Assessment of Magnetite/Carbon Composites Capacity in CO₂ Adsorption under Sound Assisted Fluidization Conditions

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Among post-combustion CO_2 capture strategies, adsorption with solid sorbents is considered to be one of the most promising options. However, the performances of solid sorbents under typical flue gas concentrations (5-15 %vol. and atmospheric pressure) have been poorly investigated. Under these operating conditions the CO_2 uptake capacity is primarily influenced by material functionality effects rather than material pore metrics, therefore, materials with a distinctive surface chemistry (presence of activated surface atoms or sites) are expected to find applications in adsorption technologies. Hence, the sorbent selection became a key point because the materials should be both convenient from the economic point of view and versatile under post-combustion conditions. Recent studies of CO_2 adsorption on low-cost iron metal oxide surfaces strongly encourage the possible use of metal oxide as sorbents, but the tendency of magnetite particles to agglomerate causes a lowering of CO_2 uptake capacity. The dispersion of magnetite nanoparticles on carbonaceous matrix appears to be a promising strategy to overcome this drawback. This work investigates the CO_2 adsorption behavior of composite materials prepared coating a low-cost commercial carbon black (CB) with magnetite fine particles. The CO_2 capture capacity of composites produced with different CB load was evaluated in terms of the breakthrough times measured at atmospheric pressure and room temperature in a lab-scale fixed bed reactor. It was established that when the amount of CB in the composite is in the range 14.3-60 % the CO_2 uptake is remarkably increased with respect to the pure magnetite. The best performing CB–FM composite (50 % of CB load) was selected to verify the possibility of carrying out a cyclic adsorption/desorption operation in a sound assisted fluidized bed. The results showed that the selected composite can undergo several CO_2 adsorption/desorption cycles without modification in its thermochemical stability and adsorption properties.

1. Introduction

Post-combustion is the most advantageous near-term CO_2 capture strategy, because it does not imply substantial modifications to the combustion process technologies currently used (Ramli et al., 2014). The use of solid sorbents offers remarkable advantages over the other separation methods because it offers great capacity, selectivity, ease of handling and reduced energy for regeneration (Raganati et al., 2014c). It was established that at low pressure (post-combustion conditions 1 bar and CO_2 10-15 % vol.) the CO_2 uptake capacity is influenced primarily by functionality effects rather than pore metrics (Banerjee et al., 2009). Magnetite (Fe_3O_4), a low cost iron metal oxide, biocompatible and non-toxic for human body has been applied in a variety of fields and recently also in gas sorption (Alfe et al., 2015). Magnetite, like other metal oxides, exhibits active sites exposed at the surface (coordinatively unsaturated metal and O sites) which can interact with gaseous molecules in terms of acid–base interactions being Lewis acid or basic sites. The tendency of Fe_3O_4 to aggregate limits its applicability in the field of adsorption technologies because it limits the exposed surface. The intercalation of carbonaceous material (graphite nanoplatelets, nanotubes, graphene) in the

metal-oxide network have been proposed in the last years and a range of carbon based-magnetite composite materials have been synthetized (Alfe et al., 2015).

The aim of this work is the synthesis and investigation of the CO_2 adsorption behavior, with CO_2 concentration and pressure typical of a post-combustion flue-gas, of carbon-magnetite composites obtained starting from a commercial carbon black (CB). CB loading was varied in order to optimize the properties of the composites for adsorption applications. The ability of such materials to act as CO_2 sorbents was rapid screened on the basis of the breakthrough curves performed in a lab-scale fixed bed reactor on small sorbent amounts (hundreds of mg). However, fixed-bed reactors do not allow a full exploitation of all the potential of an ad-hoc manufactured fine adsorbent material. On the contrary, fluidization technology is generally considered to be one of the best available techniques to handle and process large quantities of powders. However, fine powders, such as CB-FM, fall under the Geldart group C (<30 μm) classification (Ammendola and Chirone, 2010), i.e. fluidization is expected to be particularly difficult (plugging, channeling and agglomeration) because of strong inter-particle cohesive forces (van der Waals, electrostatic and moisture induced) (Raganati et al., 2011a). In this respect, sound assisted fluidization can be used to overcome these inter-particle forces and achieve a smooth fluidization regime (Raganati et al, 2011b), thus enhancing CO_2 capture on fine powders even on large scale (Raganati et al., 2014b). CO_2 uptake and desorption capacity of a selected CB-magnetite composite was evaluated in a sound assisted fluidized bed reactor. The results addressed on the material stability during a cyclic operation strategy for CO_2 adsorption and desorption.

