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Oriented Crystallisation on Supports and Anisotropic Mass Transport of the Metal-Organic Framework Manganese Formate

Mirko Arnold,*[a] Pavel Kortunov,[b] Deborah J. Jones,[c] Yannig Nedellec,[c] Jörg Kärger,[b] and Jürgen Caro[a]

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The oriented in situ crystallisation of microporous manganese(II) formate [$Mn(HCO_2)_2$] on different porous supports (e.g. porous alumina and graphite) has been investigated. The anisotropic growth of $Mn(HCO_2)_2$ was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The intracrystalline diffusion of methanol in $Mn(HCO_2)_2$ was studied by observation of the sorption kinetics by interference microscopy (IFM). It was found that untreated discs of porous alumina and graphite supports exhibit poor densities of $Mn(HCO_2)_2$ crystals per supported area. Even lower crystal densities are found for activated supports such as for alumina after basic treatment and for oxidized graphite supports. Improved results have been achieved by replacing formic acid by sodium formate in the synthesis route. Crystal growth on graphite gives results superior to those on alumina with respect to the crystal density as well as the relative orientation of the 1D channel network to the support surface. Methanol uptake from the vapour phase is similar at 25 and 40 °C and gives an adsorption capacity of about 95 mL g^{-1}. The BET surface area was found to be 280 m^2 g^{-1}. IFM indicates that diffusion occurs only along one crystallographic axis, thus proving the presence of a 1D channel system. Diffusion coefficients of about 10^{-12} m^2 s^{-1} for methanol in microporous $Mn(HCO_2)_2$ were found. These results can be used to prepare supported metal–organic framework (MOF) membranes for molecular sieving.
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Introduction

Commonly used porous materials for gas-separating membranes are zeolites and metal oxides such as Al_2O_3, TiO_2 and SiO_2. These materials offer high thermal stability and permanent porosity. Furthermore, zeolites present well-defined channels and cavities, which allow them to be used as molecular sieving membranes.[1]

Despite these outstanding properties, the demand for novel microporous materials remains high because the rational design of zeolites and other inorganic materials with pore diameters less than about 0.4 nm is still difficult and the separation of small molecules (e.g. H_2, N_2, O_2, CH_4) by molecular sieving membranes has not yet been achieved successfully. Metal–organic frameworks (MOFs), which are a new class of porous materials, are novel candidates for molecular sieving membranes. MOFs represent an interface between organic and inorganic compounds since they consist of metal ions linked by organic molecules (ligands). MOFs comprise ionic organic–inorganic hybrid materials,[2] such as the manganese formate[3,4] studied in this paper, as well as coordination polymers based on di- to tetravalent carboxylic acids.[5–8] This novel approach for preparing porous materials exhibits a rational and even more flexible design of the network compared to the already known inorganic materials. In addition to these advanced properties, access to the entire pore volume, as well as variable nanoscale pore sizes, indicates that MOFs are clearly an attractive new class of porous materials.

As might be expected, the first reports of MOFs in prospective industrial processes have already been published.[9] Possible applications for MOFs are catalysis,[10] gas purification and gas storage, which needs information on the molecular transport in MOFs.[11] The employment of MOFs as heterogeneous catalysts might be a promising field in view of their great structural and compositional variety and possible accessibility of the metal ion sites in the structure.[9] Recently, Chen reported the application of MOFs in GC columns in order to segregate alkane isomer mixtures with good separation capabilities.[12] In spite of the considerable attention given to these promising materials, only a handful MOFs with permanent porosity have been reported so far, in part because framework stability after template removal in these materials has emerged as a serious problem. Studies on functional aspects, especially the application in mem-

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[a] University of Hanover,
Callinstr. 3A, 30167 Hanover, Germany
[b] University of Leipzig,
Linnéstr. 5, 04103 Leipzig, Germany
[c] Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR CNRS 5072, Université Montpellier
2, Place E. Bataillon, 34095 Montpellier CEDEX 5, France

