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Synthesis, Characterization and Adsorption Capability of MOF-5

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ABSTRACT

Metal Organic Frameworks (MOF) are three dimensional organic-inorganic hybrid crystalline materials where a metal containing inorganic cluster is coordinated to a polydentate organic ligand. MOF-5 consists of Zn₄O inorganic moiety, that acts as secondary building unit, coordinating to benzene 1,4-dicarboxylate, a bidentate ligand that acts as spacers, to form a three dimensional structure. We report the synthesis of MOF-5 using zinc nitrate and terephthalic acid as precursors dissolved in dimethyl formamide. The synthesized MOF-5 has been characterized using Fourier Transform Infrared Spectroscopy, X-ray diffractometry, Thermal analysis, Scanning Electron Microscopy and Transmission Electron Microscopy. Surface morphology reveals well-ordered structures with large number of pores in meso-scale. Adsorption capability towards vapours and gases has been studied using ethanol and CO₂ as the model vapours using a chemi-resistive approach. Present results indicate that MOF-5 is a promising candidate for CO₂ sequestration and gas storage.

Key words: MOF-5, metal organic framework 5, CO₂ sequestration, H₂ storage

INTRODUCTION

Power generation from fossil fuels produces a large amount of CO₂ (Lashof and Ahuja, 1990), a green house gas and a major contributor to global warming. This poses a serious threat to the environment (Florides and Christodoulides, 2009). Even though alternate sources of energy are available, major portion of our energy demand is met by energy production from fossil fuels. Hence reducing CO₂ emission from power plants is necessary. The most feasible option of reducing CO₂ emission is its sequestration which can be achieved by adsorption on nanoporous materials (Saha *et al.*, 2010).

Hydrogen is a potential energy source and can be considered as an alternative to fossil fuels owing to elimination of risk of green house gas emission. Complete usage of hydrogen as an energy source can be realised if a proper storage system for hydrogen becomes available. Hydrogen, being the lightest element requires large volume to store even for a small mass. Hence, it is currently being stored as liquefied hydrogen or in the compressed form or in its hydride form or by means of adsorption on a porous carrier (Dillon and Heben, 2001). Cryogenic hydrogen storage requires large

amount of energy for condensation. Storage in the form of solid chemical hydrides requires recycling of their decomposition products and storage as metal hydrides is prone to impurities and is costly (Yaghi and Rowsell, 2005). Storage by adsorption on carbon materials is also not a powerful method as the adsorption efficiency is very low at room temperature and high pressure (Yaghi and Rowsell, 2005). Numerous efforts have been made to prepare cost-effective adsorbents from plant-based and agro-based sources (Ponnusami *et al.*, 2008; Srihari and Das, 2008a, b; Krishna Prasad and Srivastava, 2009; Ponnusami *et al.*, 2009, 2010). However, they are mostly amorphous and lack ordered pores. MOFs are good adsorbents and can be used for hydrogen storage (Rosi *et al.*, 2003).

MOF is a new class of porous materials with large surface area ranging from 1000 to 4500 m² g⁻¹ (Yaghi and Rowsell, 2005). They can be used for both hydrogen storage and carbon dioxide sequestration (Schroder *et al.*, 2010). They are basically made up of two parts: (1) an inorganic cluster-called as the node and acts as the secondary building unit and (2) an organic multidentate bridging ligand between two inorganic clusters-called as spacers (Civalleri *et al.*, 2006). Hydrogen and CO₂ can be stored in MOFs by means of physisorption (Sastre, 2010).

Li *et al.* (1999) designed MOF-5 that can be used for several applications including gas storage and separation. MOF-5, also called as IRMOF-1, is a zinc based metal-organic framework that is made up of [Zn₄O]⁶⁺ inorganic moiety as the vertex and benzene dicarboxylic acid as the bifunctional bridging ligand of the crystal (Civalleri *et al.*, 2006). MOF-5 crystal has a symmetric fcc lattice structure (Zhou and Yildirim, 2008). MOFs can be modified or functionalized to improve their pore textural and adsorption properties (Stergiannakos *et al.*, 2010).

In this study, we report the synthesis of MOF-5 by two different procedures, followed by its characterization and evaluation of adsorption capabilities by using ethanol and CO₂ as the model vapours.

MATERIALS AND METHODS

Synthesis: MOF-5 was synthesized by the first two procedures reported in the literature (Saha *et al.*, 2007), dried in vacuum oven at 120°C for 2 h and stored in vacuum desiccator. The samples obtained from the two procedures are named as Sample A and B. The precursors and solvents zinc nitrate hexahydrate, dimethyl formamide, hydrogen peroxide, triethyl amine and chloroform were bought from Merck, India and terephthalic acid was bought from Loba Chemie, India. They were used as such without further purification.