2. Experimental details

2.1 Materials

CB: CB N110 type (furnace CB) was obtained by Phillips Petroleum Co. Its density at 25 °C is 1.8 g mL^{-1}, and the surface area (SA) is 143 m^2 g^{-1} (Table 1). CB is a monodispersion of chain-like aggregates of spherical primary particles with average diameters of 15-20 nm.

All chemicals were purchased from Sigma-Aldrich, were analytical reagent grade and used as received.

Ferromagnetite (FM): FeCl$_3$•6H$_2$O (1.4 g) and FeSO$_4$•7H$_2$O (0.70 g) were dissolved in 100 mL of distilled water and kept at 30 °C for 30 minutes. After that, 10 mL of 28 % ammonia solution was added until pH 10 was reached. The mixture was kept for 1 h at 90 °C under stirring and afterward was cooled to room temperature. The solid was recovered after decantation, resuspended in water, filtered and washed with water until neutral pH was reached. The sample was dried at 100 °C. The FM yield was 0.62 g.

CB-FM composite: Five different CB-magnetite composites were produced by varying the amount of CB (0.10 g for CB-FM-1, 0.35 g for CB-FM-2, 0.60 g for CB-FM-3, 0.90 g for CB-FM-4 and 1.2 g for CB-FM-5). Composites nomenclature is reported in Table 1. CB was suspended into 200 mL of de-ionized water by sonication for 20 min and then 50 mL aqueous solution of FeCl$_3$•6H$_2$O (1.4 g) and FeSO$_4$•7H$_2$O (0.70 g) was added. The mixture was kept at 30 ºC for 30 min under stirring. After that, 10 mL 28 % ammonia solution was added in order to adjust the pH at 10. The mixture was kept for 1 h at 90 ºC under stirring. The workup of the reaction was the same applied in the case of FM preparation. The reactions yielded 0.75 g for CB-FM-1, 0.95 g for CB-FM-2, 1.2 g for CB-FM-3, 1.5 g for CB-FM-4 and 1.9 g for CB-FM-5.

2.2 Analytical methods

The C, N, H content was measured by a CHN 2000 LECO Elemental Analyzer. The quantitative determination of the Fe was obtained by ICP-MS measurements performed on a Agilent ICP-MS 7500ce spectrometer. The samples thermal stability was evaluated by thermogravimetric analysis (TGA) performed on a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer. The materials were heated in an oxidative environment (air, 30 mL min^{-1}) from 50 °C to 800 °C at a rate of 10 °C min^{-1}. Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet iS10 spectrometer. Samples were prepared as 1 % KBr pellets. The BET specific surface area and pore size distribution of the samples were measured by N_2 adsorption at 77 K by using a Quantachrome Autosorb 1-C. The samples were outgassed under vacuum at 150 °C before the analysis. Scanning electron microscopy (SEM) was performed on a FEI Inspect™ S50 Scanning Electron Microscope. Particles size distribution was determined by using a laser granulometer (Master-sizer 2000 Malvern Instruments).

