Journal of Applied Sciences

ISSN 1812-5654

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 12 (16): 1681-1685, 2012
ISSN 1812-5654 / DOI: 10.3923/jas.2012.1681.1685

Metal Organic Framework (MOF-5) For Sensing of Volatile Organic Compounds

[1]N. Iswarya, [2]M. Ganesh Kumar, [2]K.S. Rajan and [1]John Bosco Balaguru Rayappan
[1]Centre for Nanotechnology and Advanced Biomaterials, SASTRA University, India
[2]School of Electricals and Electronics Engineering,
Centre of Nanotechnology and Advanced Biomaterials, SASTRA University, India

Abstract: Metal Organic Framework-5 (MOF-5) can be used for sensing of Volatile Organic Compounds (VOCs). VOCs are emitted from biological sources, paints, coatings, etc. and they pollute the environment thus posing serious health and environmental hazards. MOF-5 is a three dimensional crystalline coordination compound made up of Zn_4O inorganic group as the vertex and benzene decarboxylate organic group as the spacer in the unit cell of the crystal. This study reported the synthesis and characterization of MOF-5 and its capability towards sensing of VOCs like ethanol, formaldehyde and acetone. Transmission Electron Micrograph reveals that the synthesized sample is highly crystalline and porous. BET surface area obtained was found to be 230 $m^2\ g^{-1}$. MOF-5 was made into pellets of thickness around 3 mm for sensing purposes. The material was found to be sensitive towards ethanol even at concentrations as low as 5 ppm, towards formaldehyde at higher concentrations and towards acetone at concentrations as low as 10 ppm. The order of increase in sensitivity is ethanol>formaldehyde>acetone.

Key words: Metal organic framework, sensing of volatile organic compounds, MOF sensors

INTRODUCTION

Volatile Organic Compounds (VOCs) are compounds with carbon and hydrogen whose boiling point ranges from 50-250°C. VOCs include acetone, formaldehyde, toluene, etc. (Health Canada, 1995). The sources of these VOCs are biogenic like plants, animals, fungi, etc. and anthropogenic like paints and coatings and chlorofluorocarbons (Goldstein and Galbally, 2007). These compounds, even in minor quantities, affect the indoor air quality (Silva *et al*., 2008). The ill effects of exposure to these compounds in humans include sick building syndrome (Silva *et al*., 2008), respiratory disorders and sensory irritation (Salonen *et al*., 2009) and cancer (Guo *et al*., 2004).

Ethanol in its native form is not a harmful agent but formaldehyde, the oxidation product of ethanol is toxic. Formaldehyde causes optical and nasal irritation and sick building syndrome (Takigawa *et al*., 2010). Formaldehyde is released into the environment from urea-formaldehyde resins of plywood in furniture, adhesives and water pre-treatment processes and as a natural metabolite (Salonen *et al*., 2009). Acetone which is harmless at lower concentrations, causes sensory irritations at very high concentrations.

A method to sense the presence of VOCs in the environment is essential. The currently available methods for sensing of VOCs are chemiresistive sensing, optical fibre sensing (Silva *et al*., 2008) and potentiometric sensing using NiO thin film electrode (Sato *et al*., 2010). Metal Organic Frameworks (MOFs) can also be used for sensing of VOCs (Zou *et al*., 2009).

MOFs are porous, crystalline and high surface area coordination compounds with an inorganic cluster in the vertex and an organic ligand as the spacer in their unit cell (Rowsell and Yaghi, 2005). MOF-5 is made up of $[Zn_4O]^{6+}$ in the vertex and terephthalic acid as the spacer in the unit cell (Civalleri *et al*., 2006). MOF sensors can be fabricated by making a self assembled monolayer of MOF on gold substrates (Shekhah *et al*., 2011) or by making pellets (Achmann *et al*., 2009).

In this study we report the use of MOF-5 pellets for sensing of VOCs like ethanol, formaldehyde and acetone.

