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Liquid-phase adsorption on metal-organic frameworks

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Abstract This work is focusing on the potential application of metal-organic frameworks as porous materials in heterogeneous catalysis where the substrate is in solution. The understanding of such a liquid-phase heterogeneous catalytic process requires adsorption equilibrium data in solution. For this purpose several metal-organic frameworks were synthesized as reference materials and tested as adsorbents for the adsorption of substrate molecules such as styrene or ethylcinnamate from the liquid phase. The adsorption capacity strongly depends on the polarity of the substrate with respect to the solvent. In several instances solvent and polarity effects are heavily superimposed on the pore size effects. Adsorption isotherms, rates and hydrogenation of the substrates are reported and discussed.

Keywords Metal-organic framework · Liquid-phase adsorption · Palladium supported catalyst · Heterogeneous catalysis · Hydrogenation

Abbreviations

bdc	1,4-benzenedicarboxylate
btc	1,3,5-benzenetricarboxylate
btb	1,3,5-benzenetribenzoate
c_0	initial concentration of substrate in solution
c_i	effective concentration of substrate in solution
dabco	1,4-diazabicyclo[2.2.2]octane
DCM	dichloromethane
DEF	*N*,*N*-diethylformamide
d_{kin}	kinetic diameter
DMF	*N*,*N*-dimethylformamide
DUT	Dresden University of Technology
HKUST	Hong-Kong University of Science and Technology
m_{ads}	amount of substrate adsorbed on adsorbent
MeIM	2-methylimidazolate
MIL	Matériaux de l'Institut Lavoisier
MOF	Metal-Organic Framework
ndc	2,6-naphthalene dicarboxylate
$Pd(acac)_2$	palladium acetylacetonate
PXRD	powder X-ray diffraction
TIPB	triisopropylbenzene
V_P	Specific total pore volume ($p/p_0 = 0.9$)
ZIF	Zeolitic Imidazolate Frameworks

1 Introduction

Metal-Organic Frameworks (MOFs) have received considerable attention as a new class of porous materials, containing metal ions or clusters linked by large organic ligands, with extremely high specific surface areas and high specific pore volume, as well as an adjustable pore size and functionality of the framework (Kitagawa et al. 2004; Li et al. 1999; Schüth et al. 2002). Due to these properties MOFs are promising materials for applications in chemical reactions in liquid phase (Corma et al. 2010; Farrusseng et al. 2009; Lee et al. 2009; Wang et al. 2009), for example for cyanosilylation (Schlichte et al. 2004), oxidation (Tonigold et al. 2009), hydrogenation (Sabo et al. 2007), Knoevenagel condensation (Gascon et al. 2009), Mukaiyama aldol (Horike

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et al. 2008) or cyclization reaction. Although the performance of MOFs as heterogeneous catalysts and catalyst support has motivated a great number of publications (Henschel et al. 2008; Hermes et al. 2006; Hwang et al. 2008; Ma et al. 2009; Wu et al. 2005; Wu and Lin 2007), only a few are focusing on the investigation of adsorption processes on MOFs in liquid phase (Alaerts et al. 2007, 2008, 2009; Cychosz et al. 2008; Horcajada et al. 2010; Klein et al. 2009; Maes et al. 2010).

MOFs show excellent capacities in gas adsorption exceeding those of activated carbon and zeolites (Thomas 2009). Several theoretical and experimental studies made a contribution to the understanding of the factors crucial for adsorption capacities and kinetics in the gas phase (Li et al. 2009; Düren et al. 2009; Murray et al. 2009). Typically, the correlation between the specific surface area or the pore volume and the amount of gas adsorbed is observed, as well as the increase of the adsorption enthalpy for MOFs with open metal sites. Adsorption from liquid solution is more complex with respect to gas phase adsorption. A number of additional factors, such as polarity and composition of host and guest, solubility of adsorbate in the solvent, temperature, adsorptive concentration, as well as competitive solvent adsorption should be taken into account. Beside of adsorbent-adsorbate interactions, the solvent (particularly in diluted solutions, where the solvent concentration is very high) dramatically influence the resulting adsorption capacity. In fact, the adsorption capacity is often dominated by selectivity. In the simplest case of multi-component liquid adsorption, a binary solution, the composition of the adsorbed phase is usually unknown. However, the design of efficient liquid-phase adsorptive separation and heterogeneous catalytic processes requires adsorption equilibrium data.