2.3 Experimental set up for CO_2 adsorption

Fixed bed reactor: a laboratory scale fixed bed reactor made of Pyrex (ID=1 cm, length=60 cm) operating under atmospheric pressure was used for the preliminary evaluation of the CO_2 adsorption capacity of different samples. N_2 and CO_2 flowrates were set by means of mass flow controllers (Bronkhorst), and subsequently mixed before entering the bed. The CO_2 concentration in the inlet and outlet gas streams was measured by an online continuous ABB infrared gas analyzer (AO2020). All adsorption tests were carried out

at ambient temperature and pressure. In a typical experiment, the sorbent (0.5 g, particle size: 180-400 μm) is loaded in the reactor. Then, a CO_2/N_2 gas mixture (15 Nl h^{-1}) at a fixed CO_2 concentration (3 % vol.) is fed through the bed. The CO_2 concentration in the column effluent gas is continuously monitored as a function of time (breakthrough curve) until the gas composition approaches the inlet gas composition value, i.e., until bed saturation is reached.

Sound assisted fluidized bed: the fluidized bed apparatus (Alfe et al., 2015) consists of a Pyrex column of 40 mm ID and 1,000 mm high, equipped with a porous plate gas distributor. A uniform distribution of gas flow has been ensured by a 300 mm high wind-box filled by Pyrex rings.

To heat the column during the regeneration step, a heating jacket is wrapped around its external surface. A thermocouple, located inside the bed 5 cm from the distributor, is connected to a temperature controller in order to maintain the temperature inside the bed at the desired value. The acoustic field is introduced inside the column through a sound wave guide located at the top of the freeboard. The CO_2 concentration in the inlet and outlet gas streams was measured by an ABB infrared gas analyzer (AO2020).

The experimental campaign was performed on a selected adsorbent which exhibits the best CO_2 adsorption capacity on the basis of the fixed bed preliminary screening. The column was initially loaded with 60 g of adsorbent, corresponding to an unexpanded bed height of about 15 cm. A cycle is a sequence of adsorption-desorption steps. All the tests were carried out at 140 dB and 80 Hz, representing the optimal values of sound parameters to maximize the fluidization quality and, then, the gas-solids contact efficiency, which, in turn, positively affects the CO_2 adsorption performance of fine solid materials (Raganati et al., 2014a). The total gas flow rate was fixed at 67.8 Nl h^{-1} to obtain a superficial gas velocity above the minimum fluidization velocity of the material both in the adsorption and in the desorption step.

Adsorption: in a pre-conditioning step of about 10 min, N_2 is fluxed in the column at ambient temperature in order to stabilize a fluidization regime at fixed operating conditions in terms of superficial gas velocity and sound parameters. Then, the adsorption run is started similarly to fixed bed adsorption tests (CO_2 10 %vol., to simulate a typical flue gas composition).

Desorption: just after each adsorption step, the column is heated up to 250 °C by means of the heating jacket. This regeneration temperature has been chosen considering that it is reported that CB-FM composites can be completely regenerated even at 150 °C but under vacuum (Mishra and Ramaprabhu, 2011). During this heating step, the acoustic field is switched off, the inlet to the column is closed and the top of the column is also sealed by a two-way valve so that all the desorbed CO_2 remains confined inside the column. When the bed reaches the desired temperature of 250 °C, the acoustic field is switched on, the inlet to the column is open (N_2 is flowed) and the column exit is unsealed (purge step). The temperature of the column was maintained constant during the purge. The adsorption-desorption sequence is repeated for 5 consecutive cycles on the same sample in order to test its stability under repeated adsorption/desorption cycles.

3. Results and discussion

3.1 Materials characterization

Table 1 reports the elemental composition of the five CB-FM composites together with the pure FM and CB. The oxygen was evaluated by difference. The amount of carbon, evaluated by TGA was also reported. The percentages of C, O, H and Fe demonstrate a quite complete incorporation of the FM into the CB. Moreover, it is also noteworthy that there is a good agreement between the nominal and the experimental amount of carbon. All samples exhibit comparable surface areas and no significant variations are detectable. The FM presents a surface are (SA) comparable to the CB one, but mostly distributed in mesopores of 20-50 Å while mesopores of 200 Å characterize CB. CB-FM-1 and CB-FM-2 present porosity similar to FM, attributable to the blocking of CB mesopores as a consequence of the FM coating. With the increase of CB loading, the pore size distribution progressively shifts toward the porosity typical of CB indicating the interspace between the CB primary particles is not obstructed. SEM imaging shows that the smooth and compact surface, typical of FM, tends to disappear with the increase of CB loading, indicating that the Fe_3O_4 particles are uniformly distributed on the CB surface. The co-precipitation strategy, exploited for the preparation of the CB-FM composites, allows the homogeneous incorporation of carbonaceous material into the composites as testified by the TG analyses in oxidative conditions. The weight loss ascribable to the oxidation of the carbonaceous part occurs at lower temperature (520-540 °C) with respect to CB (690 °C). The lower oxidation temperature of the CB embedded in the composite matrix is attributable to the iron catalytic effect. This finding confirms a good mixing between the inorganic and organic components. The FT-IR spectra of the CB-FM composites exhibit both the features of the FM and of the carbonaceous material. The FM features tend to disappear with the increase of carbon loading and the spectra of the composites become very similar to that of the pure CB.

