that takes place between CO_2 and the material: physical interaction (physisorption) and chemical interaction (chemisorption). Materials acting as physisorbent are porous carbonaceous materials, zeolites, alumina, silica gels, and MOF. Chemisorbents are usually porous surface-modified materials incorporating basic sites (carbonates and amino

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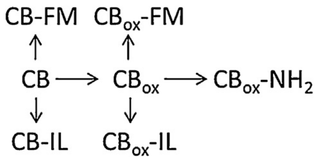

Fig. 1. Samples preparation scheme.

Table 1
Samples description.

CB	Carbon black
CB_{ox}	Oxidized carbon black
CB_{ox}–NH_2	Oxidized carbon black further functionalized with amino-groups
FM	Magnetite
CB–FM	Carbon black–Magnetite composite
CB_{ox}–FM	Oxidized carbon black–Magnetite composite
IL	Ionic liquid
CB–IL	Ionic liquid supported on carbon black
CB_{ox}–IL	Ionic liquid supported on oxidized carbon black

groups) capable of strong interactions with acidic CO_2. Typical amine-functionalized sorbents are amine-impregnated or grafted silica and amine-functionalized polymers [4]. Supported ionic liquid phase (SILP) materials are promising chemisorbents [8]. SILP are composite materials in which a film of ionic liquid (IL) is immobilized on a solid phase. This configuration combines the advantages of IL (high solvent capacity, negligible vapor pressure, high thermal stability and tunable properties [13]) with those of a solid sorbent. In a typical SILP the amount of IL is low and the ability and selectivity of CO_2 separation is unaltered with the respect to pure IL, thus limiting IL shortcomings (higher cost, mass transfer limitations due to the IL high viscosity [14]).

Recent studies of CO_2 sorption on low-cost metal oxides strongly encourage their use as chemisorbents [9,15]. Magnetite (Fe_3O_4, FM) exposes at the surface coordinatively unsaturated metal and O sites which can interact as Lewis acid with gaseous molecules as H_2O, O_2, CO, NH_3, CO_2 through acid–base interactions [16]. The tendency of magnetite particles to agglomerate is the main weak point for sorption applications because it lowers the sorption capacity. The dispersion of magnetic particles on solid matrices (polymers, inorganic minerals, carbonaceous matrices [17–21]) has been proposed to face this limitation. Recently, the sorption behavior of CO_2 was studied on composite materials prepared coating a low-cost CB with magnetite fine particles [21]. Those composites also exhibit thermochemical stability in a sound assisted fluidized bed configuration under multiple cycles of sorption and desorption steps. It was shown that the CO_2 adsorption yield is optimized when the amount of CB in the composite is higher than 14.3% and up to 60%. The results indicated that the dispersion of FM onto the CB surface plays a key role in the CO_2 adsorption behavior pointing out the importance of the substrate surface features since better performances were evidenced when both the CB and FM porosities are retained, allowing a better accessibility of the FM active sites.

Aim of this study is to investigate the role of the surface features (above all pore size distribution) of the carbonaceous material (CB) supporting different CO_2 adsorbent phases. To this aim CB microporosity was enhanced by chemical/thermal treatment and the surface further modified in mild conditions and/or coated with a CO_2-sorbent phase.

Three CB surface modifications/coatings were compared: (i) oxidation and functionalization with amino-groups, (ii) coating with magnetic iron oxides and (iii) impregnation with IL.

The ability of those materials to act as CO_2 sorbents was evaluated on the basis of the breakthrough curves performed in a lab-scale fixed bed micro-reactor.

2. Experimental

2.1. Materials

The investigated materials were prepared according to the scheme reported in Fig. 1 and labelled according to Table 1.

The materials can be gathered in three groups: (1) CB, CB_{ox} and CB_{ox}–NH_2 produced by chemical modifications of the raw CB; (2) CB–FM and CB_{ox}–FM produced by co-precipitation with FM; (3) CB–IL, CB_{ox}–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: a hydrophobic CB, a hydrophilic CB_{ox} obtained by wet oxidation of the raw hydrophobic CB and a hydrophilic CB_{ox}–NH_2 obtained by the further surface-modification with amino-groups of CB_{ox} by grafting with diethylenetriamine (DETA). Studies conducted on graphite oxide (GO) amino-functionalized with amines bearing a variable number of nitrogen atoms (ethylenediamine EDA, DETA, triethylenetetramine TETA) demonstrate that the breakthrough time for CO_2 sorption follows the sequence GO-EDA > GO-DETA > GO-TETA [22]. In this work DETA was selected as grafting agent because it represents a good compromise between the number of introducible primary amino groups and the breakthrough performances.

The second group includes carbon-based magnetite composites. The role of hydrophobic (CB) and hydrophilic (CB_{ox}) carbonaceous parts was investigated in order to evaluate their possible use as low-cost carbonaceous component in substitution of more expensive multiwalled carbon nanotubes (MWCNT) and graphene nanoplatelets to prevent the magnetite agglomeration [21,23,24] and to produce composite materials with enhanced CO_2 uptake capacity.

The third group is made up by SILP produced by using hydrophobic CB and hydrophilic CB_{ox} as supporting material. The selected basic anionic liquid was the trihexyl(tetradecyl)phosphonium triazole ($[P_{66614}][Triz]$) because of its high thermal stability (>300 °C), remarkable absorption capacity (0.95 mole CO_2 per mole IL) and good absorption enthalpy (ca. 56 kJ/mol) [25]. Moreover the use of triazole as weak nitrogen-based nucleophilic molecule is helpful for less-expensive sorbent recycling since the interaction with CO_2 results in thermodynamically less stable carbamate [25]. A solvent-free SILP preparation strategy, based on a direct impregnation of the supporting material with IL, was applied.

2.2. Samples preparation

All chemicals were purchased from Sigma–Aldrich as analytical reagent grade and used without any further purification.

CB. CB N110 type (furnace CB) was obtained by Sid Richardson Carbon Co. CB density at 25 °C is 1.8 g/mL and surface area (SA) is 143 m^2/g.

CB_{ox}. CB was oxidized according to the procedure reported by Kamegawa et al. [26]. In a typical experiment, 0.5 g of CB was treated with 10 mL of nitric acid (67 wt.%) in a round bottom flask at 100 °C under stirring for 24 h. After cooling to room temperature, the suspension was centrifuged and the solid fraction was washed with distilled water until the acid traces were removed. The product was dried at 100 °C at atmospheric pressure.

CB_{ox}–NH_2. Amino-groups were introduced on the CB_{ox} surface adapting the procedure reported by Vuković et al. [27] for carbon nanotubes. 0.4 g of CB_{ox} was dispersed in DETA (240 mL) and sonicated for 4 h at 40 °C. After sonication, the dispersion was diluted with methanol and the carbonaceous material recovered by centrifugation. The solid was washed with methanol until no traces of amine were detected.