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branes, accumulate rather slowly, and thus only one example using MOFs in a gas-separating membrane is known. In a unique approach, Won et al.[13] embedded a Cu^{II} complex in a polymer matrix to yield membranes with high H_2 selectivities and remarkable permeabilities. In the work presented here, the novel porous manganese formate, first reported by Dybtsev et al. and at around the same time by Wang et al.,[3,4] was chosen due to its high thermal stability, selective, high H_2 adsorption rates and facile preparation route. Synthesis follows a solvothermal route using formic acid, manganese(II) chloride and 1,4-dioxane as the structure-directing agent. After removal of 1,4-dioxane, the framework becomes a porous structure with a 1D channel system, where each Mn^{II} cation is coordinated by six formate ligands to give a network of corner- and edge-shared MnO_6 octahedra, as shown in Figure 1. The porous network exhibits thermal stability up to 300 °C, as indicated by XRD and TG/DTA studies (see Supporting Information). In order to use microporous materials (e.g. zeolites, porous SiO_2) as gas-separating materials in membrane technology they need to be grown on porous substrates. Commonly, zeolite crystals are grown on substrates like porous alumina and titania, which offer high thermal and mechanical stability, in order to obtain composite membranes and thus to be able to use them as gas-separating membranes. Due to the similarity between zeolites and MOFs, in this work the oriented growth of microporous manganese formate on different substrates is investigated.

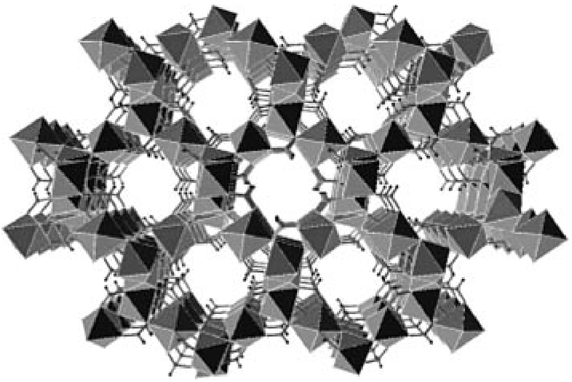

Figure 1. Schematic drawing of the guest-free framework along the *b* axis. Corner- and edge-shared MnO_6 octahedra as well as the formate ligands are shown, according to Dybtsev et al.[3]

Results and Discussion

Significant uptake of methanol from the vapour phase was observed, the total amount adsorbed being similar at 25 and 40 °C. The sorption isotherms obtained in gravimetric experiments have a shape characteristic of a microporous solid, as shown in Figure 2.

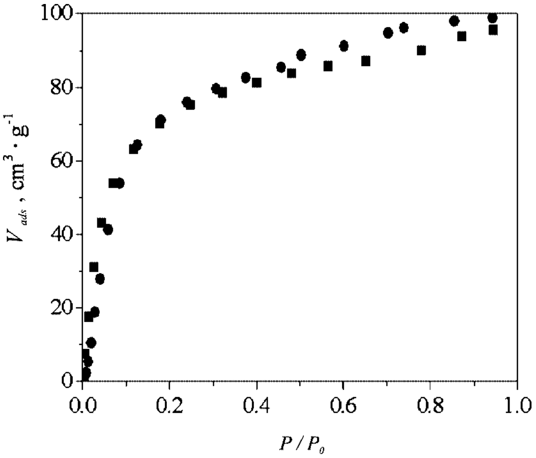

Figure 2. Adsorption isotherms of methanol in $Mn(HCO_2)_2$ at 25 °C (■) and 40 °C (●). V_{ads} represents the STP volume of the adsorbed amount of methanol.

