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HKUST-1 Metal Organic Framework as CO_2 Adsorbent in a Sound Assisted Fluidized Bed

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Among all the carbon capture and storage technologies, adsorption is considered one of the most promising alternative due to its low energy requirements, thus stimulating intense research to find suitable and highly specific adsorbents for removing CO_2 from flue gas. Much attention has been focused on metal-organic frameworks (MOF), a new class of crystalline microporous materials that has potential applications in separation processes. Therefore, a major point to be addressed is the development of a process which can handle such fine materials. In this respect, sound-assisted fluidization has been indicated as one of the best technological option to improve the gas–solid contact by promoting a smooth fluidization regime. The present work is focused on the CO_2 capture by sound assisted fluidized bed of a copper based, water stable MOF, namely HKUST-1. Tests have been performed in a laboratory scale experimental set-up at ambient temperature and pressure. The results show the capability of the sound in promoting and enhancing the adsorption process in terms of larger values of amount of CO_2 adsorbed, breakthrough time, adsorption rate and fraction of bed utilized at breakpoint. Experimental tests have also been carried out to find a suitable regeneration strategy of the sorbent, in order to study its stability to cyclic adsorption/desorption operations. An extra-situ regeneration strategy has been adopted, 150 °C under a 50 mbar vacuum. A thorough chemico-physical characterizations on a sample of HKUST-1 subjected to 10 CO_2 adsorption/desorption cycles confirms the effectiveness of this regeneration strategy and the remarkable stability of the material.

1. Introduction

CCS embodies a group of technologies consisting in the separation of CO_2 from large industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere (Ramli et al., 2014). To date a number of separation technologies could be employed: physical absorption, chemical absorption, adsorption, cryogenics separation and membranes (Raganati et al., 2014a). In this framework, adsorption using solid sorbents has been indicated as one of the most promising alternatives to the consolidated absorption technology, having the potential, due to its low energy requirement, to become the leader technology for CO_2 capture in the future (Raganati et al., 2014c). However, for this to happen, enhancement of solid sorbents efficiency represents one of the foremost challenges (D'Alessandro et al., 2012). Therefore, the necessity exists to realize new highly specific materials whose properties can be tuned at a molecular level. Over the past few decades, attention has been focused on novel-structured porous solids named metal organic frameworks (MOF) (Sumida et al., 2012). The high surface area, the high porosity, the low crystal density and potential scalability to industrial scale have made these materials an attractive target for applications towards gas adsorption, separation and storage, heterogeneous catalysis, and drug delivery (Stock et al., 2012). Among all the MOF, HKUST-1 is one of the most studied one. It contains Cu^{2+} dimers coordinated to the oxygen atoms of benzene tricarboxylate (BTC) units (Petit et al., 2011). HKUST-1 presents several advantages: high surface area, larger than that typical of common activated carbons; water stability; simple synthesis procedure (i.e. anhydrous conditions are not required); the precursors are easily available

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and not expensive. HKUST-1 has been widely used as CO_2 adsorbent from flue gas (Sumida et al., 2012), i.e. CO_2 partial pressure lower than 0.15 atm and room temperature. However, all these data available in literature refer to experimental tests performed with small amount of material (in the order of the mg) under fixed bed conditions or by means of thermobalance analysis (Raganati et al., 2014b).
Common adsorption operations are generally performed in fixed-bed reactors. However, this technology does not appear suitable to fully exploit all the potential of an ad-hoc manufactured fine adsorbent material (Alfe et al., 2015). Indeed, for these materials to be used in fixed bed operations, a previous pelletization step should be needed to overcome the prohibitively high pressure drops related to fine particles beds (Raganati et al., 2015). In this respect, sound assisted fluidization is generally considered to be one of the best available techniques to handle and process large quantities of fine powders due to an enhanced dynamic aggregate break-up and reaggregation mechanism which improves the gas-solid contact efficiency (Ammendola and Chirone, 2010). Moreover, sound assisted fluidization has already been proved to be a viable technology to promote and enhance CO_2 capture on fine powders, due to the constant renewal of the solid surface exposed to the fluid (Valverde et al., 2013).
The aim of this work is to apply sound assisted fluidization to HKUST-1 in order to evaluate its CO_2 capture efficiency using a technology alternative to those already experimented in literature. To this aim, firstly, the synthesis strategy (Petit et al., 2011) has been up-scaled to the gram-scale, for the powder to be used in a lab-scale fluidization column. Then, the fluidization quality of the powder has been characterized by carrying out fluidization tests under ordinary and sound assisted conditions (140 dB – 120 Hz). Then, adsorption tests have been performed at ambient temperature in ordinary conditions and under the effect of the above-mentioned acoustic field. In particular, effectiveness of CO_2 adsorption has been assessed in terms of the moles of CO_2 adsorbed per unit mass of adsorbent, the breakthrough time and the fraction of bed utilized at breakpoint. Finally, a regeneration strategy and HKUST-1 stability to several adsorption/desorption cycles have been assessed. In particular, after each cycle the sample has been subjected to different chemico-physical characterizations (BET, XRD, TG, FT-IR and granulometric distribution) in order to evaluate its chemico-physical stability.

