Metal-Organic Frameworks for Sensing Applications in the Gas Phase

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ABSTRACT

Several materials of the class of metal-organic frameworks (MOF) were tested for their applicability in the field of gas sensors. In particular, impedimetric gas sensor devices were studied. Various sensor configurations were investigated in a frequency range of 1 Hz -10 MHz, and additional time-continuous measurements at 1 Hz were performed. In the temperature range from 120 °C to 240 °C, the sensors were exposed to O_2, CO_2, C_3H_8, NO, H_2, ethanol and methanol concentrations and tested under various humidity conditions of the carrier gas N_2. The materials did not show any signal to O_2, CO_2, C_3H_8, NO, and H_2. However, promising pronounced and reversible responses in the electric properties to changes in humidity were obtained for some selected MOF materials. Of particular interest is the linear response curve observed at 120 °C.

Keywords: metal organic frame work; MOF; impedance spectroscopy; humidity; gas sensor.

1. INTRODUCTION

Metal-organic frameworks are well-known for their ability to store quite large amounts of hydrogen [1,2] or for their use in gas purification applications [3]. The reason for high storage capacity of this materials class is its high specific surface area, resulting from its high and ordered porosity. As small molecules like hydrogen are only adsorbed and not covalently bound to the surface, they can be released completely, for example at lower partial pressures. In this work, the change of the capacity of the materials, caused by the adsorbtion or desorbtion of molecules on the inner surface of the MOF, is utilized to detect small amounts of gaseous analytes by monitoring the electric impedance of the material.

2. EXPERIMENTAL

2.1. Sensor preparation

Different types of metal organic frameworks were provided as powders or pelletized by the BASF Group. From these materials, two different sensor set-ups were prepared as described in Fig. 1. Materials in powder form were processed in thick film technology and applied on top of Au-interdigital electrodes (IDEs) via screen-printing. In this study, IDE structures with a line width and spaycing of 50 µm were used (50/50 IDE). The electical connection to the measurement equipment was provided by two Au-wires, welded on top of the contact pads of the Au-IDEs (Fig. 1a).
The pellets (Ø = 6 mm, *d* = 2mm) were contacted directly by metal-discs (Ø= 6 mm). Contact to the analysis system was again provided by two Au-wires (Fig. 1b).

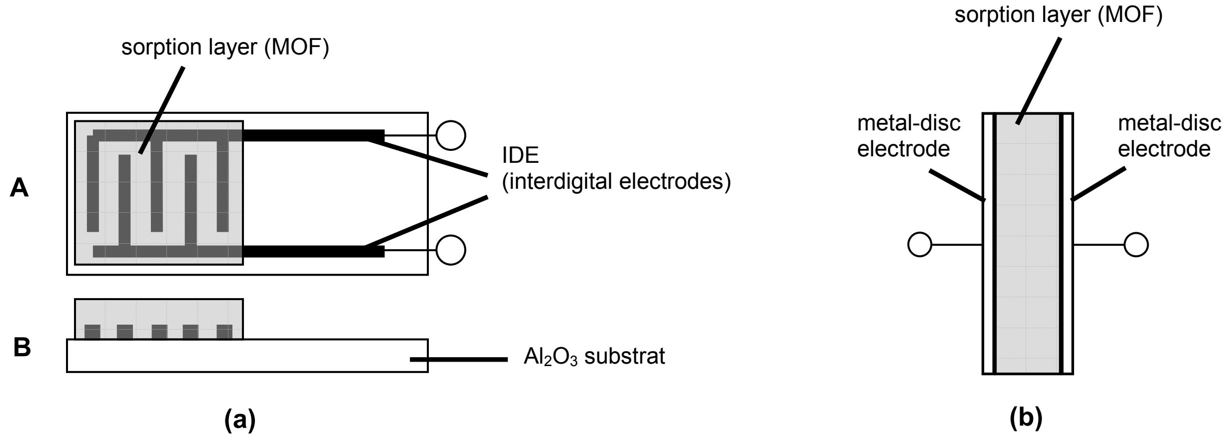

Figure 1. Sensor setup: (a) Sensor in thick film technology; MOF paste screen-printed on top of Au-interdigital electrodes (IDEs, 50/50), A: top view, B: cross section. (2) MOF pellet contacted by metal-disc electrodes.

2.2. Sensor characterization

Both sensor set-ups were passively heated in a furnace (120 °C - 240 °C) and characterized in N_2 carrier gas similar to the method reported in [4]. Different gas concentrations of O_2, CO_2, NO, C_3H_8, H_2, ethanol, and methanol were admixed to the carrier gas (Table 1). For the variation of humidity of the test gas between 0 - 3 %vol an assambly similar to [5] was utilized.

Table 1. Concentrations of test gas atmospheres.

test gas	concentration of test gas in N_2 carrier gas
O_2	10 %vol.
CO_2	10 %vol.
NO	1000 ppm
C_3H_8	1000 ppm
H_2	1000 ppm
ethanol	0 - 18 %vol.
methanol	0 - 35 %vol.

An impedanze analyzer (Novocontrol) was used to monitor the frequency dependent impedancce of the sensor between 1 Hz and 10 MHz. In addition, time-continuous measurements were conducted at 1 Hz, to evaluate the change of the complexe impedance or the capacity of the materials as a function of variations in the surrounding gas atmosphere. Gas atmospheres were monitored by an FTIR analysis system (Nicolet 6700, Thermo) downstream the sensing device.