Volumetric experiments were also performed (not shown), and a small hysteresis was observed between adsorption and desorption branches. The BET surface area was calculated to be 278 $m^2 g^{-1}$, which is in excellent agreement with that obtained from previously reported H_2 (240 $m^2 g^{-1}$) or CO_2 (297 $m^2 g^{-1}$) sorption isotherms.[3]

IFM studies were performed to gain more information about the diffusion kinetics as well as to demonstrate the presence of a 1D channel system. Figures 3b and c show the time-dependent intracrystalline concentration profiles of methanol (0–10 mbar) in an $Mn(HCO_2)_2$ single crystal (Figure 3a). Uptake was found only along the *y* axis, with no significant transport along the *z* and *x* axes. This result confirms the existence of a 1D channel system along the crystallographic *b* axis in Figure 1. Furthermore, no evidence for an intergrowth structure was observed, and methanol was found to be distributed homogeneously throughout the whole crystal. The molecular diffusivity evaluated in the middle part of the chosen crystal from Fick's Second Law does not depend on the methanol concentration, and its average value (9.15×10^{-13} $m^2 s^{-1}$) is in good agreement with data obtained from the uptake rate (1.05×10^{-12} $m^2 s^{-1}$) using the $t^{1/2}$ approach. However, the sorption uptake concentration profiles cannot be described exclusively by intracrystalline diffusion. The sorption uptake is determined to a minor extent by surface permeability, which, most remarkably, is found to depend on the methanol concentration. Values for the surface permeability of 2×10^{-1} $m s^{-1}$ for 0.2 of the final loading and 3×10^{-1} $m s^{-1}$ for 0.9 of the final methanol loading (95 $mL g^{-1}$) are estimated.

Initial attempts to prepare a composite membrane of $Mn(HCO_2)_2$ grown on alumina and graphite were carried out without any treatment of the support surfaces. The growth of $Mn(HCO_2)_2$ crystals on alumina discs resulted in only poor densities (10 crystals/mm^2). In situ crystallisation on graphite shows, in general, a more distinct growth of $Mn(HCO_2)_2$ crystals on support surfaces (80 crystals/mm^2).

