# DESIGN OF MOF HETEROSTRUCTURES FOR EXPANDING APPLICATION OPPORTUNITIES

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## ABSTRACT

Metal-organic framework (MOF) structures can be immobilized into different hydrophobic porous matrices in order to enhance their structural stabilities in humid environment and thus widen their application opportunities. Herein, two paths of immobilization were exemplified: (1) the confined crystallization of Cu-based benzene-1,3,5-tricarboxylate (HKUST-1) within the mesoporous FDU-12 silica; (2) incorporation of Fe-based benzene-1,3,5-tricarboxylate (MIL-100) within polyHIPE membrane. Both composites show enhanced structural stability. The adsorption properties and catalytic activity performed on HKUST-1@FDU-12 and MIL-100@polyHIPE heterostructures respectively, showed that sorption sites of MOF's micropores are completely accessible for hosting molecules.

Keywords: metal-organic framework, heterostrucutures, HKUST-1, MIL-100.

## INTRODUCTION

Metal-organic frameworks (MOFs) are a fast developing class of nanoporous materials constructed from nodes of metal ions and multidentate organic ligands forming the crystalline hybrid nets. Their unique structure properties such as high eternal surface areas, void accessibilities and high density of open-metal sites enable versatile application opportunities. [1-5] However, MOF's implementation in industrial scale is still rather limited. One of the main reasons for this is in most cases their chemical instability in solvo- or hydrothermal conditions.[6-8] Various post-synthesis modification approaches have been already used in order to improve this properties. The preparation of different MOF-containing composites is one of the possible paths.[9,10]

In this contribution, the examples of MOF incorporation into mesoporous silica and macroporous polymer membrane are described. Both heterostructures were structurally characterized and tested for sorption and catalytic properties.

## EXPERIMENTAL

MOF heterostructures were prepared using two different paths. (1) **HKUST-1@FDU-12.** Mesoporous FDU-12 silica matrix was prepared according to the previously published procedure.[11] Surface of the silica framework was $NH_2$-modified by grafting with (3-aminopropyl)triethoxisilane (APTES) in order to generate binding sites for $Cu^{2+}$ cations. $Cu^{2+}$ was grafted on $NH_2$-functionalized FDU-12 by stirring $Cu(NO_3)_2 \cdot 3H_2O$ in $EtOH/H_2O$ solution. Cu/FDU-12 product was mixed with the $EtOH/H_2O$ solution of benzene-1,3,5-tricarboxylic acid (BTC) and solvothermally treated by microwave heating. (2) **MIL-100@polyHIPE.** Dicyclopentadiene and Pluronic L-121 were stirred together with MIL-100(Fe) which was prepared according to the literature.[12] After the slow, drop-wise addition of water, Ru-based

initiator (M2) was added to induce the polymerization. The mixture was casted onto the proper support and heated at 80 °C to form a membrane with the thickness of 200 μm.

## RESULTS AND DISCUSSION

**HKUST-1@FDU-12.** XRD pattern of the composite confirms the presence of HKUST-1 phase within the sample (Fig. 1a). $N_2$ sorption isotherms of silica matrix, bulk HKUST-1 and the composite material are shown on Figure 1b. The isotherm of FDU-12 matrix (red curve in Fig. 1b) pronounced desorption hysteresis typical for 'ink-bottle' shaped mesopores with narrowed entrances and negligible contribution of the micropores ($S_{BET} = 72$ m$^2$/g). On the other hand, bulk HKUST-1 represents typical type I isotherm indicating highly microporous nature of the material ($S_{BET} = 1211$ m$^2$/g). The isotherm of the composite material shows a significant increase of the micropore contribution and BET surface (374 m$^2$/g) area relative to the FDU-12 (72 m$^2$/g). The delayed evaporation gives rise to the less pronounced sorption hysteresis with respect with the silica matrix, without any observable tailing of the desorption curve that could indicate the partial plugging of the silica mesopores. The sorption results implies that part of the mesopores are completely filled with HKUST-1 phase and the rest of the mesopores remains unoccupied.
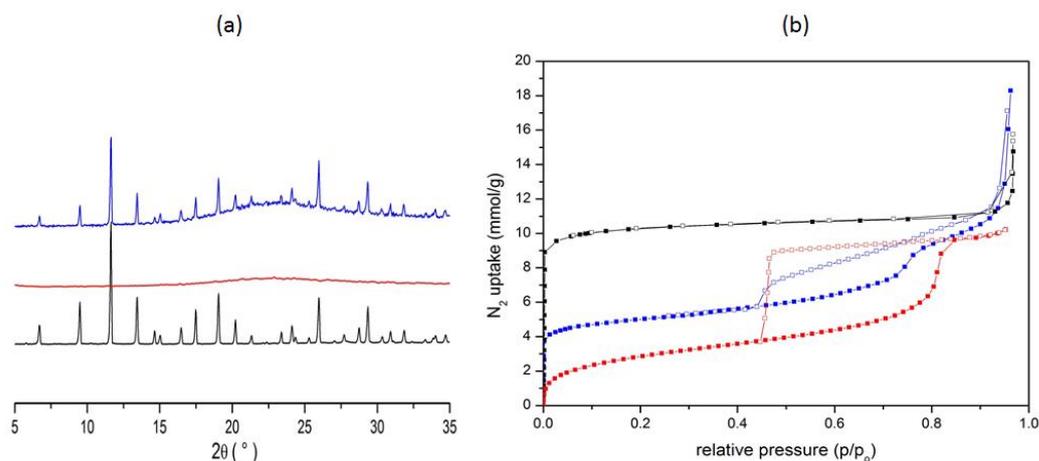


