MAGNETIC NANOPARTICLES ENCLOSED IN METAL-ORGANIC FRAMEWORKS FOR MAGNETIC INDUCTION SWING ADSORPTION SEPARATION TECHNOLOGY

E. Tordi[1], G. Scipioni[1], M. Albino[2], A. Masi[3], C. Innocenti[2], D. Peddis[4], C. Sangregorio[2], F. Varsano[1], M. Bellusci[1]

[1]ENEA, C.R. Casaccia Via Anguillarese 301, Roma, Italy

[2]ICCOM-CNR and Dept. Of Chemistry Univ. Of Florence, via della Lastruccia 3, 50019 Sesto Fiorentino

[3]ENEA, C. R. Frascati Via Enrico Fermi 45, 00044 Frascati (RM), Italy

[4]Univ. of Genova, Dept. of Chemistry and Industrial Chemistry, Genova, Italy

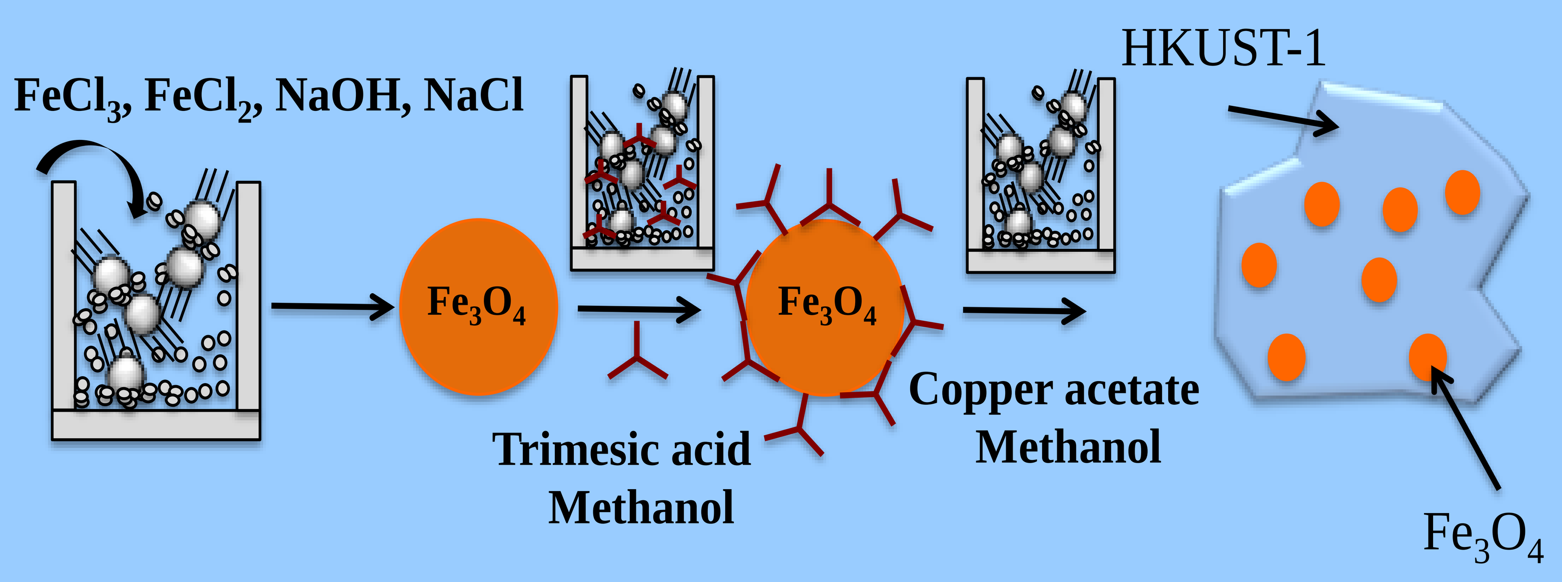
mariangela.bellusci@enea.it

Aim

The CO_2 separation processes currently used in the industrial sector result in a 25-50% increase in the energy needs of a power plant, this can substantially impact the energy costs of all production processes that require decarbonisation. It is in this context that has been recently proposed a novel separation process based on innovative sorbent materials capable of releasing the captured molecules under the stimulus of an alternating electromagnetic field. This separative technology named MISA (Magnetic Induction Swing Adsorption) by Saddiq et al [1], is based on the use of composite materials consisting of an organic component with high adsorption capacity for the molecule of interest and magnetic nanoparticles capable of heating up under the action of a magnetic field. The advantage of applying MISA instead of conventional heating is represented by the greater and proven efficiency of magnetic induction, compared to other heating methods, in the transfer of energy, thus prefiguring energy savings. We report the synthesis of magnetic Fe_3O_4@HKUST-1 metal-organic framework (MOF) nanocomposites by a simple, fast and sustainable mechanochemical process, its thermal, magnetic and morphological characterization and its functional properties, i.e its response to an externally applied magnetic field. The MOF HKUST-1 ($Cu_3(C_6H_3(COO)_3)_2(H_2O)_3$) was one of the first to be studied and used to separate CO_2/N_2 mixture from post combustion processes, has a high selectivity for CO_2 and the carbon dioxide uptake at 0.15 bar, typical of post combustion capture processes, is ranked among the best [2, 3].