2. Materials and methods

2.1 Experimental apparatus

CO_2 adsorption experiments have been carried out in a laboratory scale sound assisted fluidized bed apparatus (Raganati et al., 2014a). The fluidized bed consists of a Plexiglas column of 40mm ID and 1000mm high, equipped with a porous plate gas distributor located at the bottom of the column. N_2 and CO_2 flowrates have been set by means of mass flow controllers (Bronkhorst), and subsequently mixed before entering the bed; a uniform distribution of gas flow has been ensured by a 300 mm high wind-box filled by Pyrex rings. The bed pressure has been measured by a pressure transducer installed at 5 mm above the gas distributor. The acoustic field is introduced inside the column through a sound wave guide located at the top of the freeboard. The sound-generation system is made of a digital signal generator to obtain an electric sine wave of specified frequency whose signal is amplified by means of a power audio amplifier rated up to 40 W. The signal is then sent to a 8 W woofer loudspeaker placed downstream the sound wave guide. The CO_2 concentration in the inlet and outlet gas streams has been measured by an ABB infrared gas analyzer (AO2020).

2.2 Material and chemico-physical characterization

HKUST-1 was prepared adapting the procedure reported in literature (Petit et al., 2011). HKUST-1 as prepared and after 10 cycles of CO_2 sequestration has been characterized by a large array of analytical techniques. Particles size distribution was obtained by using a laser granulometer (Master-sizer 2000 Malvern Instruments) on the HKUST-1 crystals dispersed in water under mechanical agitation with or without the application of ultrasound (US). Pore size distribution and surface area were evaluated by means of a QUANTACHROM 1-C analyzer according to the BET (Brunauer Emmet Teller) method using Ar at 87K. Before each measurement the sample was outgassed for 12 h under vacuum at 150 °C. Morphological features were evidenced by Scanning Electron Microscopy (SEM) performed by means of a FEI Inspect™ S50 Scanning Electron Microscope. The thermal stability of the samples was assessed by thermogravimetric analyses performed on a Perkin-Elmer Pyris 1 thermobalance. The analyses were performed heating the samples in inert atmosphere (N_2, 40 mL min^{-1}) from 50 °C up to 750 °C at a rate of 10 °C min^{-1}. X-Ray diffraction (XRD) characterization was also performed in order to control the samples crystallinity, using a Philips PW1710 diffractometer operating between 5°2θ and 60°2θ with a Cu Kα radiation. Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet iS10 spectrometer using the attenuated total reflectance (ATR) method by using a germanium crystal. CO_2 Temperature Programmed Desorption (TPD) experiments

were carried out with a Micromeritics AutoChem 2920 II equipped with a thermoconducibility (TCD) detector. Samples (100mg) were pretreated in He up to 150/250 °C at 10 °C min^{-1}. The material was kept 1 h at this temperature and then cooled to ambient temperature. After that the material was subjected for 1 h to an adsorption step with a 15 %vol. CO_2/N_2 mixture. Then the flow was switched again to He and the samples were heated up to 150/250 °C at 10 °C min^{-1} and kept for 1 hour at this temperature.