Figure 1: (a) XRD patterns of HKUST-1@FDU-12 (blue), FDU-12 matrix (red) and the bulk HKUST-1 material (black). (b) $N_2$ sorption isotherms of the corresponding materials.

As it is shown in Figure 2, the bulk HKUST-1 structure is sensitive to moisture and undergoes structural transformation into nonporous $Cu_2OH(BTC)(H_2O)]_n \cdot 2nH_2O$ phase in humid environment. On the other hand, significant improvement of the structural stability towards water can be observed in HKUST-1 confined within the silica matrix. The structure remains preserved even after the direct contact with water at 50 °C for 1 day. The sorption capacities for $CO_2$ and $H_2$ of HKUST1@FDU12 were compared with the ones of pure HKUST-1 as well. Gas uptakes for the composite decrease for approximately 50% when compared with the parent HKUST-1 material. Since EDS and TG analyses indicate that the weight contribution of HKUST-1 within the silica matrix is 50% as well (not shown here), it can be concluded that decrease in sorption capacities of the composite is exclusively caused by the presence of silica

matrix. Thus, the sorption sites of HKUST-1 within the silica matrix seem to be fully accessible for gas molecules.
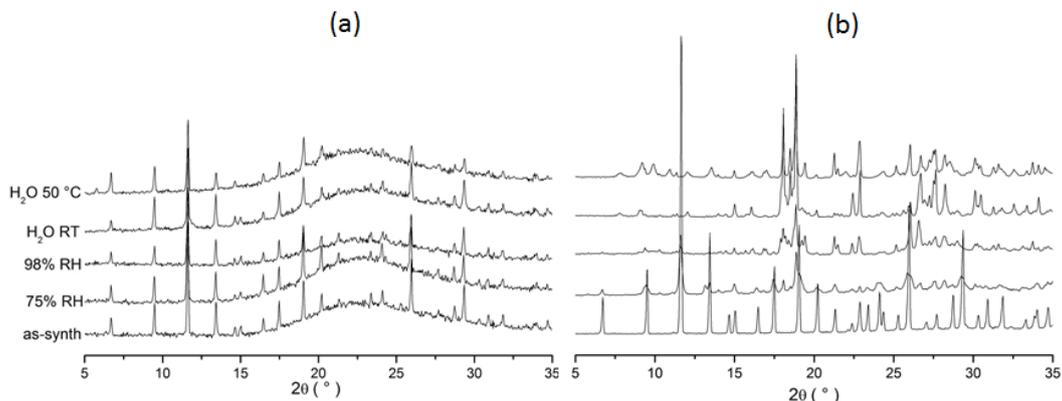


Figure 2: XRD patterns of (a) HKUST-1@FDU-12 and (b) bulk HKUST-1 (blue) treated under different relative humidity for 1 day, and after stirring in water at room temperature and 50 °C for 1 day.