Experimental

The synthesis of magnetite (Fe_3O_4) nanoparticles was carried out in a stainless steel grinding jar internally coated with Teflon as reported in our previous paper [2] in a SPEX 8000M shaker mill. With the intention of obtaining a magnetite with larger particle size, the "as synthesized" product was treated at 400° C for 10 min in He flow (50ml/min), such temperature was chosen on the basis of the thermal analysis. Magnetite nanoparticles have also been synthesized by developing a colloidal synthesis approach based on the thermal decomposition of iron acetylacetonate.



The Fe_3O_4@HKUST-1 magnetic framework composites (MFCs) have been synthesized by ball-milling. Operationally, the developed mechanochemical process involves two grinding phases; the first one consisted in the milling of the pre-synthesized magnetite in the presence of only trimesic acid and methanol (0.5ml, 10 minutes). This milling step induced a superficial functionalization of Fe_3O_4 nanoparticles. In the second stage (30 minutes milling), copper acetate was introduced with the addition of 4.5 ml of methanol, to carry out the actual synthesis of HKUST-1 on the nanoparticles. Both grindings were carried out under argon atmosphere with 6 zirconia balls (10 mm).The role of the functionalization step of the nanoparticles, is related to the idea of directing the growth of the MOF crystalline structure right on the surface of the magnetite particles, exploiting the principle whereby the nucleation of crystalline structures tends to occur preferentially on any particles present in the system, which act as "crystallization germs". The final product was left to air dry overnight, to proceed to purification the next day according to the method set up for the MOF HKUST-1. The scheme 1 shows a graphic description of the synthesis process. The reagents ratio was calculated to produce composites containing approximately 20wt% magnetite under dehydrated conditions. The produced samples are labeled, Fe_3O_4@HKUST-1, $Fe_3O_4$400@HKUST-1 and Fe_3O_4TD@HKUST-1 depending on the embedded magnetite nanoparticles. The produced nanomaterials were characterized in their structural, morphological, and thermal properties and were tested for CO_2/N_2 mixture separation.