In this work the liquid-phase adsorption properties of several MOFs which differ in polarity, pore size, and pore volume were examined. The substrates are chosen due to the consideration of applicability in hydrogenation reaction. Ethylcinnamate is often used as substrate. By using of palladium supported catalysts the hydrogenation of the α,β-unsaturated double bond is preferred to the ester functionality. It was shown recently, that the specific activity of palladium supported MOF-5 in hydrogenation of ethylcinnamate with molecular hydrogen at elevated pressure, was twice as high as that for commercial Pd/C catalyst with almost the same Pd content (Opelt et al. 2008). The styrene hydrogenation has been chosen as test reaction due to its practical interest, for example in the hydrogenation of pyrolysis gasoline in order to remove extremely reactive unsaturated species, such as styrene, mono and di-olefins. Styrene hydrogenation is often used as a representative reaction due to its slower reacting behavior in comparison to other unsaturated species of pyrolysis gasoline.

The solvents are selected because of different polarity (ranging from high dielectric constant ε of 8.9 for DCM, to lower of 1.9 for *n*-heptane), molecule size, and the solubility of the substrates.

1.1 Materials

Figure 1 shows the structures of metal-organic frameworks used in this study.

The investigated materials (Fig. 1) can be split into two different groups: (1) metal-organic frameworks, where the coordination sphere of the metal atoms comprise water or other solvent molecules which can be removed in vacuum at elevated temperatures (so-called open metal sites); (2) metal-organic frameworks with coordinatively saturated metal clusters. To the first group belong: copper trimesate $Cu_3(btc)_2$ (HKUST-1, Chui et al. 1999), the chromium based terephthalate $Cr_3F(H_2O)_2O(1,4\text{-bdc})_3$ (MIL-101, Férey et al. 2005), and the nickel based benzene tribenzoate $Ni_5O_2(btb)_2$ (DUT-9, Gedrich et al. 2010). The clusters available in these MOFs are shown in Fig. 2. As reported in previous work HKUST-1 and MIL-101 are suitable materials for heterogeneous catalysis and open metal sites available can potentially coordinate substrate molecules used in catalytic reactions (Henschel et al. 2008; Schlichte et al. 2004).

The second group include the Zn_4O^{6+}-based MOFs such as MOF-5 (Fig. 1d, Li et al. 1999), DUT-6 (Fig. 1f, Klein et al. 2009), and $Zn_4O(btb)_2$ (Fig. 1e, Caskey et al. 2008), as well as aluminium based MOF DUT-4 (Fig. 1g, Senkovska et al. 2009), a pillared MOF $Zn_2(bdc)_2(dabco)$ (Fig. 1h, Dybtsev et al. 2004), and the zeolitic imidazolate ZIF-8 (Fig. 1i, Park et al. 2006). ZIF-8 and $Zn_2(bdc)_2(dabco)$ adopt exceptional positions. In contrast to the other MOFs there are no carboxylic groups in the ligand of ZIF-8 involving the strong hydrophobic character of the framework, as was shown in water adsorption experiments (Küsgens et al. 2009). The major feature of the $Zn_2(bdc)_2(dabco)$ framework is its flexibility. It shows a guest-depending structure transformation which is fully reversible (Dybtsev et al. 2004; Uemura et al. 2007).

Not only the chemical composition, but also the pore geometry of metal-organic frameworks has an essential effect on the adsorption since the diffusion of reactants to the active reaction centre is a crucial point for heterogeneous catalysis in the liquid phase. The shape of pore in $Cu_3(btc)_2$ (Fig. 1a), MIL-101 (Fig. 1c), DUT-6 (Fig. 1f) and ZIF-8 (Fig. 1i) is quasi spherical. For such systems the size of the pore window and not of the pore itself is the rate-determining step for adsorbing and desorbing larger molecules. In contrast the limiting factor in channel-built MOFs like MOF-5 (Fig. 1d), $Zn_4O(btb)_2$ (Fig. 1e), DUT-4 (Fig. 1g), or $Zn_2(bdc)_2(dabco)$ (Fig. 1h) is the dimension of the channel.

