Assessment of fine sorbents performances for CO\textsubscript{2} capture in a sound assisted fluidized bed

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Abstract

The aim of the present work is to compare the adsorption performances of different materials (two activated carbons, four zeolites and a metal organic framework) under sound-assisted fluidization conditions (140 dB–80 Hz) in order to maximize the gas–solid contact efficiency and, in turn, minimize the limitations to the intrinsic adsorption capacity of the sorbents. All the tests were performed at ambient temperature and pressure with values of CO\textsubscript{2} concentration typical of flue gases (5–10 vol.%). The different behaviors exhibited by the materials were explained on the basis of their textural properties. In particular, the microporosity falling in the range of 8.3–12 Å strongly affects the CO\textsubscript{2} adsorption performances under the investigated operating conditions.

Introduction

Among all the post-combustion technologies, adsorption processes on solid sorbents are attractive due to their low energy requirements. Great interest is focused on ultra-fine materials, whose chemico-physical properties can be tuned at the molecular level. However, the capture capacity of these fine materials strongly depends on the technology adopted for the adsorption tests. Common techniques, such as thermogravimetric analysis or fixed bed operation, end up underestimating it, since these fine powders are organized in structures (aggregates), which can be difficultly permeable to the gaseous phase. Therefore, the choice of the proper adsorption technique becomes crucial. In this framework sound-assisted fluidization has already been proved to maximize the CO\textsubscript{2} adsorption capacity of fine sorbents with respect to common technologies, due to the higher exploitation of the exposed surface. In particular, the application of the sound greatly enhances the break-up and re-aggregation mechanism of fluidizing aggregates [1,2], thus making the surface of the fine sorbent particles more readily available for the adsorption process. The aim of this work is to compare the adsorption performances of different materials under sound-assisted fluidization conditions (i.e. conditions which are capable to maximize their adsorption performances). In particular, two commercial activated carbons characterized by similar chemical functionalities but different pore size distributions and four commercial zeolites with different chemical functionalities were used. The aim is to find the key parameters determining the intrinsic CO\textsubscript{2} capture capacity under typical post-combustion operating conditions. The performances of these commercial materials were also compared to that of a synthesized metal organic framework (MOF) [3].
The differences among the performances of all these sorbents were correlated to their different chemico-physical properties, and in particular to the pore size distribution.

**Materials and Methods**

Two kinds of activated carbons and four zeolites were used to investigate the effect of their different chemico-physical properties on the adsorption performances. The activated carbons are: an activated carbon DARCO FGD (Norit) and an activated charcoal powder (Sigma Aldrich), which will be addressed hereafter as AC Norit and AC Sigma, respectively. They are characterized by a similar surface area but different pore size distribution. Two zeolites were selected: a Zeolite H-ZSM-5 (Zeolite Int.), i.e. an acid high Si/Al ratio (140) zeolite, and a Molecular sieves-13X powder (Sigma Aldrich), i.e. a basic low Si/Al ratio (1.25) zeolite characterized by Na+ ions as extraframeworks cations. The effect of the extraframework cation was also studied by performing a limited number of tests on a zeolite Y (Si/Al ratio = 2.43) in the ammonium (NH4-Y) and sodium form (Na-Y) (UOP). Then, these common adsorbents were compared to a new-concept adsorbent material, i.e. HKUST-1 (or MOF-199), synthetized in the laboratories of the Istituto di Ricerche sulla Combustione (CNR) of Naples. More specific details about the synthesis procedure can be found elsewhere [3]. All the materials were characterized by different techniques. The particles size distribution was obtained by using a laser granulometer (Master-sizer 2000 Malvern Instruments). Superficial area measurements were carried out according to the BET (Brunauer Emmet Teller) method using N2 at 77 K with a QUANTACHROM 1-C analyzer.

Experiments were carried out in a laboratory scale sound-assisted fluidized bed apparatus [4]. The CO2 concentration in the inlet and outlet gas streams was continuously measured by an ABB infrared gas analyzer (AO2020). All the powders were previously characterized to assess their fluidization quality both in ordinary and sound-assisted conditions (120-140dB and 10-300 Hz). For all the tests about 100 g of powder were loaded in the fluidization column in order to obtain a bed height of about 15 cm. Also adsorption tests were carried out at ambient temperature and pressure. In a pre-conditioning step of about 10 min, N2 is fluxed in the column in order to stabilize a fluidization regime at fixed operating conditions in terms of superficial gas velocity and sound parameters. This is followed by the adsorption step in which a CO2/N2 gas mixture at a fixed CO2 concentration is fed through the column. The CO2 composition in the column effluent gas is continuously monitored as a function of time (breakthrough curve) until bed saturation. Each adsorption test was performed under sound-assisted fluidization conditions (140dB-80Hz), corresponding to the best fluidization quality for all the materials. Moreover, tests were performed at three different CO2 inlet concentration (5, 10 and 15 %vol. in N2) with a total gas flow rate of 67.8 Nl h⁻¹ to obtain a superficial gas velocity (1.5 cm s⁻¹).
Results and discussion

