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Carbon dioxide gas detection by open metal site metal organic frameworks and surface functionalized metal organic frameworks

Venkateswarlu Pentyala[a,b,*], Polina Davydovskaya[a,c], Martin Ade[d], Roland Pohle[c], Gerald Urban[a,b]

[a] Department for Microsystem Engineering, University of Freiburg, Freiburg, Germany
[b] Freiburg Materials Research Center, University of Freiburg, Freiburg, Germany
[c] Siemens AG, Corporate Technology, Munich, Germany
[d] Institute of Inorganic and Analytical Chemistry University of Freiburg, Freiburg, Germany

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ABSTRACT

Novel nanoporous materials known as Metal-Organic Frameworks (MOFs) are currently attracting wide attention due to their potential applications such as gas storage, gas separation and catalysis. Recently, MOF materials were also developed for chemical sensors. In this work, for the first time iso-structural MOFs M-MOF-74 (where M = Mg, Ni, Co and Zn) and ethylenediamine functionalized Mg-MOF-74 were investigated as selective CO2 gas sensing material for the work function read-out based method at ambient temperature and different humidity levels. M-MOF-74s are very interesting MOFs because they contain coordinatively unsaturated metal centers where adsorbates can interact strongly with their affinity towards gas molecules. Interaction of the CO2 molecules with open metal sites or amine-functional groups changes the work function ($\Delta\Phi$) of sensing layer which can serve as a signal for gas sensors. Results show that ethylenediamine functionalized Mg-MOF-74 exhibited enhanced CO2 gas sensing properties compared to other M-MOF-74 with respect to sensitivity, reversibility and stability.

1. Introduction

In recent years, there has been an uprising of research and developmental activities on detection of carbon dioxide (CO_2). It is a challenge to develop highly sensitive, stable, selective, low power consuming and cost effective CO_2 sensors at room temperature. Detection of CO_2 at room temperature is very important in many applications such as process control in the food industry, indoor and outdoor air quality control, and air quality monitoring in mines [1–3].

Solid-state gas sensors are widely used based on metal oxide materials for the detection of CO_2 gas at elevated temperature [4]. In this paper focused on the development of low power sensors for the detection of CO_2 at room temperature, which not only avoids the need for heating power during operation, but also makes the assembly of the sensors much simpler, cheaper and more portable.

The development of CO_2 sensors is of great interest, particularly if low cost and low power consumption is to be achieved. Further detection and control of combustion processes of carbon-based fuels and materials could be a prospective application field.

MOFs are highly ordered solid-state crystalline compounds consisting of metal or metal clusters connected by organic linkers to form porous three-dimensional networks with large pore volumes and high inner surface areas [5]. The combination of these properties explains the broad applications in areas such as gas storage [6], catalysis [7], gas separation and purification [8], sensing [9,10], and drug release [11]. The structure and properties of MOFs can be tuned by selection of metal ions and organic linkers. MOF's are good adsorbents compared to zeolites and carbon materials because of their high surface area, and the possibility of ligand functionalization. [12].

MOFs have seen extensive developments with rapid progress over the past two decades with a focus on CO_2 storage and separation [13,14]. The adsorption of CO_2 gas molecule into the MOFs depends on several factors such as ligand functionalization, open metal insertion, amine grafting and pore size [15]. Open metal insertion and surface functionalization are common approaches to

* Corresponding author. Tel.: +49 17655410817.
E-mail address: venkat.haipv@gmail.com (V. Pentyala).

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improve the gas selectivity of the MOF. The open metal sites are typically obtained from the synthesized MOFs by removing metal-coordinated solvent molecules at elevated temperatures and/or under vacuum. The iso-structural compounds M-MOF-74 (M = Mg, Ni, Co and Zn) have shown excellent selectivity of CO_2 adsorption over other gases like methane and nitrogen [13,16–19]. Dietzel et al. [18] performed a systematic study with M-MOF-74 and showed that the nature of the divalent metal plays an important role for the CO_2 gas adsorptive properties of the material. The important and crucial factor for CO_2 gas sensing applications is selectivity over other gases. Compared to the other gases CO_2 exhibits a linear molecular structure, a high quadrupolar moment and non-polar nature. This difference can be employed to separate CO_2 from other gases by introducing functional groups into the pores of MOFs. In principle, cross sensitivities against strong oxidizing gases (NO_2,O_3) are not expected due to the nature of CO_2.

Recently various materials have been investigated as CO_2 sensors based on amine functionalized polymers [4,20,21]. Stegmeier et al. [4] explained the change in work function observed in such polymers in contact with CO_2 by carbamate formation as the underlying chemical reaction at room temperature. For the first time we combine such an approach with MOFs as a sensing material. In this work, ethylenediamine was employed as a grafting reagent to functionalize the open coordination sites of Mg-MOF-74.