MATERIALS AND METHODS

MOF-5 was synthesized by the second procedure reported in literature (Saha *et al*., 2009; Iswarya *et al*., 2012). The precursors used for the synthesis of MOF-5 were zinc nitrate hexahydrate, terephthalic acid, triethyl

---

Corresponding Author: K.S. Rajan, School of Electricals and Electronics Engineering,
Centre of Nanotechnology and Advanced Biomaterials, SASTRA University, India

amine, hydrogen peroxide and chloroform. All the precursors were procured from Merck, India except terephthalic acid which was procured from LobaChemie, India. They were used as such without further purification.

CHARACTERIZATION

Fourier transform infra-red (FTIR) spectroscopy: FTIR spectrum was recorded in FTIR spectrophotometer (Spectrum-100, Perkin-Elmer, USA) to confirm the presence of the required functional groups in the synthesized sample. The sample was scanned over the spectral region of 400 to 4000 cm^{-1} (10 scans).

X-ray diffraction analysis: X-ray diffraction pattern of the synthesized sample was recorded in a X-ray diffractometer (D8 Focus, Bruker, Germany) with CuK source over the range of $5° < 2\theta < 40°$.

Transmission electron microscopy: The sample was imaged in a 200 kV Field Emission Transmission Electron Microscope (JEM 2100F, JEOL, Japan) to confirm its porous nature. The sample was dispersed in ethanol and a drop of the dispersion was placed on a copper grid for imaging.

Micrometrics: Pore size, pore size distribution, pore area and volume analysis were done in a mercury intrusion porosimeter (AutoPore IV 9500 V 1.07, Micromeritics, USA). Analysis was done based on the amount of mercury that intrudes into the pores at pressure in the range of 0-25000 psi.

Sensing studies: Pellets of 6 mm diameter and 3 mm thickness were made from the synthesized material in a tablet pressing machine (KI356, Khera Instruments, India). Electrical contacts were made to the pellet and resistance change on exposure to gases was measured using an electrometer (6517A, Keithley Instruments Inc., USA). Measurements were made by keeping the pellet in a home made sensing chamber of 6.4 L capacity with a septum for introducing the gases as described in our earlier work (Sivalingam *et al.*, 2012).

Sensing studies for ethanol (Merck, India) at 5 ppm, formaldehyde (Merck, India) at 5-100 ppm and acetone (Merck, India) at 5-15 ppm were done in the above described chamber by introducing the gas through the septum.

RESULTS

Fourier transform infra-red spectrum: Figure 1 shows FTIR spectrum of MOF-5 sample. Two sharp intense peaks were seen at 1581 and 1361 cm^{-1}. Several small peaks in the range of 1225-950 cm^{-1} and 800-650 cm^{-1} and 500 cm^{-1} were seen. A broad peak at 3403 cm^{-1} was observed.

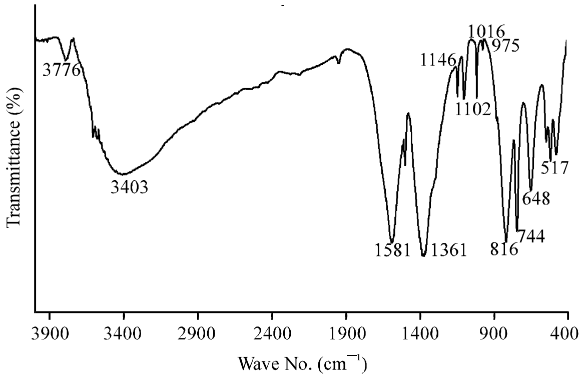

Fig. 1: FTIR spectrum of MOF-5

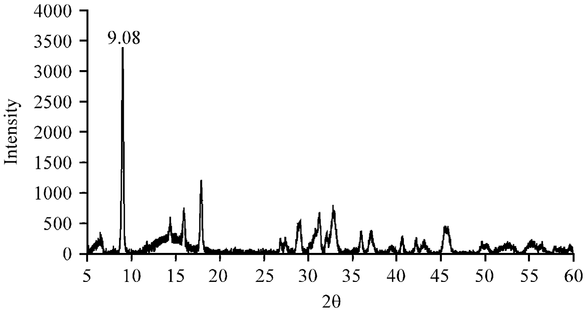

Fig. 2: X-ray diffractogram of MOF-5

X-ray diffractometry: Figure 2 shows the X-ray diffractogram of MOF-5. A sharp intense peak at 2 (theta) = 9.08 was seen.