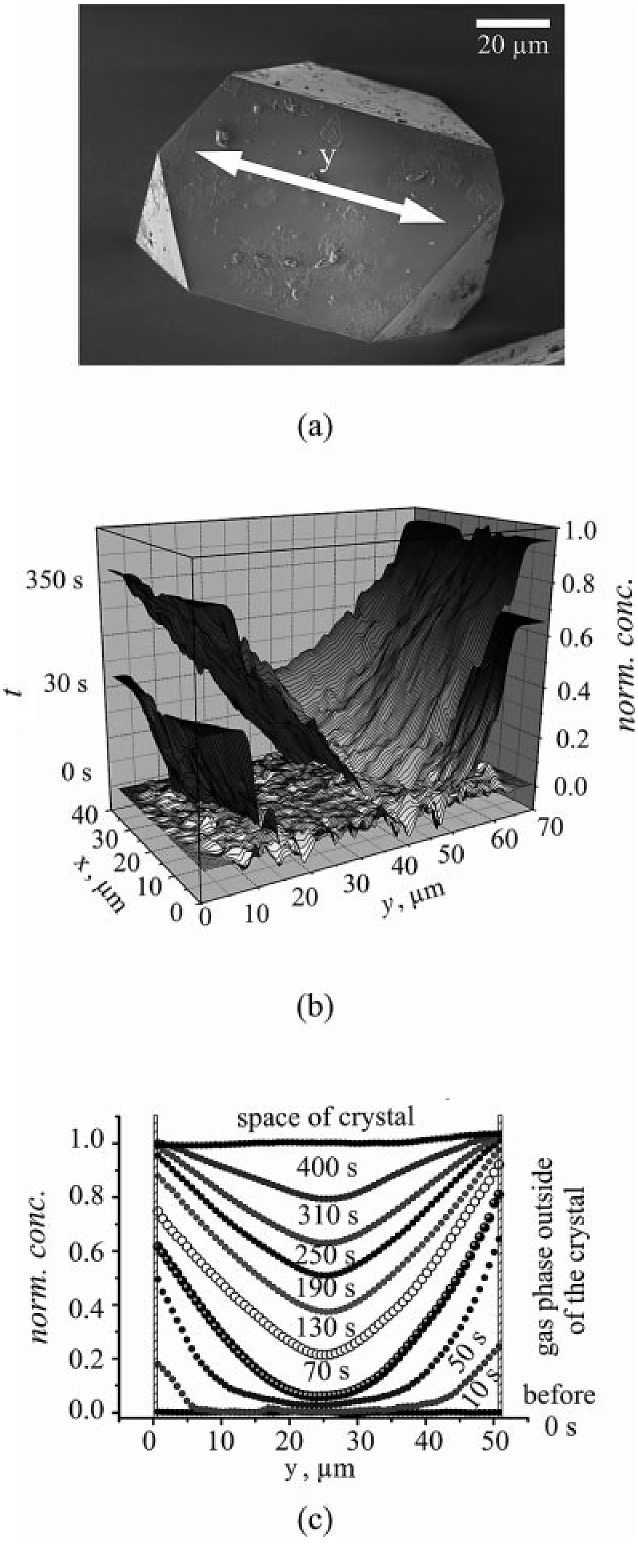

Figure 3. SEM micrograph of an $Mn(HCO_2)_2$ crystal used for IFM (a). Arrows indicate the 1D channel system along the *b* axis. 2D intracrystalline concentration profiles for methanol sorption by an $Mn(HCO_2)_2$ single crystal in the same orientation as shown in (a), obtained by IFM at room temperature (b), and the corresponding 1D intracrystalline concentration profiles (c).

To increase the crystal density, different methods for support activation were evaluated.