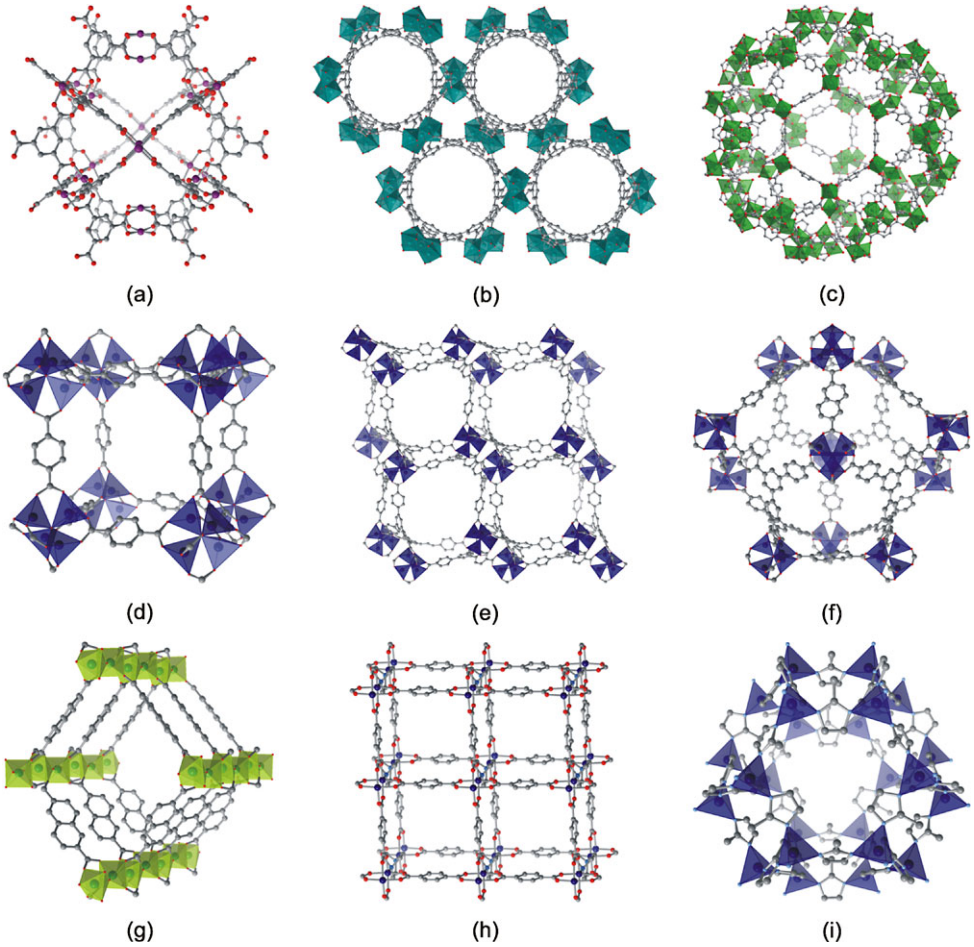

Fig. 1 Crystal structures of MOFs: (**a**) $Cu_3(btc)_2$, (**b**) DUT-9, (**c**) MIL-101, (**d**) MOF-5, (**e**) $Zn_4O(btb)_2$, (**f**) DUT-6, (**g**) DUT-4, (**h**) $Zn_2(bdc)_2(dabco)$ and (**i**) ZIF-8 (carbon, oxygen, nitrogen atoms are coloured *grey*, *red*, and *pale blue*, respectively. Metal atoms (or coordination polyhedra) are represented as follow: copper in *purple*, zinc in *dark blue*, nickel in *teal*, chromium in *green*, aluminium in *light green*

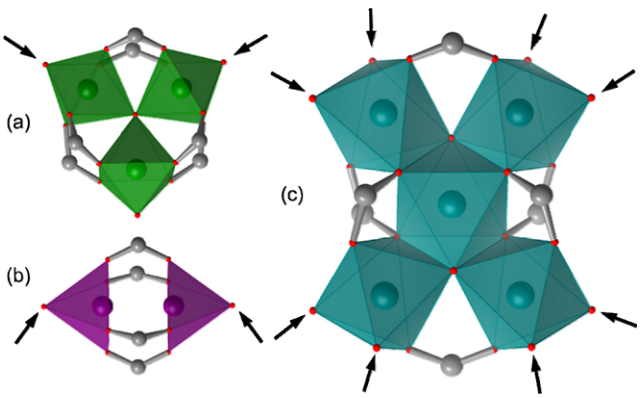

Fig. 2 The clusters comprise open metal sites in: (**a**) MIL-101, (**b**) $Cu_3(btc)_2$ (HKUST-1), and (**c**) $Ni_5O_2(btb)_2$ (DUT-9) (*arrows* point to removable solvent)