Chemico-physical characterization

All the powders are characterized by dimensions lower than 100 µm with Sauter diameters always lower than 20 µm (see Table 1), thus meaning that all the powders belong to Group C of Geldart’s classification. Table 1 reports the BET and total pore volume of all the sorbents. The two activated carbons exhibit similar values of total pore volume and BET surface area, even though the pore size distribution is quite different. They are both characterized by a significantly broad pore size distribution; indeed, besides the pores in the mesoporosity (20 Å < d < 500 Å) they also have micropores (d < 20 Å). With regard to the microporous region, the distribution is bimodal for both the activated carbons: AC Norit shows micropores in the ranges 3.5-9 Å and > 11 Å, whereas, AC Sigma micropores fall in the ranges 7-10.5 Å and > 13 Å.

Table 1. Chemico-physical properties of all the adsorbent materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>D&lt;sub&gt;SAUTER&lt;/sub&gt;</th>
<th>BET surface area</th>
<th>Total pore volume</th>
<th>Volume of micropores in the range 8.3-12 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC Norit</td>
<td>0.39 µm</td>
<td>1060 m²/g</td>
<td>1.34 cm³/g</td>
<td>1.06·10⁻² cm³/g</td>
</tr>
<tr>
<td>AC Sigma</td>
<td>15.4</td>
<td>1038 m²/g</td>
<td>1.14 cm³/g</td>
<td>1.43·10⁻² cm³/g</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>12.6</td>
<td>400 m²/g</td>
<td>0.41 cm³/g</td>
<td>1.79·10⁻² cm³/g</td>
</tr>
<tr>
<td>13X</td>
<td>3.1</td>
<td>960 m²/g</td>
<td>0.41 cm³/g</td>
<td>4.03·10⁻² cm³/g</td>
</tr>
<tr>
<td>Na-Y/NH₄-Y</td>
<td>2.7</td>
<td>756 m²/g</td>
<td>0.41 cm³/g</td>
<td>6.92·10⁻³ cm³/g</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>4.3</td>
<td>680 m²/g</td>
<td>0.66 cm³/g</td>
<td>1.54·10⁻¹ cm³/g</td>
</tr>
</tbody>
</table>

With regard to the four zeolites, they are basically microporous (d < 20 Å) and characterized by unimodal pore size distributions, as typically observed for zeolites. In particular, almost all H-ZSM-5 pores have a dimension lower than 6 Å, the 13X exhibits pores in the range 6 - 8.5 Å, whereas the Y zeolites are characterized by a peak in the range 7 - 8.5 Å. As reported in Table 1, all the zeolites have quite the same total pore volume, which is, however, remarkably lower than that of the two activated carbon. Besides, zeolite 13X is characterized by a BET surface area larger than that of H-ZSM-5 and Na/NH₄-Y and slightly lower than that of the two activated carbons. HKUST-1 is characterized by a surface area lower than that of the activated carbons and zeolites 13X and it is a microporous material, with all the pores lower than 20 Å. In particular, it exhibits a total pore volume intermediate between the activated carbons and the zeolites. Regarding the fluidization quality, for all the materials the fluidization quality is very poor (channeling phenomena occur inside the bed) without the application of any acoustic field. Therefore, the application of the sound is required to achieve a proper fluidization regime, which is closely related to an efficient break-up of the large aggregates yielded by cohesive forces into smaller structures easily to be fluidized [4].

Adsorption performances

For each adsorbent material typical CO₂ breakthrough curves were obtained and
some parameters were evaluated in order to compare the adsorption performances of all the materials: the moles of CO\textsubscript{2} adsorbed per unit mass of adsorbent, n\textsubscript{ads}; the breakthrough time, t\textsubscript{b}; the time difference t\textsubscript{95} - t\textsubscript{b} between, being t\textsubscript{95} the time it takes for CO\textsubscript{2} to reach the 95% of the inlet concentration at the adsorption column outlet; the fraction of bed utilized at breakpoint, W; n\textsubscript{ads} at t\textsubscript{b}, namely the amount of CO\textsubscript{2} adsorbed at the breakpoint. All these values were plotted in the bars graphs reported in Figures 1 at C\textsubscript{0}=10%vol. (similar results were obtained at 5 and 15%vol.).