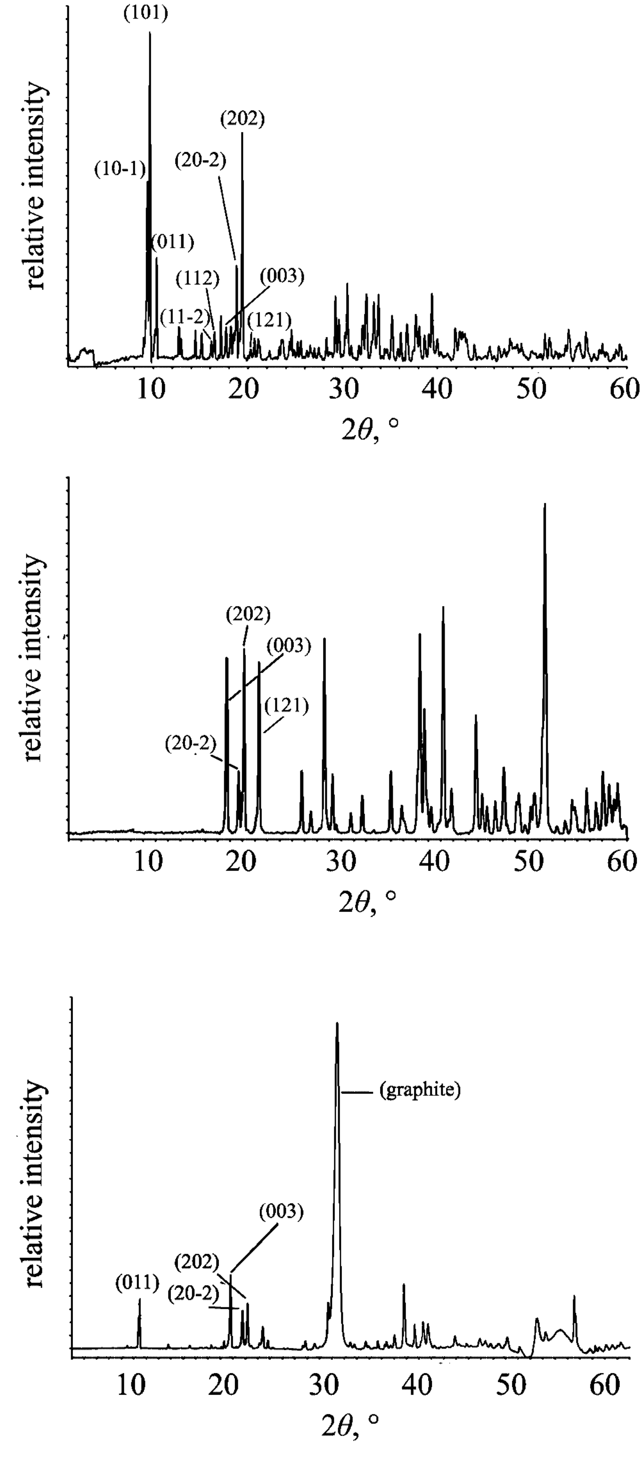

Figure 4. Powder XRD pattern of as-synthesised $Mn(HCO_2)_2$ (a), $Mn(HCO_2)_2$ grown on alumina support discs showing the peaks for the (202), $(20\bar{2})$ and (003) planes are dominant (b) and $Mn(HCO_2)_2$ grown on graphite supports by the "formate" route showing an additional dominant peak for the (011) plane (c).

In order to increase the crystal growth on alumina, the supports were treated with sodium hydroxide. Alumina surfaces treated with sodium hydroxide are even less suitable for $Mn(HCO_2)_2$ crystal growth as virtually no crystals were observed after in situ crystallisation on those supports

(1 crystal/mm^2). The commonly used seeding method resulted in an increase in the crystal density to 150 crystals/mm^2. It must be stressed, however, that despite an improved density of $Mn(HCO_2)_2$ crystals on the surface, the orientation of the 1D channel system was undesirable. This was concluded by comparing the XRD pattern of $Mn(HCO_2)_2$ grown on the alumina support (see Figures 4a and b). This indicates that the 1D channel system lies parallel to the support surface. With this orientation, no mass transfer would occur through membranes prepared with this method. Oxidised graphite supports show a trend similar to the alumina supports treated with sodium hydroxide, since crystal growth on these supports exhibits a lower crystal density than the untreated ones (40 crystals/mm^2).

The crystal density achieved by this method underlines the influence of electrostatic interactions during the growth of $Mn(HCO_2)_2$ on these supports. As activated supports – treatment with sodium hydroxide in the case of alumina and oxidation in the case of graphite – lead to poor crystal densities, a different synthesis method using sodium formate rather than formic acid was developed. This is based on the assumption that positively charged surfaces could inhibit the formation of crystals on the surface because of electrostatic repulsion. $Mn(HCO_2)_2$ crystals grown on oxidized carbon supports by the formate route are characterised by advanced crystal densities (see Figure 5a) as well as a reasonable tilt angle of 34° of the 1D channel system to the support surface (see Figures 4a and c). Additionally, it was found that $Mn(HCO_2)_2$ crystals were grown into the porous graphite to a certain extent, which suggests a proper connection to the support (see Figure 5b).