Characterization

FTIR spectroscopy: FTIR spectra were recorded in FTIR spectrophotometer (Spectrum-100, Perkin-elmer, USA) to ascertain the presence of functional groups in the synthesized samples. The sample was scanned over the spectral region of 400 to 4000 cm⁻¹(10 scans).

X-Ray diffractometry: X-Ray diffraction analysis was done to study the crystal structure in a powder X-Ray diffractometer (X'PERT-PRO, PANalytical, Netherlands) with CuK_α (λ-1.54Å) source over the range of 5°<2θ<40°.

Thermal analysis: Thermogram of the samples was recorded by increasing the temperature from 25 to 1000°C at the rate of 10°C min⁻¹ under nitrogen purge using a simultaneous Thermo Gravimetry-Differential Thermal Analyser (SDT Q600, TA instruments, USA).

Scanning electron microscopy: The morphology and surface texture of the samples were analysed using a Field Emission Scanning Electron Microscope (JSM 6701F, JEOL, Japan). Samples were mounted on a brass stub with double sided carbon tape and platinum was sputter coated onto the samples at a current of 20 mA to form a thin conducting layer. Sputter coated samples were introduced into the specimen chamber of the electron microscope through the exchange chamber. Samples were imaged using the secondary electron detector under ultra high vacuum at an accelerating voltage of 3kV.

Transmission electron microscopy: Porous nature of the samples was analysed in a 200 kV Field Emission Transmission Electron Microscope (JEM 2100F, JEOL, Japan). The samples were dispersed in ethanol and a drop of the dispersion was placed on a copper grid for imaging.

Adsorption studies: Sample B was made into a pellet with a thickness of 3 mm and diameter of 6 mm in a tablet pressing machine (KI356, Khera Instruments, India).

Adsorption capability of sample B was tested by passing ethanol vapour at 5 ppm in a home made sensing chamber as detailed in our earlier papers (Sivalingam *et al.*, 2011a, b and c). Similarly, CO₂ adsorption capability of the same sample was studied by passing CO₂ at 100 ppm into a vacuum chamber (12A4D, Hind High Vacuum Co. (P) Ltd., India). Resistance without passing any gas was also measured in respective chambers for comparison. In both the cases change in resistance due to adsorption of gases on the surface was studied using an electrometer (6517A, Keithley Instruments Inc., USA).

RESULTS

FTIR spectra: Figure 1 shows the FTIR spectra of samples A and B. The spectra confirm the presence of MOF-5 in both the samples. Two sharp peaks were obtained at 1582 and 1374 cm⁻¹ in sample A and 1579 and 1365 cm⁻¹ in sample B. Several small peaks were seen in the range of 1225 to 950 cm⁻¹, 900 to 670 and 500 cm⁻¹ in both the samples. A sharp narrow peak at 3603 cm⁻¹ and a broad peak at 3409 cm⁻¹ in sample A and 3380 cm⁻¹ in sample B were also seen.