References

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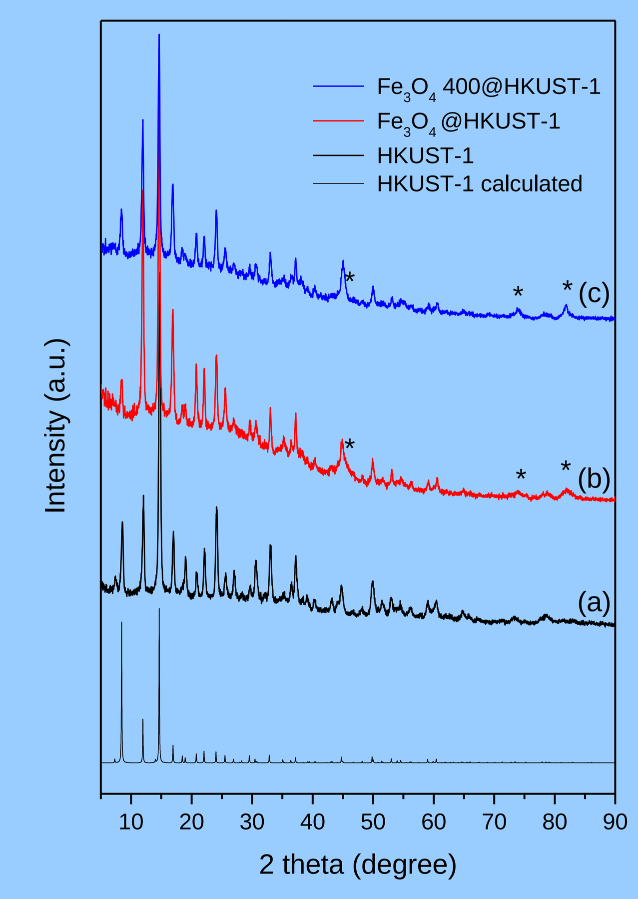
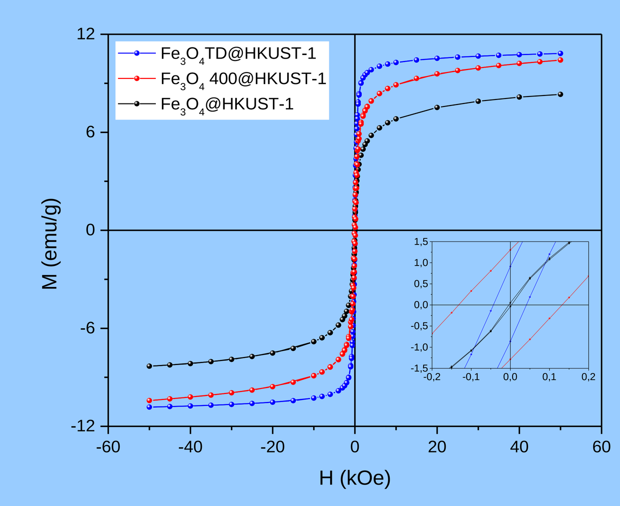
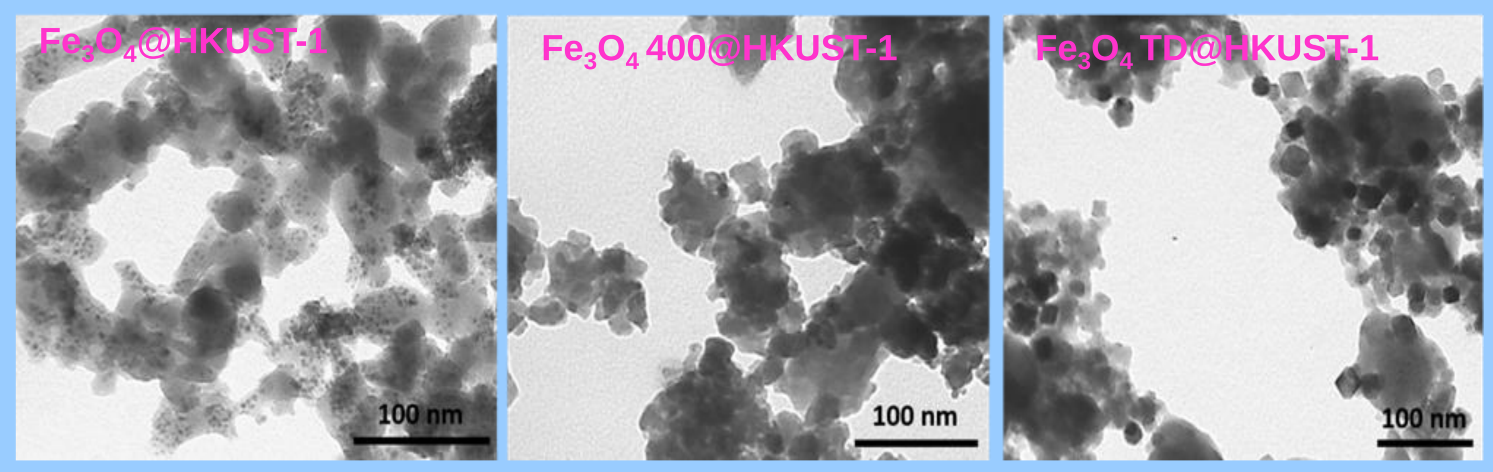
Results



Sample	Specific Surface BET (m^2/g)	Adsorption capacity CO_2 P=0.15bar (mmol/g)	Adsorption capacity N_2 P=0.75bar (mmol/g)	Selectivity	Temperature (K)
HKUST-1	1800±90	2,87 1,23 0,65	0,37 0,22 0,13	39 28 26	273 298 323
Fe_3O_4@HKUST-1	830±40	1,59 0,67 0,32	0,29 0,18 0,10	28 19 15	273 298 323
Fe_3O_4 400@HKUST-1	870±40	1,53 0,62 0,40	0,32 0,21 0,16	24 14 12	273 298 323
Fe_3O_4 TD@HKUST-1	960±50	1,29 0,60 0,44 0,06	0,30 0,18 0,15 ND	22 17 14 ND	273 298 308 403