Table 1: Samples characteristics

Sample	CB nominal amount (wt.%)	Elemental composition					SA (m²/g)
		H (wt.%)	C (wt.%)	O (wt.%)	Fe (wt.%)	C (TG) (wt.%)	
CB	100	0.48	98.9	0.62	0	100	143
FM	0	0.39	0	34.9	64.7	0	154.3
CB-FM-1	14.3	0.43	11.9	35.1	52.6	13	160
CB-FM-2	36.8	0.46	34	25.6	39.9	38	148.3
CB-FM-3	50	0.49	41.5	29.7	28.3	43	156.7
CB-FM-4	60	0.48	55.5	20.7	23.3	57	157.4
CB-FM-5	66.7	0.46	60.4	20.3	18.8	64	145.4

All the fresh-prepared samples are in the form of fine powders. For the fixed bed tests they have been previously pelletized. On the contrary, the selected sample used in the fluidized bed (CB-FM-3) has been used in its original form. The granulometric analysis performed on this sample shows that the powder is characterized by a particle size distribution lower than 40 μm and a Sauter diameter of about 350 nm.

3.2 CO_2 adsorption screening tests in fixed bed and CO_2 adsorption-desorption cycles tests under sound assisted fluidization conditions

Figure 1a reports the breakthrough curves (i.e. C/C_0 versus time, C and C_0 are the CO_2 concentration in the effluent and feed stream, respectively) obtained for all the materials in the fixed bed reactor.
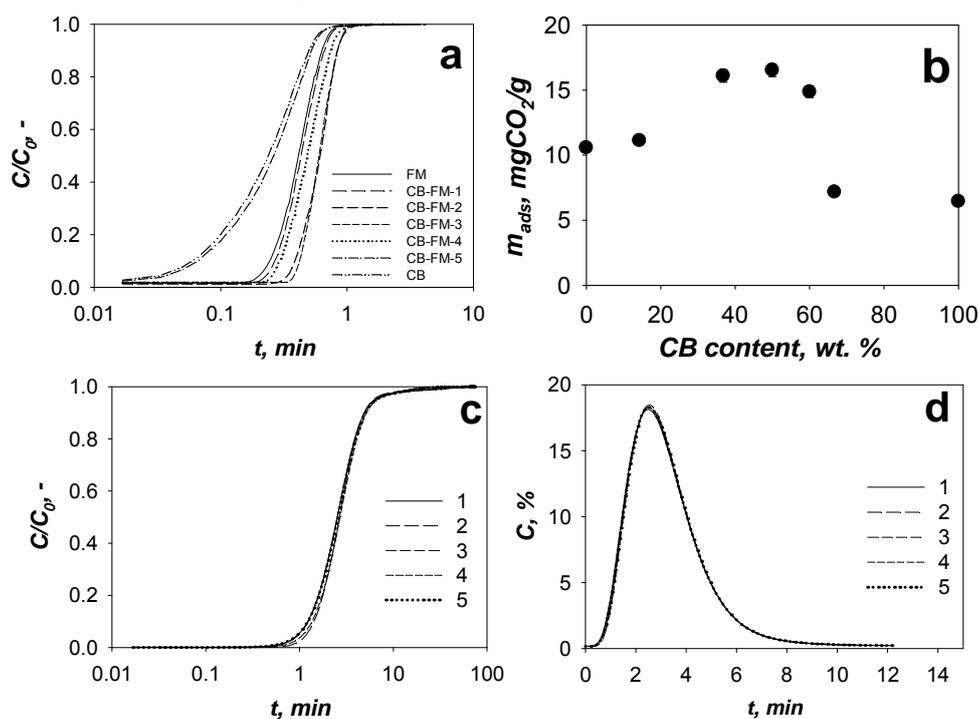