**MIL-100@polyHIPE.[13]** XRD patterns (Fig. 3, left) of the composite material compared with the referenced MIL-100(Fe) powder indicate the presence of MOF phase within the composite polymer. The structural correlation between MIL-100(Fe) phase and the polymer matrix in the MIL-100@polyHIPE composite was performed by SEM analysis (Figure 3, right). Observations at low accelerating voltage (1 kV) show that the polymer matrix contains spherical-shaped macropores and smaller windows with the estimated dimensions up to 10 μm and 1 μm, respectively (Figs. 3a and 3b, right). The close-up observations of the membrane's cross-section revealed the presence of nanoparticle aggregates incorporated within the walls of the polymer (Figure 3b, right). The composite was observed also at 10 kV where the contrast in the image related to the areas with different elemental compositions (Z-contrast) becomes visible. Figures 3c and 3d reveal bright spots corresponding to Fe-rich domains which are densely and more or less evenly distributed throughout the polymer matrix on the surface as well as in the inner part of the polymer.
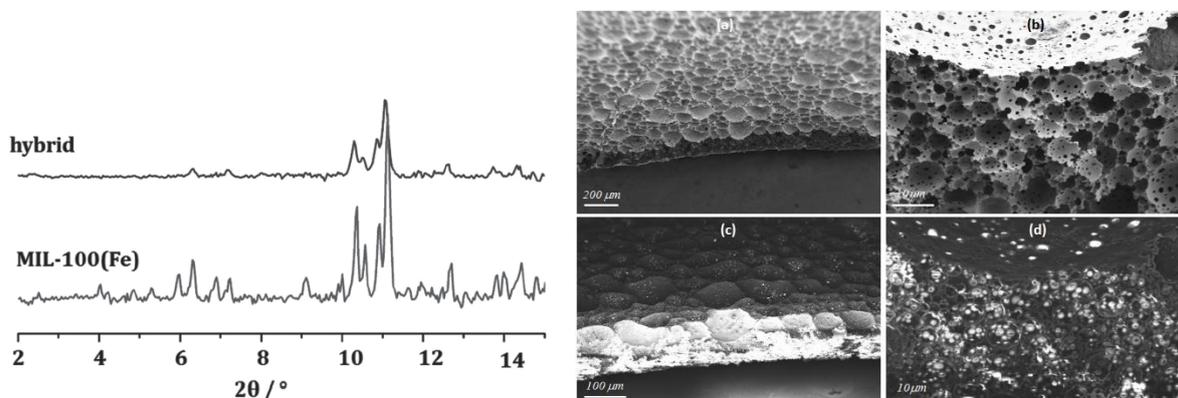


Figure 3: Left; XRD patterns of the referenced MIL-100(Fe) (below) and MIL-100@polyHIPE material (above). Right; SEM micrographs of the composite: a) membrane surface, b) interior both observed at 1 kV, c) membrane surface and d) membrane interior both observed at 10 kV.

The composite membrane was tested for flow-through Friedel-Crafts alkylation of p-xylene with benzyl bromide to yield 2-benzyl-1,4-dimethylbenzene (Fig. 4). At the residence time of 2 s on the membrane with the flow rate of 0.01 mL/min a 7% conversion is reached. No leaching or degradation of MOF phase was observed after the reaction. Relatively low degree of the conversion can be assigned to the low content of MIL-100(Fe) phase within the polymer matrix (14 wt.% according to TG analysis) rather than to the blocking of the acid sites with the polymer.
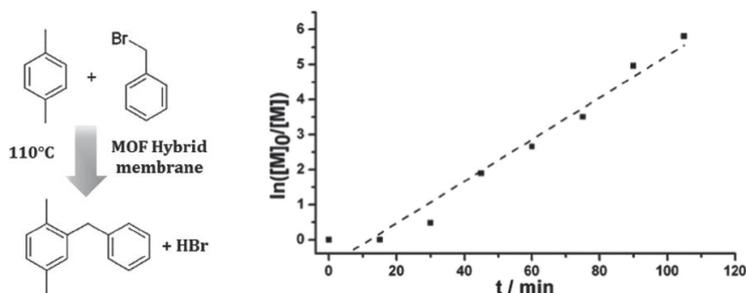


Figure 4: Benzyl bromide coupling reaction with p-xylene on the MIL-100(Fe) hybrid membrane (left), the first-order kinetic plot of the performed reaction for MIL-100@polyHIPE in a batch mode (right).[13]

## CONCLUSION

Two examples of MOF heterostructure designs were presented; (1) the confined crystallization of HKUST-1(Cu) within FDU12 mesoporous silica matrix, (2) incorporation of MIL-100(Fe) within the macroporous polymer membrane. In both cases, MOF phases were successfully immobilized within the matrices retaining their accessibility of sorption and catalytic sites. The described paths of MOF shaping into the composites are a promising way of to enhance their functionality.

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