**Figure 2.** (a) CO\textsubscript{2} adsorption performances of the sorbents under sound-assisted conditions (140dB-80 Hz) at C\textsubscript{0}=10%; (b) Adsorption isotherms. u = 1.5 cm/s. Figure 1b shows CO\textsubscript{2} adsorption isotherms obtained for all the materials fitted by the Langmuir equation. HKUST-1 is by far the adsorbent characterized by the highest CO\textsubscript{2} adsorption capacity, as clearly confirmed by the most favorable adsorption isotherm, whereas, the activated carbons and the zeolites follow, respectively. With regard to the activated carbons, the Sigma one is characterized by the best adsorption performances. Indeed, in all the investigated conditions, it adsorbs a higher amount of CO\textsubscript{2} in considerably less time. Moreover, it also gives the highest t\textsubscript{b}, W and kinetics. The observed different adsorption performances between the two activated carbons are mainly due to their different pore size distribution. The results obtained for the zeolites 13X and H-ZSM-5 agree with several works reported in literature, which rank zeolites among the fastest adsorbents, reaching equilibrium capacity within minutes, being t\textsubscript{95}-t\textsubscript{b} very small. They are both characterized by faster adsorption kinetics with respect to AC Norit, whereas, their kinetics are comparable to that of AC Sigma. In particular, the 13X is the zeolite giving the best adsorption capacity, t\textsubscript{b}, W and n\textsubscript{ads} at t\textsubscript{b}. The difference between 13X and H-ZSM-5 could be due the different structure and nature of the extraframework cation of the two zeolites. In the case of zeolite 13X (Si/Al = 1.25) these cations are Na\textsuperscript{+}, which are capable of generating strong electrostatic interactions with CO\textsubscript{2}. On the contrary, the H-ZSM-5 is characterized by a prevalence of Si atoms with respect to Al ones (Si/Al = 140) and the extraframework cations are H\textsuperscript{+}, which give the zeolite an acid character, thus reducing the affinity towards CO\textsubscript{2} molecules with respect to zeolite 13X. However, the different behaviour shown by the two zeolites could also be due to their
different pore size distribution. A limited number of tests was performed on a zeolite Y exchanged in the ammonium (NH$_4$Y) and sodium form (Na$_2$Y). The obtained results show that the two zeolites are characterized by very similar adsorption performances (about 0.19 mmol/g), thus meaning that the adsorption process is not affected by the chemical nature of the extraframework cation under the investigated operating conditions. On the basis of the above-mentioned considerations, none of the textural properties, BET surface area and the total pore volume, can be considered as key adsorption parameters. Sure enough, AC Norit is characterized by the best textural properties (Table 1). On the contrary, HKUST-1 has a BET surface area lower than both the activated carbons and zeolites 13X and Y. Likewise, its total pore volume is remarkably lower than that of both the two activated carbons. However, despite these average characteristics, HKUST-1 shows the best CO$_2$ uptake. This means that although the total pore volume is the highest in the activated carbons, not all the pores are effective for an optimum adsorption capacity. As a matter of fact, the amount of CO$_2$ adsorbed is practically independent of the total volume of pores and BET surface area, respectively. Figure 2 shows the relationship between the adsorbed amount of CO$_2$ and the total volume of micropores falling in the range 8.3 - 12 Å (Table 1). In this case, an increasing correlation can be clearly observed, thus confirming the importance of a specific porosity for CO$_2$ adsorption under the investigated operating conditions, i.e. at low CO$_2$ partial pressure. In light of all these considerations, the excellent performance observed for HKUST-1 under the investigated operating conditions can be explained. This sample, with an average BET surface area (680 m$^2$/g) as well as total pore volume (0.66 cm$^3$/g) with respect to the activated carbons and zeolites, exhibits the maximum volume (0.15 cm$^3$/g) of that specific micropores (8.3 - 12 Å). In summary, the total amount of CO$_2$ adsorbed increases with increasing the volume of these specific micropores. This result is in agreement with literature works reporting that adsorbent materials characterized by a high volume of narrow micropores (< 1 nm) exhibited high CO$_2$ adsorption capacity [5], even though they refer to CO$_2$ partial pressure as high as 1 atm, i.e. larger than that typical of a post-combustion flue-gas (CO$_2$ 1 - 15 %vol. and atmospheric pressure). On the other side, performances of solid sorbents under typical flue gas conditions were poorly investigated. In particular, Sevilla et al. [5] reported that the CO$_2$ adsorption process inside narrow micropores may be enhanced because of the stronger interaction of CO$_2$ molecules with the pore surfaces with this enhancement being negligible for micropore widths larger than around three/four times the molecular diameter of CO$_2$ molecules (3.3 Å). Therefore, in agreement with the results obtained, the size limit can be reasonably established at about 12 Å for CO$_2$. On the contrary, other pores present in the adsorbent materials, such as larger micropores (> 12 Å) or mesopores (> 20 Å), are most likely not relevant for CO$_2$ capture under post-combustion operating conditions (i.e. P$_{CO2} ≤ 1$ atm).
In this work the CO₂ capture performances of different fine adsorbent materials were compared. In particular, sound-assisted fluidization was used in order to enhance the gas-solid contact efficiency, thus minimizing the limitations to the intrinsic adsorption capacity of the sorbents. All the adsorption tests were performed at ambient temperature and pressure with CO₂ concentration typical of flue gases. The results obtained show that HKUST-1 is by far the adsorbent characterized by the highest CO₂ adsorption capacity, whereas, the activated carbons and the zeolites follow, respectively. Their different behaviours were explained on the basis of their textural properties. In particular, under the investigated operating conditions the adsorption process is mainly affected by a specific microporosity (8.3 - 12 Å).

References