3. RESULTS AND DISCUSSION

None of the tested materials showed any cross-interfering effects in their electric properties at varying O_2, CO_2, C_3H_8, NO or H_2 concentrations in the surrounding gas atmosphere. Sensor elements equipped with Fe-BTC-MOF showed significant effects when hydrophilic gases like ethanol, methanol and water were applied (Fig. 2).

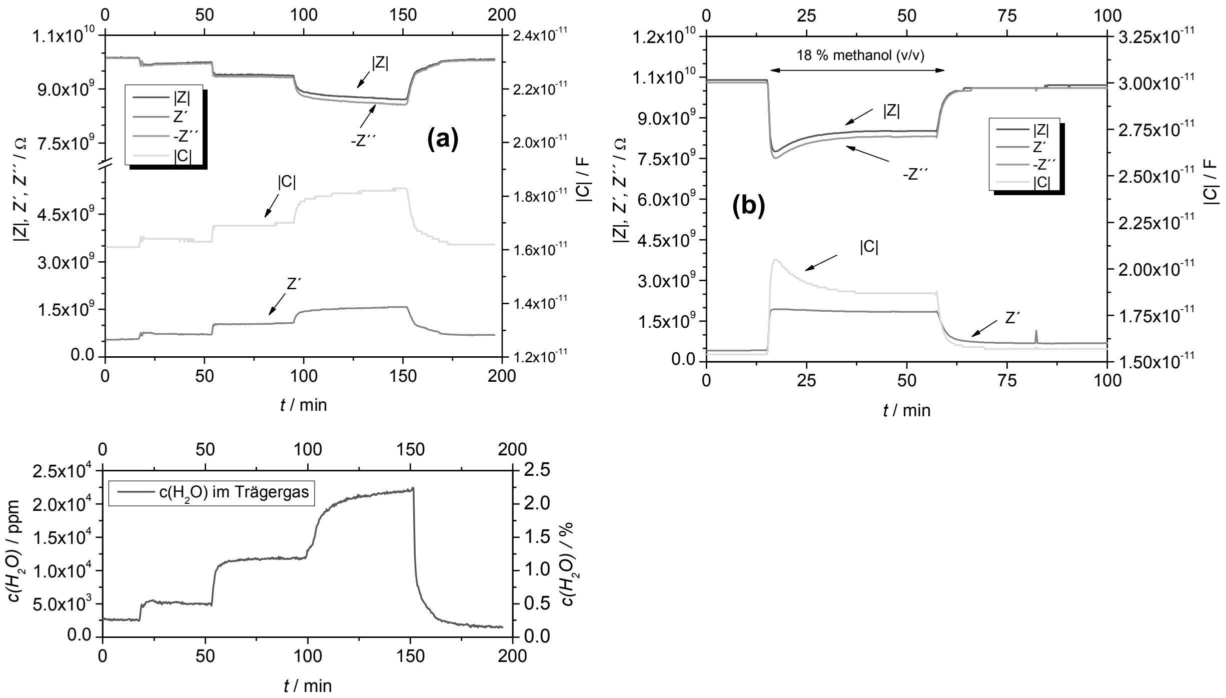

Figure 2. Characteristic impedimetric sensor signal for a Fe-BTC-MOF at different (a) H_2O and (b) methanol concentration in the N_2 carrier gas at 120 °C.

For example, at 120 °C there was a linear and reversible change in the complex impedance (IZI) of 1.5 GΩ when humidity was varied between 0 - 2.5 % H_2O (Fig. 3a). With an increase in sensor temperature up to 240 °C, the dependence of the sensor signal from the humidity of the surrounding gas can be approximated linear in a double logarithmic plot (Fig. 3b).
At 120 °C, the response to the test gas increased in the order of methanol > ethanol > H_2O, whereby most stable and best reversible signals where obtained for variations in the water content.

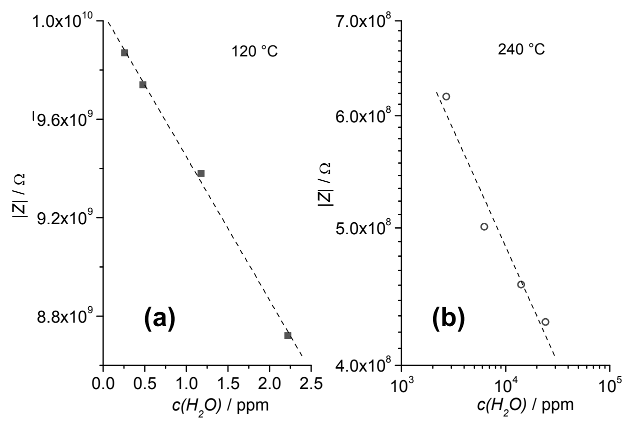

Figure 3. Sensor response curve for different concentrations of H_2O (0 - 2.5 %) in N_2 carrier gas at 120 °C and 240 °C. At 120 °C a linear dependence of the complex impedance from the humidity of the test gas was observed.

4. CONCLUSION

Different materials from the class of metal-organic frameworks have been investigated for the first time as sensor materials for impedimetric humidity sensors. In this study, metal-organic frameworks were identified as promising materials for the detection of hydrophilic gases in the atmosphere in a temperature range between 120 - 240 °C. Moreover, at 120 °C a linear dependence of the sensor signal from the humidity of the test gas was observed. As MOFs can be synthesized as mass-products and can easily be applied to plain transducers via thick film technology, they are promising candidates for the application as recognition elements in gas sensors.

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