Magnetic nanoparticles incorporated in CALF-20 MOF for MISA assisted separation of CO_2/N_2 in post combustion mixtures

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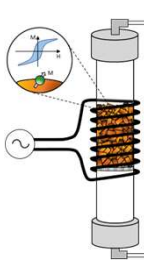
INDUCTION HEATING CAN TRIGGER THE REGENERATION OF SORBENT BEDS: Classically, the heat in a Temperature Swing Adsorption (TSA) process is supplied indirectly by using a pre-heated purge gas. Such method implies energy wastes at the outlet and the need to upgrade or purify the output stream from the purge dilution. By implementing **MAGNETIC COMPOSITES ADSORBENTS** such as magnetic nanoparticles embedded in MOF, heat can be generated in-situ by applying an alternating magnetic field. This is a fully electrified regeneration process named Magnetic Induction Swing Adsorption (MISA).



Main advantages

- **Heat is generated directly inside the sorbent bed; no heat transfer resistance**
- Very quick start up of desorption ($\Delta T>100°C/min$) allows increased productivity
- Helps decarbonizing chemical industry using sustainable electricity

Calgary Framework CALF-20 was demonstrated to preferentially adsorb CO_2 over H_2O in post-combustion mixtures.

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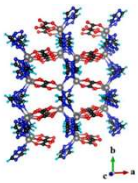
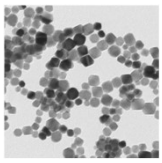


Synthesis and shaping of Fe_3O_4 @ CALF-20 composite

Sustainable synthesis by Liquid Assisted Grinding: **1 hour milling** in Spex Mixer/Mill. Ball to powder weight ratio 10. Washing in water

The Fe_3O_4 nanoparticles were synthesized by thermal decomposition of iron acetylacetonate in high boiling solvent, in the presence of surfactants



Fe_3O_4 nanoparticles (0.29g)

Triazole 1.25g
Zinc Oxalate =1.65g
Methanol = 2ml

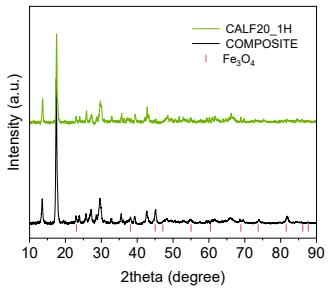
Magnetic MOF

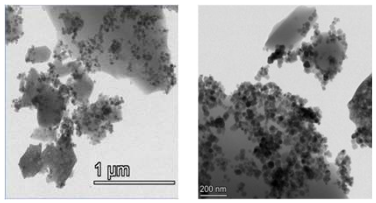
Powder

Granules

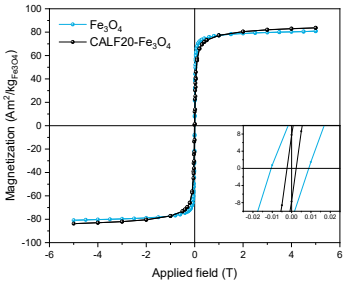
The Fe_3O_4 @ CALF-20 composite was shaped into granules using a 5% (w/w) Poloxamer acqueos solution. The solution was sprayed onto the powder placed in a specifically developed jar and kept rotating (80Hz for 8 hours) using a roll jar mill.

Characterization of Fe_3O_4 @ CALF-20 composite

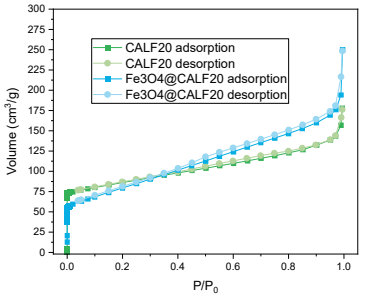




XRD Analysis performed on powders degassed at 180°C and closed in glass capillary show the typical diffractogram of CALF-20 with additional peaks belonging to Fe_3O_4.
The **TEM** images show that the magnetic nanoparticles are well dispersed on the surface of the MOF.

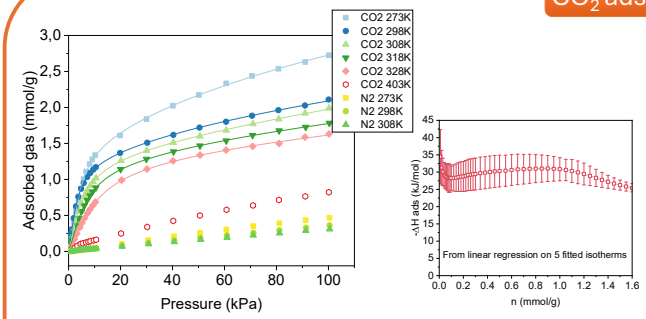


Magnetic properties of the composites and bare magnetite nanoparticles

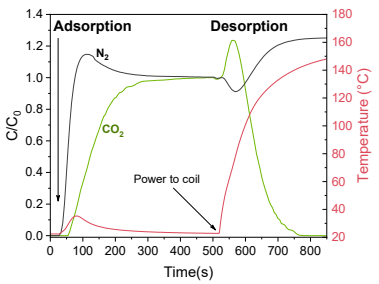


Nitrogen adsorption/desorption **isotherms at 77K** exhibits a type-I + type II (IUPAC) shape, typical of microporous materials followed by non horizontal plateau with negligible mesoporosity. The more pronounced inclination of the adsorption curve at intermediate pressure regimes measured for the composite is attributable to the presence of nanoparticles that contribute to a non microporous surface.
The specific surfaces of CALF20 and Fe_3O_4@CALF20 calculated by BET method are 320±16 m^2/g^{-1} and 280±16 m^2/g respectively.

CO_2 adsorption/desorption



CO_2 adsorption isotherms have been fitted by a dual-site Langmuir model.
CO_2 / N_2 Selectivity (308K) = 37
Working Capacity (308K-403K) = 0.35mmol/g
ΔH_{CO2}=-30 ± 4 kJ/mol



CO_2 desorption by induction heating
Ip= 105A, B=16.5mT, P=200W,
Fe_3O_4@ CALF-20 = 0.6g.
CO_2 20sccm N_2 110sccm

CONCLUSIONS
Fe_3O_4@CALF-20 magnetic composite has been produced by mechanochemical synthesis in 1 hour. The obtained material heats up under the effect of an alternating magnetic field allowing a fast desorption of the adsorbed carbon dioxide.

ENEA ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES, ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

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