Transmission electron microscopy: Figure 3 shows the Transmission Electron Micrograph of MOF-5. The image reveals the presence of unordered pores of dimensions below 10 nm.

Micrometric analysis: Figure 4 shows the graph of cumulative pore area ($m^2\ g^{-1}$) vs. pore size diameter (μm). BET surface area obtained from porosimeter analysis is 230 $m^2\ g^{-1}$. The sample was found to be 66.86% porous and the total pore area was 4.754 $m^2\ g^{-1}$.

Sensing studies: Figure 5 shows the graph representing the response of MOF-5 towards acetone, formaldehyde and ethanol at 5 ppm. The response was found to be 0.0872, 0.5216 and 30.36 for acetone, formaldehyde and ethanol, respectively.

Figure 6 shows the graphical representation of response of MOF-5 on presenting formaldehyde gas at

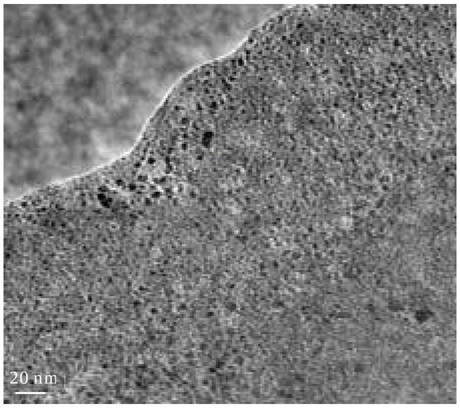

Fig. 3: Transmission electron micrograph of MOF-5

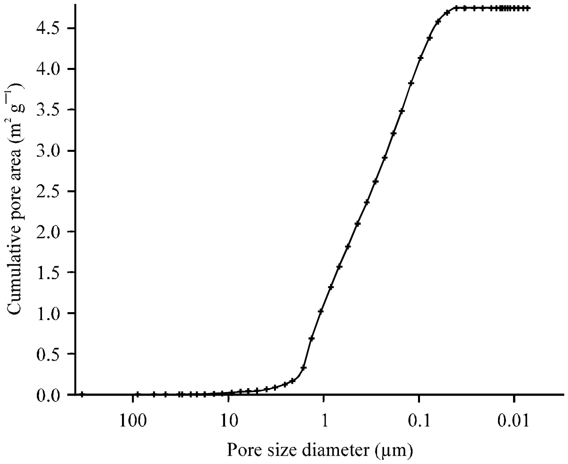

Fig. 4: The cumulative pore area at various pore size diameter for cycle 1 intrusion