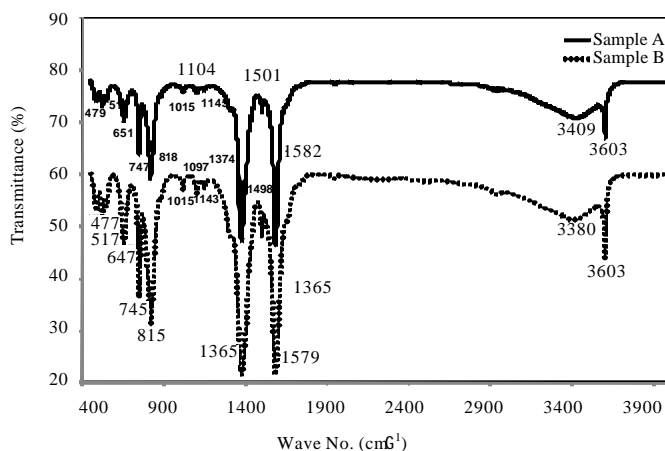


Fig. 1: Fourier transform infra red spectra of samples A and B

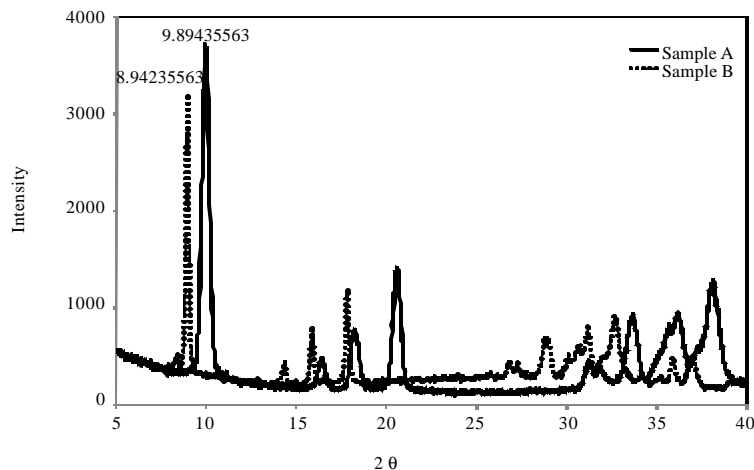


Fig. 2: Powder X-ray diffraction pattern of samples A and B

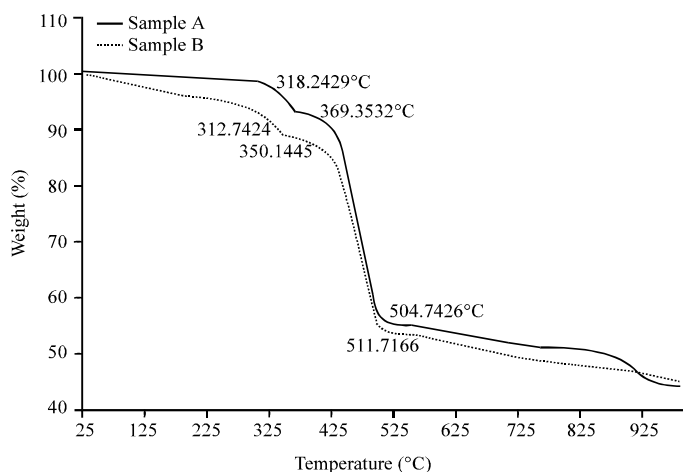


Fig. 3: Thermogram of samples A and B

X-Ray diffraction: The X-Ray diffractograms of the samples A and B are shown in Fig. 2. Sample A and B showed a sharp intense peak at 9.89° and 8.94° , respectively.

Thermal gravimetric analysis: Figure 3 represents the thermogram of samples A and B. Weight loss occurred at 2 stages: around 330°C and 360 to 512°C in sample A and 311°C and 350 to 512°C in sample B.

Scanning electron microscopy: The scanning electron micrographs of samples A and B are shown in Fig. 4. Particles in the size range of 10 to 15 nm were found decorating the surface.

Transmission electron microscopy: The transmission electron micrographs of samples A and B are shown in Fig. 5. The figure shows that MOF-5 possessed many small pores of the order of 2 to 4 nm.

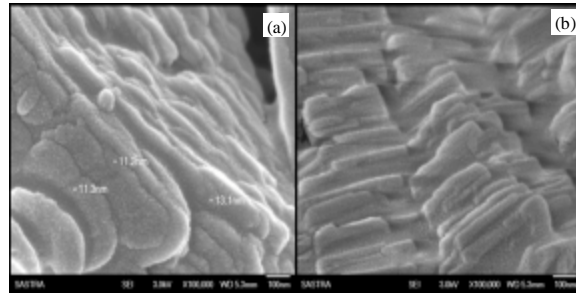


Fig. 4(a-b): Scanning electron micrographs of samples A and B

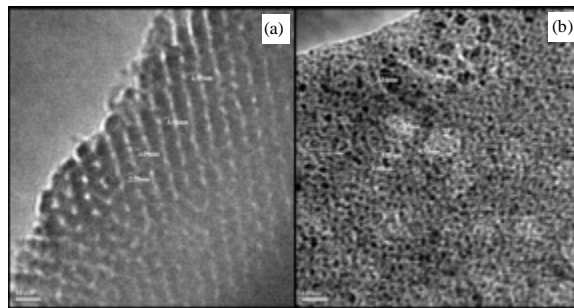


Fig. 5(a-b): Transmission electron micrographs of samples A and B

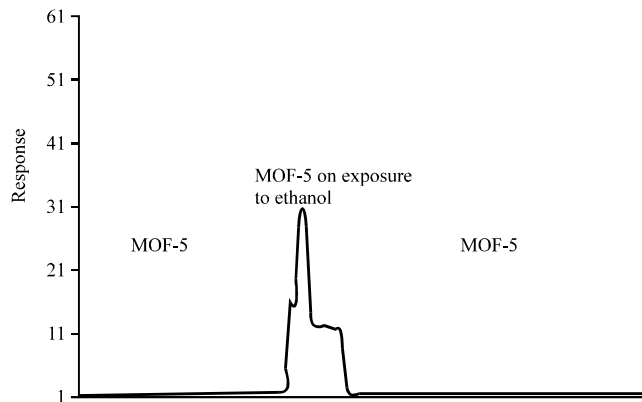


Fig. 6: Plot representing the response of sample B while presenting ethanol vapour