2.3 Experimental procedures

Preliminary fluid-dynamic characterization: HKUST-1 has been previously characterized to assess its fluidization quality both in ordinary and sound assisted conditions. The values of SPL (140 dB) and sound frequency (120 Hz) have been chosen on the basis of a previous experimental campaign on sound assisted fluidization of ultra-fine powders (Raganati et al, 2011a). All the tests have been performed at ambient temperature and pressure using N_2 as fluidizing gas in order to prevent any intensification of the powder cohesiveness due to air moisture. For all the tests 50 g of HKUST-1 has been loaded in the fluidization column in order to obtain a bed height of about 15 cm. For each test, pressure drop curves have been obtained.
Adsorption tests: all adsorption tests have been carried out at ambient temperature and pressure. In a typical experiment, HKUST-1 (50 g) is loaded in the column in order to obtain a bed height of 15 cm. Then, in a pre-conditioning step of about 10min, N_2 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 CO_2/N_2 gas mixture at a fixed CO_2 concentration is fed through the column.
The CO_2 composition in the column effluent gas is continuously monitored as a function of time (breakthrough curve) until the composition approaches the inlet gas composition value, i.e., until bed saturation is reached. CO_2 concentration profiles have been obtained as a function of time, which has been counted from the time the gas mixture takes from the fluidized bed to the analyzer. Each adsorption test has been performed both in ordinary and sound assisted fluidization conditions. All the adsorption tests (both with and without sound application) have been performed on the same batch of adsorbent material, thus carrying out a cyclic adsorption/desorption operation. In particular, after each adsorption test the material has been regenerated according to the procedure described below.
Sorbent regeneration strategy: a mixed regeneration strategy combining mild temperature (150 °C) and vacuum (50 mbar) has been adopted. This treatment has not been performed in the fluidized bed apparatus but extra-situ. The sample was fully characterized from a chemico-physical point of view after each regeneration step in order to confirm the effectiveness of this regeneration strategy. The sample regenerated only by thermal treatment (150 °C and 250 °C) without the application of vacuum has also been characterized to compare the regeneration strategies.

3. Results and discussion

3.1 Preliminary chemico-physical and fluid-dynamic characterization

Figure 1a reports the cumulative size distributions of the fresh powder. The application of US has only a slight effect reducing the Sauter mean diameter from 5.6 μm to 4.3 μm. According to the obtained particle size distribution, the powder belongs to Group C of Geldart classification. HKUST-1 is characterized by BET surface area of 680 m^2/g, lower than that reported in literature (up to values of 900 m^2/g, Petit et al., 2011), most likely due to the fact that it was prepared in large amount for this experimental campaign, thus leading to a lower control on its chemico-physical characteristics. The SEM investigation (Figure1b) shows that the powder is formed by irregular crystals with a quasi-octahedral shape confirming a lower control on the crystal growth parameters. However, the sample preparation seems not to affect the HKUST-1 crystal formation as shown by XRD spectrum (Figure 1c). The comparison between our HKUST-1 XRD pattern and a simulated HKUST-1 one (Petit et. Al., 2011) confirms the HKUST-1 crystallographic pattern. The observed deviations in the relative intensities are due to variations in the degree of hydration. The FT-IR spectrum of the HKUST-1 (Fig. 1d) is also consistent to those reported in literature (Petit et. al., 2011). The bands at 1,645 and 1,590 cm^{-1} and at 1,450 and 1,370 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups in BTC, respectively. The HKUST-1 is predominantly a microporous material (Fig. 1e) with pore size between 6 and 12 Å, which is in agreement with the structural model of cavities (Petit et. al., 2011). Pores with sizes between 40 and 50 Å (not shown) are also found and attributed to a distortion in the structure of HKUST-1. As regards the HKUST-1 thermal stability, the thermogravimetric curve in inert environment (Fig. 1f) exhibits that HKUST-1 structure is stable up to 350 °C. In particular, the structure of the material collapses at 350 °C, but already for temperature higher than 250 °C the material starts a degradation process.