Figure 1: (a) Adsorbents Breakthrough curves in the fixed bed; (b) m_{ads} vs nominal CB loading. (c) CB-FM-3 breakthrough curves and (d) CO_2 desorption profiles in the fluidized bed.

These curves were worked out to evaluate: i) the mass of CO_2 adsorbed per unit mass of adsorbent, m_{ads}, calculated by integration; ii) the breakthrough time, t_b, or breakpoint, which is the time it takes for CO_2 to reach the 5% of the inlet concentration at the adsorption column outlet. As clearly shown in Figure 1a, the CO_2 capture performance of FM (m_{ads}=10.6 mgCO₂/g, t_b=13 s) is remarkably better with respect to CB (m_{ads}=6.5 mgCO₂/g, t_b=3 s). However, in spite of this evidence, the results obtained demonstrate that the presence of carbonaceous matrix inside the composites does not compromise FM ability to fix CO_2 molecules.

Table 2: Results of adsorption/desorption cycles under sound assisted fluidization conditions. C_0=10 % vol.; Inlet flow rate=67.8 Nl h^{-1}; Desorption temperature=250 °C; Sound =140 dB - 80 Hz

Cycle	m_{ads} (mgCO$_2$/g)	t_b (min)	t_{95} - t_b (min)	r_{ads} (mg/min)	m_{des} (mgCO$_2$/g)
1	19.94	0.97	5.3	2.04	19.92
2	20.03	1.2	5	2.04	19.95
3	19.99	1	5.6	1.93	19.97
4	19.8	1.1	5.6	2.01	19.75
5	19.86	0.95	5.7	1.99	19.85

Indeed, CB-FM-1 adsorbs rather the same amount of CO_2 than pure FM even if it contains a lower amount of pure FM. Whereas, amount of CB in the composite higher than 14.3 % and up to 60 % (i.e. CB-FM-2, CB-FM-3 and CB-FM-4) makes it possible to obtain CO_2 uptakes and t_b (about 25 s) remarkably increased with respect to the pure FM. This result indicates that the CB loading used in CB-FM-2, CB-FM-3 and CB-FM-4 is optimal to enhance the dispersion of Fe_3O_4 particles into the composites allowing a better CO_2 uptake. On the contrary, a CB amount larger than 60 % causes a dramatic decrease of CO_2 capture performances of the composite (CB-FM-5) being the composite textural properties similar to CB. In particular, it is also clear from the inset of Figure 2a that the CO_2 capture performances of the composites reach a plateau for CB content between 14.3 % and 60 %. Experimental evidences (above all pore size distribution) indicate that the dispersion of FM onto the CB surface plays a key role in the CO_2 adsorption behaviour (Alfe et al., 2015). Better performances are evidenced when both the CB and FM porosity are retained, allowing a better accessibility of the FM active sites. On the basis of fixed bed results, tests in the fluidized bed experimental set-up have been carried out on the CB-FM-3 sample, which is characterized by the highest CO_2 capture capacity. Figures 1c and d report the CO_2 breakthrough curves and regeneration profiles obtained for all consecutive adsorption/desorption cycles. It is clear that CB-FM-3 is very stable to cycles.