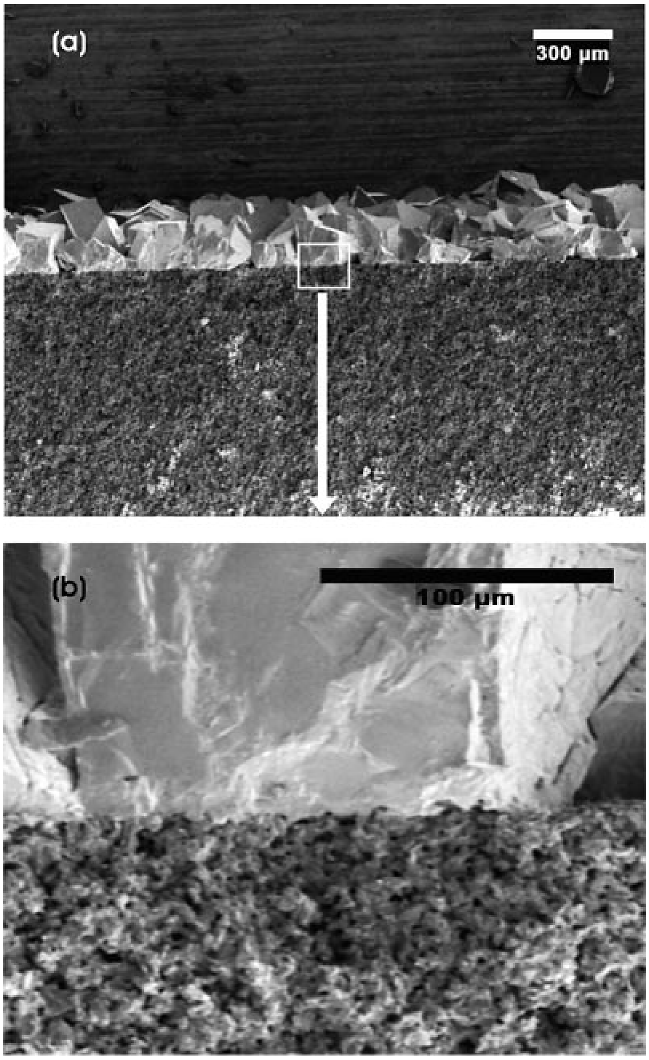

Figure 5. Profile of $Mn(HCO_2)_2$ crystals grown on a graphite support disc after two in situ crystallisations by the "formate" route (a). The magnified image shows intergrowth between the carbon support and $Mn(CO_2)_2$ (b).

Conclusions

It has been shown that the synthesis of supported MOF composite membranes based on manganese(II) formate [$Mn(HCO_2)_2$] is possible in principle. The amount of crystals grown on the supports and the orientation of the 1D channel system on the surface depends strongly on the selected support as well as on the synthesis route. While membrane-quality coatings have still not been achieved, this study has identified factors that are important for the production of continuous layered $Mn(HCO_2)_2$ membranes. Future work should focus on a detailed examination of the surface charges during synthesis, and the obtained results can be applied in a direct modification of in situ synthesis and/or surface treatment in order to increase the amount of crystals on the supports. Additionally, in situ crystallisation of other promising MOFs for new composite molecular sieving membranes seems to be reasonable. For instance, Pan et al. have published the synthesis of a porous, lanthanum-containing MOF with stability up to 450 °C and high and selective H_2 adsorption rates.[14]

Experimental Section

Porous $Mn(HCO_2)_2$ was synthesised according to Dybtsev et al.[3] in a steel autoclave with Teflon-lined insert ("formic acid" route). $MnCl_2\cdot 2H_2O$ (2.5 g, 12.5 mmol) and HCO_2H (0.94 mL, 25 mmol) were dissolved in 1,4-dioxane (25 mL) and 50 mL of *N*,*N*-diethylformamide (50 mL). The solution was then autoclaved at 115 °C for 48 h. The obtained crystals were filtered and washed with acetone. In order to remove the 1,4-dioxane template molecules, the crystals were heated to 150 °C for 24 h under reduced pressure. All employed chemicals were used as delivered without any purification.

In order to maintain the advantage of the high thermal stability of $Mn(HCO_2)_2$, the in situ crystallisation was performed on supporting discs of porous α-Al_2O_3 (Inocermic GmbH, Germany) and porous graphite (Poco Graphite Inc., USA) with a diameter of 18 mm and a thickness of 1 mm to form composite membranes in the same manner as zeolite membranes. Before in situ crystallisation, supports were cleaned with deionised water and acetone to remove impurities from the surface. Finally, they were dried at 80 °C for 1 h.