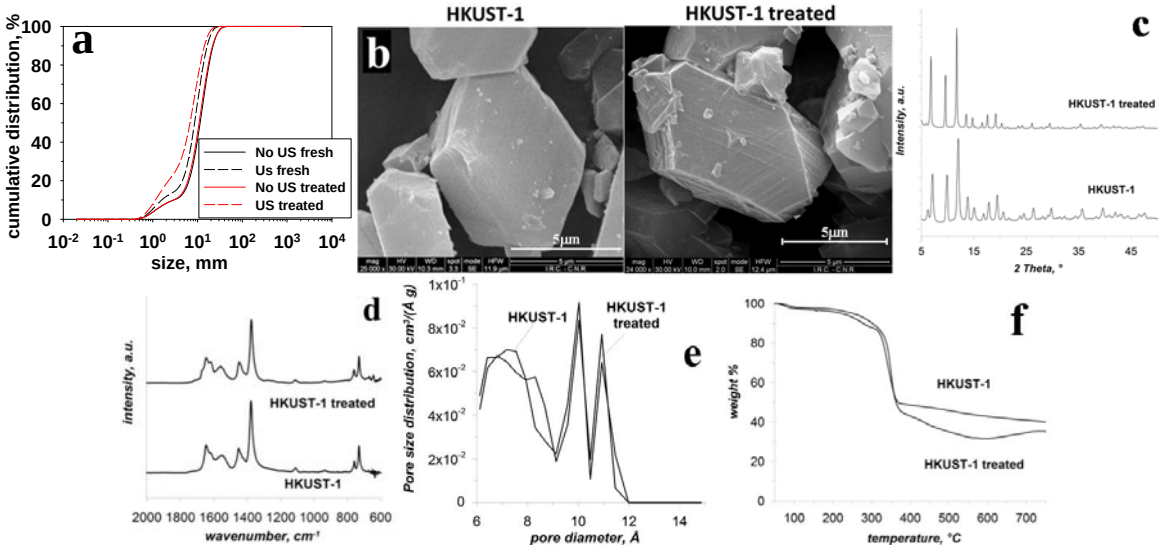

Figure 1: Freshly prepared HKUST-1 and regenerated after 10 cycles granulometric distribution (a), SEM image (b), X-ray diffraction (XRD) pattern (c), FT-IR spectra (d), pore size distribution (e) and thermogravimetric analysis in N_2 (f)

In Figure 2a the dimensionless pressure drops ($\Delta P/\Delta P_0$) curves (being ΔP and ΔP_0 the pressure difference across the bed and the static weight of the bed, respectively) obtained in ordinary conditions, by increasing (UP) and decreasing (DOWN) the superficial gas velocity (u), are reported. In these conditions the material cannot be fluidized (channelling occurs inside the bed) as clearly confirmed by the pressure drop curves, which do not reach an asymptotic value. 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 (Raganati et al, 2011b) enhancing at the same time the gas-solid contact efficiency. This is clearly confirmed by the regular fluidization curves typically obtaine