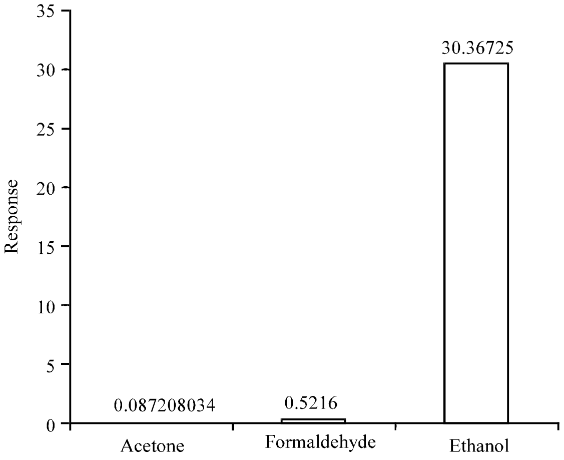

Fig. 5: The response of MOF-5 towards acetone, formaldehyde and ethanol at 5 ppm

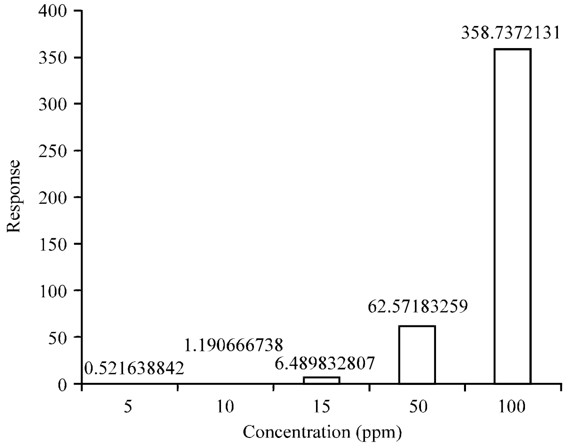

Fig. 6: The response of MOF-5 towards formaldehyde at various concentrations

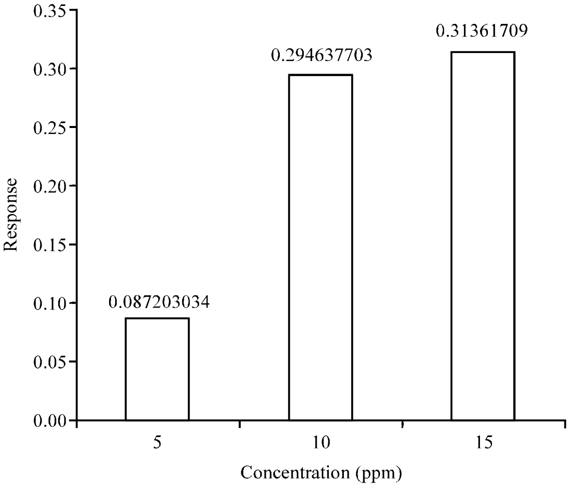

Fig. 7: The response of MOF-5 towards acetone at various concentrations

different concentrations. The response increased linearly and it was 358.73 at 100 ppm of formaldehyde.

Figure 7 shows the graphical representation of response of MOF-5 towards acetone at different concentrations. The response was found to be 0.087, 0.294 and 0.313 for 5, 10 and 15 ppm of acetone, respectively.

DISCUSSION

FTIR spectrum (Fig. 1) confirms the presence of the required functional groups present in MOF-5. The peaks at 1581 and 1361 cm^{-1} are characteristic of the symmetric and asymmetric stretching of C-O bonded to benzene ring present in the linker (Sabouni *et al*., 2010). Several small peaks seen in the region of 1225-950 cm^{-1} and

800-650 cm^{-1} are because of the in-plane and out of the plane stretching of the aromatic C-H groups of the benzene ring present in terephthalic acid (Coates, 2000). The peaks around 3000 cm^{-1} are because of the adsorbed moisture content (Coates, 2000).

The X-ray diffractogram (Fig. 2) is similar to the one obtained by Saha *et al.* (2009). The peak at $2\theta = 9.08°$ with $d = 9.73$ Å is characteristic of MOF-5 and confirms that it is highly crystalline.

Transmission electron micrograph (Fig. 3) shows that the sample is highly crystalline and porous with unordered pores. The presence of large number of pores contributes to the high surface area of MOF-5.

The porous nature of the sample is confirmed by the total porosity of 66.86% obtained from porosity analysis. BET surface area of 230 m^2 g^{-1} (Fig. 4) is a reasonably good surface area and it makes MOF-5 suitable for sensing experiments.

Figure 6 shows that the sensitivity towards ethanol is better than that of formaldehyde and acetone. So the response of MOF-5 at higher concentrations of acetone and formaldehyde were tested. Sensitivity towards formaldehyde increases linearly as the concentration of formaldehyde increases from 5-100 ppm. There is an increase in the sensitivity towards acetone when the concentration of acetone increases from 5-10 ppm and the increase at 15 ppm is very low.

CONCLUSION

MOF-5 shows good sensitivity towards ethanol even at concentrations as low as 5 ppm. MOF-5 shows a linear increase in response as concentration of formaldehyde increases. Increase in response at increasing concentrations of acetone stabilizes at 10-15 ppm and the highest concentration at which it can sense acetone is 10 ppm. The material is highly selective towards ethanol. From the results obtained it is evident that MOF-5 is a promising candidate for sensing of VOCs in testing indoor air quality.