To improve the crystal growth on the support, they were treated differently before in situ crystallisation: α-Al_2O_3 supports were autoclaved at 150 °C for 4 h with a solution of 50% NaOH to increase the concentration of free OH groups, which are possible connecting nodes for $Mn(HCO_2)_2$. Another approach for increasing the crystal growth on alumina supports consists of placing seed crystals on the surface. For this purpose, ground $Mn(HCO_2)_2$ was simply rubbed onto the alumina surface.

The activity of graphite supports was increased by heating in air at 300 °C for 12 h to increase the concentration of several different functional groups, especially carbonyl, carboxyl and hydroxy groups, on the carbon surface.[15] Since a positively charged surface might reduce the crystal growth, an alternative synthesis method that replaces formic acid with sodium formate was also developed ("formate route").

The adsorption–desorption isotherms of methanol in microporous $Mn(HCO_2)_2$ were measured by monitoring the mass uptake of the sample, recorded with a Sartorius S3D-V microbalance, following successive injections of known amounts of methanol in the vapour phase. To monitor the equilibrium pressure and to calculate the amount of injected vapour, two pressure gauges (Edwards) were used, with ranges from 10^{-5} to 1 Torr and from 10 to 1000 Torr. Secondary vacuum was achieved with a Varian Turbomolecular drag pump coupled to a dry primary pump. Prior to each experiment, the sample was introduced into a specially designed glass cell and weighed. The cell was then fixed to the suspending rod of the microbalance, and equilibrated with a reference cell. After a short time to allow the balance to stabilize, the sample was heated in situ at 150 °C, and out-gassed under vacuum for 24 h.

To confirm the structure of $Mn(HCO_2)_2$ crystals and to determine the orientation of the crystals on supports, X-ray diffraction data were obtained with a Philips X′PERT diffractometer and evaluated using the software WinXPOW. Reflections were collected in the range from $2\theta = 5$ to 90° (step width: 0.01°; time per step: 10 s) at a voltage of 40 kV and a current of 40 mA. In order to confirm the structure of the obtained $Mn(HCO_2)_2$ crystals, powder XRD data were collected from ground samples. The obtained data were used to determine the preferred orientation of crystal growth on the applied supports. The dominant planes in the XRD pattern obtained from $Mn(HCO_2)_2$ on the employed supports were taken to be perpendicular to the surface. The tilt angle between the 1D channel system and the support surface could then be determined by calculating the angle between the 1D channel system and the vertical to the support plane of $Mn(HCO_2)_2$.

Both the crystal morphologies and the quantitative growth of $Mn(HCO_2)_2$ on different supports were evaluated with a field-emission scanning electron microscope (JEOL JSM 6700F). In view of the metal–organic nature of the $Mn(HCO_2)_2$ only low accelerating voltages (1 kV) were applied in order to avoid decomposition of the structure and charging of the sample surface.

Interference microscopy (IFM) measurements allow in situ observation of the sorption uptake of gaseous species in porous media with a spatial resolution of 0.5 µm.[16,17] Methanol sorption was studied with a pressure step from 0 to 10 mbar at room temperature. For these measurements, the calcined MOF sample was introduced into an optical cell and prior activated under reduced pressure at 150 °C for 24 h. The IFM setup consists of a vacuum system, a Carl Zeiss Jenapol interference microscope and a Mach-Zehnder type interferometer. Interference patterns were recorded with a CCD camera (XC-77CE, Sony).

Supporting Information (see footnote on the first page of this article): Figure S1 shows the TG/DTA analysis of as-synthesised $Mn(HCO_2)_2$ still containing 1,4-dioxane template molecules. The first weight loss (140–280 °C, 16.5%) is clearly related to the selective removal of the template molecules. The XRD patterns before (a) and after template removal (b) (Figure S2) show that even after template removal the framework remains stable.

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