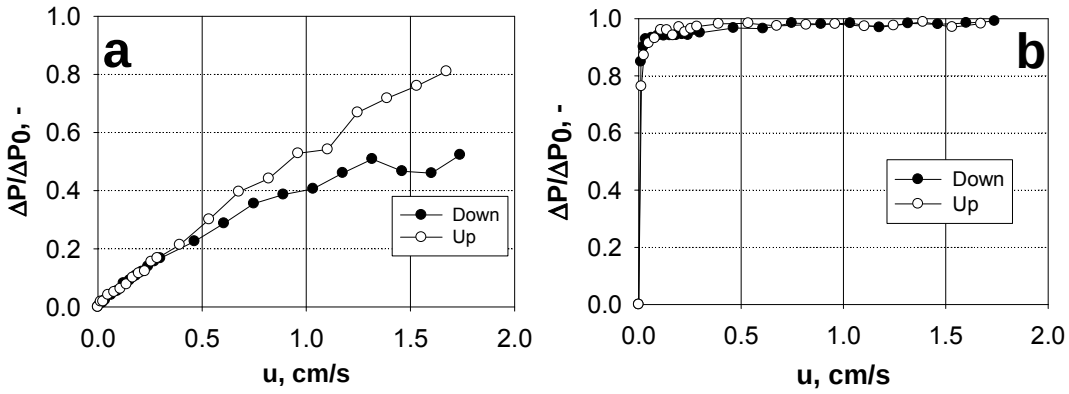

Figure 2: HKUST-1 pressure drop curves for (a) ordinary and (b) sound assisted, 140 dB - 120 Hz, tests

3.2 Adsorption tests and regeneration strategy

Figure 3a reports the typical breakthrough curves (i.e. C/C_0 versus time, C and C_0 being the CO_2 concentration in the effluent and feed stream, respectively) obtained in ordinary and sound assisted tests (140 dB – 120 Hz) at 1.5 cm/s and 15 %vol. of CO_2. These curves have been worked out to calculate: i) the moles of CO_2 adsorbed per unit mass of adsorbent, n_{ads}, calculated by integrating the breakthrough curves; ii) the breakthrough time, t_b, or break point, which is the time it takes for CO_2 to be detected at the adsorption column outlet (5 % of the inlet concentration); iii) the fraction of bed utilized at breakpoint, W, namely the ratio between the CO_2 adsorbed until t_b and that adsorbed until saturation; iv) the rate of the adsorption process, evaluated as the difference between the time it takes for CO_2 to reach the 95 % of C_0 at the adsorption column outlet, t_{95},

and t_b. The analysis of the curves suggests that the application of the sound greatly enhances t_b, which, in the sound assisted test (141 s) is more than five times that obtained in ordinary conditions (26 s).

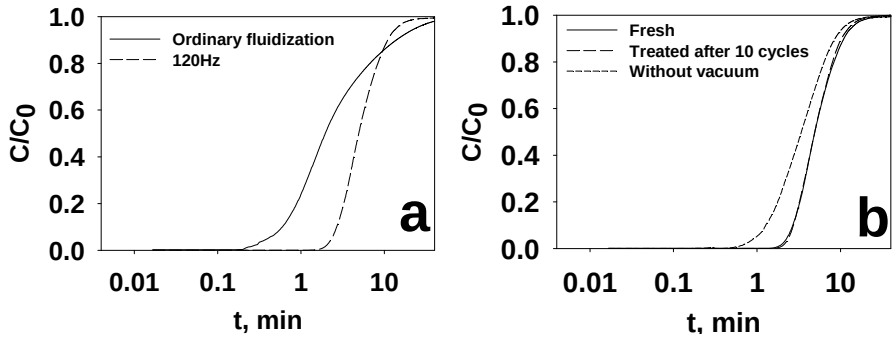

Figure 3: (a) HKUST-1 breakthrough curves under ordinary and sound assisted; (b) Effect of the regeneration strategy (140 dB – 120 Hz). C_0 = 15 %; u = 1.5 cm/s