Adsorption capability: Figure 6 and 7 show the resistance variation that occurred during the adsorption of ethanol vapour and CO_2 on sample B. The adsorption and desorption ability of the synthesized MOF-5 was tested by presenting various concentrations of ethanol vapour and CO_2 at room temperature in static condition. An appreciable change in resistance with reference to baseline resistance was observed when 5 ppm of ethanol and 100 ppm of CO_2 were presented. The response was found to be 30.

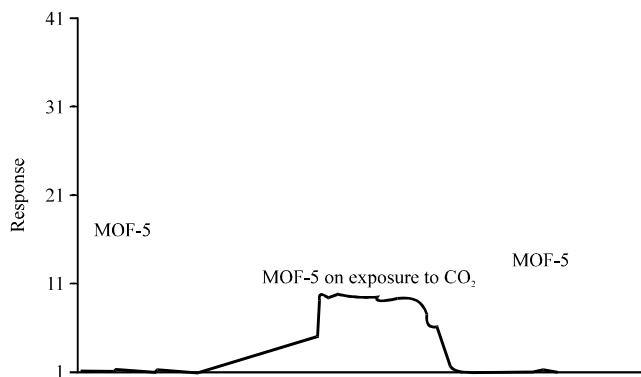


Fig. 7: Plot representing the response of sample B while presenting CO_2

DISCUSSION

FTIR spectra (Fig. 1) confirm the presence of all the functional groups present in MOF-5. The two sharp peaks obtained at 1582 and 1374 cm^{-1} in sample A and 1579 and 1365 cm^{-1} in sample B correspond to the symmetric and asymmetric stretching of C-O bonded to Zn, respectively (Sabouni *et al.*, 2010). Several small peaks occurring in the range of 1225 to 950 cm^{-1} correspond to the in-plane bending of the C-H group present in the benzene ring of the BDC linker (Coates, 2000). Similarly, the small peaks occurring in the range of 900 to 670 cm^{-1} are because of the out of plane bending of the C-H group of the benzene ring of the BDC linker (Coates, 2000). Peaks occurring around 500 cm^{-1} are characteristic of Zn-O stretching. The broad peak at 3409 cm^{-1} in sample A and 3380 cm^{-1} in sample B denote the minor quantity of adsorbed O-H groups on the MOF structure. The sharp narrow peak at 3603 cm^{-1} is because of the O-H stretch of the non-bonded hydroxy groups (Coates, 2000).

The X-Ray diffractograms (Fig. 2) correspond with that of the pattern obtained by Saha *et al.* (2007). It is evident from the diffractograms that both the samples were crystalline in nature. The sharp peak at 9.89° in sample A is similar to the one got by Sabouni *et al.* (2010). Spectra of sample B shows more similarity to the spectra obtained by Saha *et al.* (2007). This is characteristic of [220] plane with $d = 8.89\text{ \AA}$ in sample A and 10.59 \AA in sample B confirming the highly porous nature of MOF-5 (Buso *et al.*, 2011).

Weight loss in two stages observed during thermal analysis (Fig. 3) can be attributed to the evaporation of non volatile adsorbed species like DMF during the first stage and decomposition of the framework structure during the second stage (Choi *et al.*, 2006). Both the samples showed overall thermal stability up to 350°C .

It is evident from the SEM images (Fig. 4) that the powder morphology is well ordered for both the samples. TEM images (Fig. 5) reveal that sample B contains larger number of pores (0.5 to 4 nm) implying potentially high surface area. Hence sample B has been chosen for further adsorption studies. The large change in resistance (Fig. 6, 7) upon exposure to lower concentrations of ethanol and CO_2 demonstrate the availability of large number of sites for interaction between MOF-5 and ethanol/ CO_2 . This confirms the high surface area and the adsorption capability of MOF-5 towards these species.

CONCLUSION

MOF-5 samples synthesized by two different methods are similar in composition but have different crystal and pore structure. The MOF-5 samples were found to be stable at temperatures up to 350°C and hence they can be used in high temperature applications. Adsorption studies show that they are capable of adsorbing gases and hence can be used for CO₂ sequestration and H₂ storage.

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