2 Experimental section

2.1 Materials

The Metal-Organic Frameworks used in this study were synthesised as reported earlier: $Cu_3(btc)_2$ (Schlichte et al. 2004), MIL-101 (Férey et al. 2005; Llewellyn et al. 2008), DUT-9 (Gedrich et al. 2010), MOF-5 (Li et al. 1999), DUT-6 (Klein et al. 2009), $Zn_4O(btb)_2$ (Caskey et al. 2008), DUT-4 (Senkovska et al. 2009), $Zn_2(bdc)_2(dabco)$ (Dybtsev et al. 2004). For more details to synthesis and characterisation see Supplementary Material. ZIF-8 (BasoliteZ1200) was purchased from Sigma Aldrich.

2.2 Characterisation

Powder X-ray diffraction (PXRD) patterns were obtained in transmission geometry using a Stoe StadiP X-ray diffractometer equipped with an imaging plate position sensitive detector and CuKα_1 ($\lambda = 1.5405$ Å) radiation (40 kV, 30 mA).

Nitrogen physisorption isotherms were measured at 77 K using Quantachrome AUTOSORB 1 C or QUADRASORB apparatus. The specific total pore volume was estimated at $p/p_0 = 0.9$.

The liquid-phase adsorption and the hydrogenation reaction were controlled using GC/MS analysis (SHIMADZU GCMS QP5000) equipped with a non-polar BPX5 column (5% Phenyl polysilphenylene-siloxane from SGE company).

2.3 Liquid-phase adsorption

After the synthesis and activation, the MOFs were consequent handled and stored under argon atmosphere in a glove box.

Typically liquid-phase experiments were carried out in an argon flushed 10 ml Schlenk flask at 298 K. To achieve one point of the adsorption isotherm, approximately 100 mg of MOF were contacted with a solution (10 ml) of adsorptive with known concentration.

After addition of substrate solution to the activated adsorbent the mixture was stirred. The adsorption process was monitored by sampling 0.1 ml of the solution using a syringe and a 0.45 µm PTFE filter after certain periods of time. We assumed that the equilibrium was reached, if no changes in the concentration of the solution could be detected *via* GC/MS analysis.

To estimate the amount of substrate adsorbed 0.2 ml of a standard solution (hexadecane in *n*-heptane, 44 mmol l^{-1}) was added to the taken sample. Applying gas chromatography (GC), the initial and effective concentrations were determined using a calibration curve. The amounts of adsorbed substrate (m_{ads}) were calculated from the differences of these two concentrations. The volume change due to the sampling was neglected.

The amount of substance adsorbed per unit mass of the MOF was calculated by (1)

$$m_{ads} = \frac{M \cdot V_0 \cdot (c_0 - c_i)}{m_s} \quad (1)$$

where m_{ads} (called the excess adsorption) is the amount of the substance adsorbed as compared with its content in an equal volume of equilibrium solution per unit mass of the adsorbent; c_0—the initial concentration of the substrate in the starting solution; c_i—the effective concentration of the substrate in the solution at measuring point (time); V_0—volume of the solution; m_s—mass of the activated MOF material; M—molecular weight of substrate.

Calculating m_{ads} for various concentrations of substrate in the equilibrium state the excess adsorption isotherms could be plotted.

2.4 Hydrogenation

2.4.1 Sample preparation

For hydrogenation reaction the activated MOFs were first impregnated with a chloroform solution of palladium precursor (palladium acetylacetonate, $Pd(acac)_2$) *via* incipient wetness technique as reported before (Henschel et al. 2008; Sabo et al. 2007) (see Supplementary Material). 50 mg of dried, fine powdered $Pd(acac)_2$/MIL-101 were placed in a glass flask and heated in a H_2 flow at 473 K for 1 h to obtain MIL-101 containing 1 wt% Pd.

2.4.2 Reaction

After cooling to 308 K, 50 ml *n*-heptane and 5 g of the substrate ($c_0 = 1$ mol l^{-1}, precursor catalyst to substrate weight ratio 1:100) were added to the flask.