The application of the sound also affects the global adsorption capacity. Indeed, the total amount of CO_2 adsorbed until saturation (1.14 mmol/g) is increased up to values of 53 % with respect to the tests performed in ordinary conditions (0.78 mmol/g). Moreover, in spite of the up-scaled synthesis procedure, which led to a lower control on HKUST-1 chemico-physical characteristics, the results obtained are remarkably higher than the values typically reported in literature for P_{CO_2}=0.1-0.15 atm (0.52-0.56 mol/kg, Sumida et al., 2012). This evidence is a further confirmation of the fact that the capture capacity of these types of materials (i.e. group C powders of Geldart's classification) strongly depends on the technology adopted for the adsorption tests. Most likely the peculiar fluid-dynamic conditions present inside a sound assisted fluidized bed make it possible to maximize the surface of solids exposed to the gas phase (by a continuous break-up of aggregates), thus significantly increasing the amount of CO_2 adsorbed until complete saturation of the bed. W is also greatly enhanced by sound, moving from 8 %,under ordinary conditions, up to 29 % under sound assisted conditions. Finally, the application of the sound greatly improves the kinetics of the entire process. Indeed, the application of acoustic fields allows to speed up the adsorption process: under sound assisted conditions the time for CO_2 to approach the saturation value is remarkably decreased, as confirmed by the lower value of t_{95}-t_b (18min) with respect to that obtained in ordinary conditions (30min), being the value of n_{ads} increased.
An accurate study has also been carried out in order to select an efficient regeneration strategy for HKUST-1. From the thermogravimetric analysis (Figure 1f) it is clear that 350 °C is a thermal limit of the material. So, two temperatures, 250 and 150 °C have been investigated as possible regeneration temperatures. However, before testing the material in the fluidization column, a CO_2 TPD analysis has been performed to have more detailed information about possible damages to the HKUST-1 structure. In both cases HKUST-1 has been found to be unstable: a temperature of 250 °C is too high since the sample starts decomposing at around 220 °C, according to the thermogravimetric analysis in inert atmosphere, whereas the treatment at 150 °C is too mild to properly regenerate the material by completely desorbing the CO_2 trapped into the pores.
On the basis of these results, it clearly emerges that the sole thermal treatment is not effective to properly regenerate HKUST-1. Therefore, a mixed regeneration strategy has been adopted: a bland temperature and vacuum have been combined by heating up the sample to 150 °C under a vacuum of 50mbar. This treatment has not been performed in the fluidized bed apparatus but extra-situ. In order to verify the repeatability of the adsorption tests and the effectiveness of this regeneration strategy (bland temperature and vacuum) the two tests performed at 140 dB-120 Hz (with 5 and 15 % CO_2 inlet concentration) have been carried out once again after 10 adsorption/desorption cycles and the obtained results have been compared to those relative to the first adsorption test under the same operating conditions. The adsorption effectiveness can be properly reproduced as confirmed by the overlap of the repeated test breakthrough curve with the original one (Figure 3b). As a further confirmation the same test has been repeated but regenerating the sample without vacuum, namely only heating the powder up to 150 °C. In this case the powder cannot be entirely regenerated and the adsorption effectiveness is remarkably worsened.
All these remarks regarding the effectiveness of the regeneration process and the repeatability of the adsorption tests have been confirmed by characterizing the sample after it has been subjected to several adsorption-desorption cycles (Figure 1). The XRD and FT-IR analyses (Figure 1c and d) showed that the sample keeps its crystallographic and chemical structure even after several adsorption-desorption treatments. This is also confirmed by the SEM image (Figure 1 b), which shows that the crystal is not affected by the treatments. Finally, the TG (Figure 1 f) plot confirms that the structure is the same as the fresh sample, indeed

the same collapse of the HKUST-1 structure can be observed at 350 °C. The particle and pore size distributions are also substantially unvaried (Figure 1a and f) as well as the BET surface area.

4. Conclusions

In this work sound assisted fluidization has been applied to HKUST-1 in order to evaluate its CO_2 capture efficiency under more realistic process conditions than those already experimented in literature. To this aim, the synthesis strategy has been up-scaled to the gram-scale, for the powder to be used in a lab-scale fluidization column. The experimental results show that the application of the sound confirms its ability to improve the gas-solid contact as well as the adsorption efficiency and that, in spite of the up-scaled synthesis procedure, HKUST-1 capture capacity is remarkably higher than the values typically reported in literature for P_{CO2}=0.1-0.15 atm. With reference to the regeneration strategy, it was shown that HKUST-1 starts decomposing around 220 °C, whereas 150 °C is too low to entirely regenerate it. Therefore, an extra-situ mixed regeneration strategy has been adopted: the sample has been heated up to 150 °C under a vacuum of 50mbar. The adsorption tests performed using a sample, which has been subjected to 10 adsorption/desorption cycles, confirm the effectiveness of this regeneration strategy. Indeed, HKUST-1 adsorption effectiveness can be properly reproduced. A further characterization of the cycled sample confirms that HKUST-1 keeps its chemico-physical features.

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