ACKNOWLEDGMENT

This study was supported by (i) PG teaching grant No. SR/NMPG-16/2007 of Nano Mission Council, Department of Science and Technology (DST), India.

REFERENCES

Achmann, S., G. Hagen, J. Kita, I.M. Malkowsky, C. Kiener and R. Moos, 2009. Metal-organic frameworks for sensing applications in the gas phase. Sensors, 9: 1574-1589.

Civalleri, B., F. Napoli, Y. Noel, C. Roettia and R. Dovesi, 2006. Ab-initio prediction of materials properties with CRYSTAL: MOF-5 as a case study. Cryst. Eng. Comm., 8: 364-371.

Coates, J., 2000. Interpretation of Infrared Spectra, A Practical Approach. In: Encyclopedia of Analytical Chemistry, Meyers, R.A. (Ed.). John Wiley and Sons Ltd., New York, pp: 10815-10837.

Goldstein, A.H. and I.E. Galbally, 2007. Known and unexplored organic constituents in the earth's atmosphere. Environ. Sci. Technol., 41: 1514-1521.

Guo, H., S.C. Lee, L.Y. Chan and W.M. Li, 2004. Risk assessment of volatile organic compounds in different indoor environments. Environ. Res., 10: 57-66.

Health Canada, 1995. Indoor air quality in office buildings: A technical guide. A Report of the Federal-Provincial Advisory Committee on Environmental and Occupational Health. Minister of National Health and Welfare.

Iswarya, N., M.G. Kumar, K.S. Rajan and R.J.B. Balaguru, 2012. Synthesis, characterization and adsorption capability of MOF-5. Asian J. Sci. Res., 5: 247-254.

Rowsell, J.L.C. and O.M. Yaghi, 2005. Strategies for hydrogen storage in metal-organic frameworks. Angew. Chem. Int. Ed., 44: 4670-4679.

Sabouni, R., H. Kazemian and S. Rohani, 2010. A novel combined manufacturing technique for rapid production of IRMOF-1 using ultrasound and microwave energies. Chem. Eng. J., 165: 966-973.

Saha, D., S. Deng and Z. Yang, 2009. Hydrogen adsorption on metal-organic framework (MOF-5) synthesized by DMF approach. J. Porous Mater., 10: 141-149.

Salonen, H., A.l. Pasanen S. Lappalainen, H. Riuttala, T. Tuomi, P. Pasanen, B. Back and K. Reijula, 2009. Volatile organic compounds and formaldehyde as explaining factors for sensory irritation in office environments. J. Occup. Environ. Hyg., 6: 239-247.

Sato, T., V.V. Plashnitsa, M. Utiyama and N. Miura, 2010. Potentiometric YSZ-based sensor using NiO sensing electrode aiming at detection of volatile organic compounds (VOCs) in air environment. Electrochem. Commun., 12: 524-526.

Shekhah, O., J. Liu, R.A. Fischer and C. Woll, 2011. MOF thin films: existing and future applications. Chem. Soc. Rev., 40: 1081-1106.

Silva, L.I.B., T.A.P. Rocha-Santos and A.C. Duarte, 2008. Sensing of volatile organic compounds in indoor atmosphere and confined areas of industrial environments. Global NEST J., 10: 217-225.

Sivalingam, D., J.B. Gopalakrishnan and J.B.B. Rayappan, 2012. Structural, morphological, electrical and vapour sensing properties of Mn doped nanostructured ZnO thin films. Sens. Actuators B Chem., 166-167: 624-631.

Takigawa, T., W. Bing-Ling, K. Morimoto, K. Nakayama, M. Tanaka, E. Shibata and T. Yoshimura *et al*., 2010. Relationship between indoor chemical concentrations and subjective symptoms associated with sick building syndrome in newly built houses in Japan. Int. Arch. Occup. Environ. Health, 83: 225-235.

Zou, X., G. Zhu, I.J. Hewitt, F. Sun and S. Qiu, 2009. Synthesis of a metal-organic framework film by direct conversion technique for VOCs sensing. Dalton Trans., 16: 3009-3013.