M-MOF-74 (M = Mg, Ni, Co and Zn) and ethylene diamine functionalizedMg-MOF-74(en-Mg-MOF-74) were investigated for the work function read-out based sensing towards CO_2 gas under different humidity levels. Amine functionalization MOFs compounds was undertaken in order to improve sensitivity and selectivity and to reduce the influence of humidity on the CO_2 gas sensing properties

2. Material and methods

2.1. MOF synthesis and layer deposition

All chemicals were purchased from Sigma Aldrich GmbH, Germany and used without further purification. The chemicals used for synthesis of M-MOF-74 were 2-5-di-hydroxy terephthalate (DHTP), magnesium nitrate, cobalt nitrate, zinc nitrate, nickel nitrate, ethylenediamine, toluene, methanol and ethanol. M-MOF-74 with different divalent metals (M = magnesium, cobalt, nickel and zinc) were synthesized based on published procedure [22]. Briefly for Mg-MOF-74 MOF, magnesium nitrate hexahydrate and DHTP were allowed to react in a mixture of dimethylformamide (DMF), ethanol and water (15:1:1) at 125 °C for 20 h. The resulting microcrystalline product was washed with DMF, and then soaked in methanol at room temperature. The solvent was changed four times over a period of three days. The material was collected by filtration and was heated to 250 °C for 6 h under vacuum. The same procedure was also used for preparing Co, Ni and Zn-MOF-74 MOFs with a slight change in temperature (120 °C) and time (25 h). Functionalization of Mg-MOF-74 with ethylenediamine was carried-out by using a previously published procedure [23]. The as synthesized Mg-MOF-74 was mixed with ethylenediamine in toluene and held under reflux with vigorous stirring for 10 h. The resulting crystals were filtered and washed with DI water and ethanol and dried overnight at room temperature.

TiN sputtered Al2O3 substrates were used. Sensing layers were obtained by drop-coating of TiN sputtered Al_2O_3 substrates with a dispersion of M-MOF-74 powder in methanol.

The layer thickness may differ from sample to sample. The aim of these studies was the qualitative investigation of the films regarding reversibility and response stability but not quantitative evaluations.

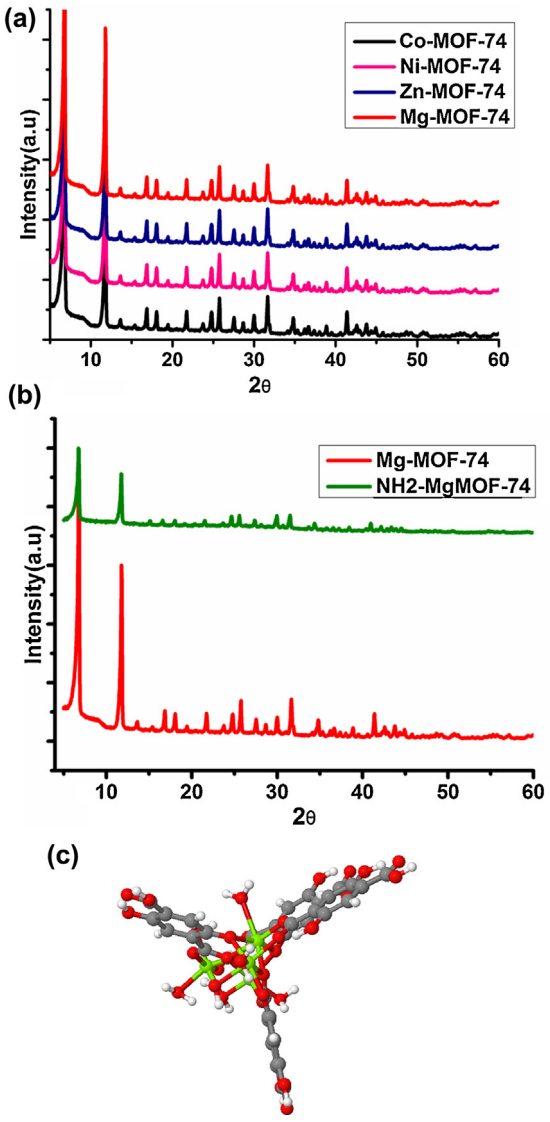

Fig. 1. (a) XRD of M-MOF-74(M = Mg, Co, Ni and Zn). (b). The structure around the metal in M-MOF-74 (Mg-green, carbon-grey, oxygen-red and hydrogen-white) (c) XRD pattern comparison of ethylenediamine functionalized-Mg-MOF-74 and Mg-MOF-74.

2.2. Characterizations

2.2.1. Powder X-ray diffraction (PXRD)

The as-synthesized material was characterized by powder X-ray diffraction (PXRD) measurements. The powdered samples were glued on a foil of polyvinyl acetate and X-ray powder diffraction data recorded on a STOE STADIP diffractometer (STOE, Darmstadt, Germany) using copper radiation (Kα1; λ = 1.5405 Å) in transmission geometry, with a Ge (1 1 1) monochromator and a wide range (0–130°) image plate detector with 0.02° resolution.

2.2.2. Morphology and thermal investigation

As prepared MOF sensing layers were analyzed by scanning electron microscopy (SEM) (FEI Quanta 250 FEG). The specific surface area and pore size distribution were estimated from N_2 adsorption/desorption measurements performed at 77 K on a Soptomatic 1990 instrument (Thermo Scientific GmbH, Germany). The sample powder was degassed for 5 h at 363 K and 5 mm Hg. The adsorption branches in the relative pressure range of 0.05–0.3 and 0.05–0.2 respectively. The total pore volume was estimated from the amount