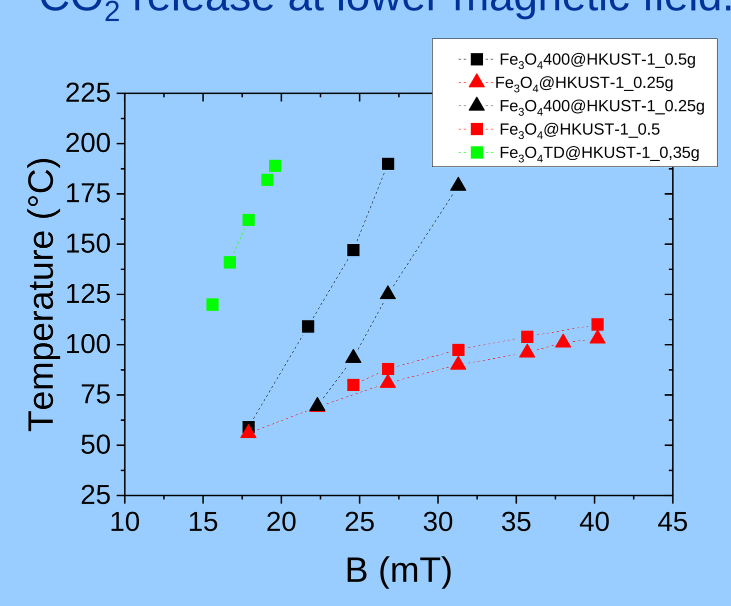


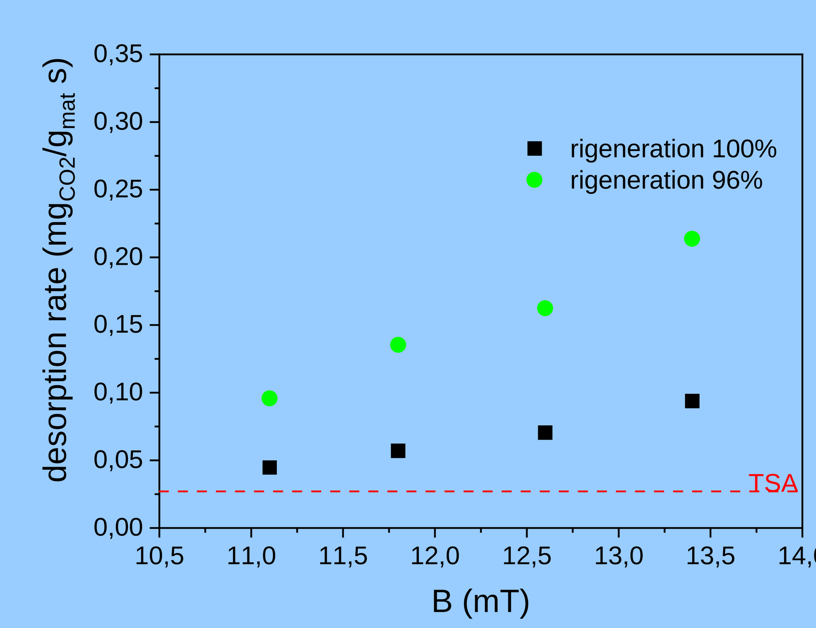
-The X-ray diffraction pattern on the synthesized MOF(a) and its composite with Fe_3O_4 together with a simulated pattern show that the structure of the material produced is in accordance to that expected. The diffraction patterns of the obtained composites show only the characteristic reflections of HKUST-1 and magnetite (*). The XRD profile of the composite obtained with Fe_3O_4 by thermal decomposition is the same.

-TEM images of the nanocomposites display the presence of a large number of inorganic nanoparticles, with the same morphology and average size of the pristine one, homogeneously distributed in the MOF.

-Specific BET area, adsorption capacity and selectivity are reported in table. The selectivities of the nanocomposites are lower than those measured for HKUST-1, confirming that the decrease of surface area observed in the nitrogen adsorption isotherms at 77K is due to a lower structural order of the organic component in the composite material. In fact, it can be easily argued that structural disorder has a greater influence on CO_2 adsorption, which tends to be favored in the microporous volume, compared to nitrogen adsorption, characterized by less specific interactions at room temperature and probably therefore less linked to the structuring of the porosity in the presence of the nanoparticles.

-The composite developed with nanoparticles obtained by liquid method show show better magnetic properties. This results in better heating properties and CO_2 release at lower magnetic field.





Composites materials showed comparable carbon dioxide adsorption capacity, indicating that for the same amount of incorporated magnetic material there is no appreciable influence on the sorbent capacity of the composite. On the contrary, the carbon dioxide desorption amount as a function of the applied magnetic field, for both composites measured under the same experimental conditions, reflects the observed difference between the maximum temperatures that can be reached by the two composites with the same energy supplied by the induction furnace. The composite Fe_3O_4@HKUST-1 in the reported experimental conditions is not 100% regenerable even at the highest applied magnetic fields. The composites made using magnetite treated at 400 °C or by liquid method on the contrary are 100% regenerable.

For the best sample (Fe_3O_4TD@HKUST-1), it is evident that for each field value applied the productivity of the heating process by induction is always higher than the traditional process (Thermal Swing Adsorption).