Table 2 reports the values of m_{ads}, t_b, t_{95}-t_b, r_{ads} and m_{des} obtained from the tests performed in the fluidized bed, t_{95}-t_b, r_{ads} and m_{des} being the difference between the time it takes for CO_2 to reach the 95 % of the inlet concentration at the adsorption column outlet, t_{95}, and t_b, the adsorption rate evaluated on the basis of the CO_2 adsorbed in t_{95}-t_b and the mass of CO_2 desorbed per unit mass of adsorbent, respectively. In particular, the sample completely keeps its capture performances: not only the CO_2 uptake and desorbed CO_2 are not affected by the increasing number of cycles but also all the kinetic parameters (t_b, t_{95}-t_b and r_{ads}). The CB-FM-3 showed better CO_2 adsorption performances than those of a commercial activated carbon tested under the same experimental conditions; in particular, m_{ads} is about 23 % higher (Raganati et al., 2014a).

Regarding the adsorption step, it can be seen that CB-FM-3 goes to saturation in about 30 minutes, whereas the t_b is about 1 minute. The CO_2 uptake obtained is higher than that obtained from the test carried out on the same sample in fixed bed. This enhancement is from one hand due to the larger CO_2 partial pressure adopted in the fluidized bed tests, which is the thermodynamic driving force, and from the other hand due to the improvement of gas-solid contact efficiency and mass transfer coefficients yielded by sound assisted fluidization with respect to the tests performed in fixed bed conditions (Valverde et al., 2013). In particular, the application of the sound greatly enhances the break-up and re-aggregation mechanism of aggregates, thus constantly renewing the surface exposed to the fluid and making it more readily available for the adsorption process. The sound parameters, affecting the fluidization quality, can, in turn, influence the adsorbent performance, due to the tight link existing between the adsorption efficiency and the fluid-dynamics of the system. As a general result, the adsorption process is enhanced as sound intensity is increased (> 120 dB) and when sound frequencies fall in an optimum range (50–120 Hz). Indeed, for too high frequencies the acoustic field is not able to propagate inside the bed, while for too low frequencies the relative motion between smaller and larger sub-aggregates is practically absent (Raganati et al., 2015a). Regarding the regeneration step, it is clear that a temperature of 250 °C is enough to completely regenerate the sample, i.e. the amount of CO_2 desorbed is the same as the amount adsorbed in the previous adsorption step (Table 2). In particular, the concentration pattern reaches a maximum in CO_2 outlet concentration, which is remarkably higher than the inlet value of 10 % vol., for relatively low desorption times (about 2 min), indicating that most of the adsorbed CO_2 is quickly removed from the samples. After this fast stage, the curves show a relatively longer tail (the whole regeneration process lasts about 10 min) indicating that the residual CO_2 desorption takes place slowly as a result of driving force reduction (Raganati et al., 2015b). It is noteworthy that the time needed to adsorb 95 % of the total CO_2 uptake (about 11 min) is comparable to that required to completely regenerate the

sample. This result is of a practical interest in the case of a cyclic operation in two interconnected fluidized beds.

4. Conclusions

Five different carbon-magnetite composites obtained from a commercial CB were synthesized by co-precipitation strategy and characterized. The synthesis approach allowed the homogeneous incorporation of both the carbonaceous material and iron oxide particles into the composites. The investigation of the CO_2 adsorption behavior using typical post-combustion flue-gas pressure and composition (1 bar and CO_2 10-15 % vol.), indicated that carbon-magnetite composites are promising CO_2 adsorbents, with good CO_2 uptake capacity with respect to common adsorbent materials (i.e. activated carbons), and demonstrated that the presence of carbonaceous matrix inside the composites does not compromise FM ability to fix CO_2 molecules. In particular, it was established that when the amount of CB in the composite is higher than 14.3 % and up to 60 % the CO_2 uptakes is remarkably increased with respect to the pure magnetite. Sound assisted fluidization, applied on the best adsorbing composite (50 % of CB load), enhances the CO_2 uptake (about 20 mgCO_2/g). The composite can undergo several adsorption and desorption of CO_2 cycles without modification in adsorption properties, demonstrating its suitability for practical applications. The obtained results are interesting in prospect of a cyclic operation in two interconnected fluidized beds, since the time needed to achieve almost the total CO_2 uptake is comparable to that necessary to completely regenerate the adsorbent.

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