3 Results and discussion

3.1 Pore volume effect

Since the adsorption is a surface phenomenon and it was often documented, that the adsorption capacity directly depends on the porosity of material, it was important to check this relation for chosen MOFs.

Figure 3 shows liquid-phase adsorption of ethylcinnamate in *n*-heptane (left) and *i*-octane (right) for an initial adsorbate concentration (c_0) of 0.1 mol l^{-1}. For MOFs of the second group without open metal sites (DUT-4, $Zn_4O(btb)_2$, MOF-5, DUT-6) a nearly linear dependency between the amount of substrate adsorbed and total pore volume is detected. MIL-101, the palladium loaded compound (denoted Pd/MIL-101) and DUT-9 show an outstanding better performance. Also $Zn_2(bdc)_2(dabco)$, due to the flexibility of the framework shows slightly anomalous behaviour.

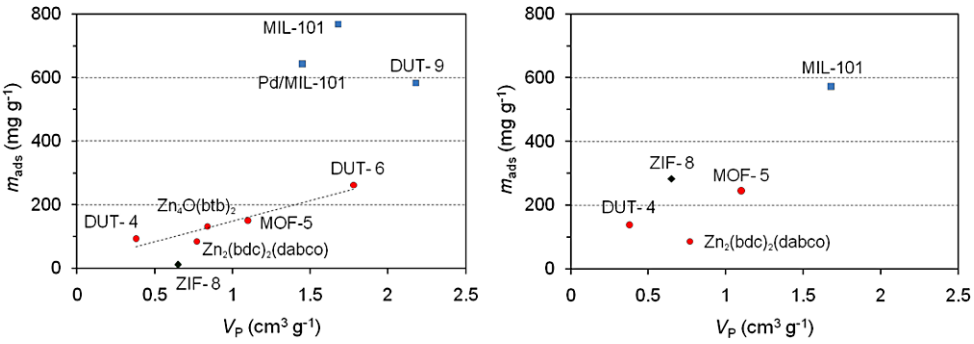

Fig. 3 Adsorption of ethylcinnamate in *n*-heptane (*left*) and *i*-octane (*right*) on selected MOFs (initial concentration of 0.1 mol l^{-1})

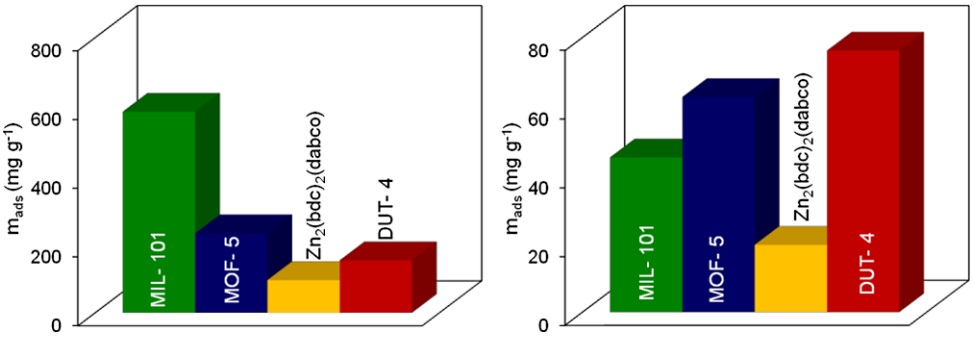

Fig. 4 Adsorption of ethylcinnamate (*left*) and styrene (*right*) in *i*-octane on selected MOFs (initial concentration of 0.1 mol l^{-1})

3.2 Adsorption of nonpolar substances

It is also known, that the polarity of the adsorbate and adsorbent has a huge influence on the adsorption properties. As an example the differences in the shape of adsorption isotherms for nitrogen gas and water vapour on activated carbons could be named.

In contrast to the polar ethylcinnamate, the amount of a nonpolar molecule like styrene, adsorbed from *i*-octane in investigated MOFs, turns out about a tenth less pointing on the hydrophilic character of the frameworks (Fig. 4). Furthermore in case of nonpolar molecules it takes much longer till the adsorption equilibrium state is reached. For example, in case of DUT-4 the reaching equilibrium took about three times longer for styrene than for ethylcinnamate in *i*-octane (Fig. S1).

3.3 Solvent effect

The influence of the nature of solvents (like polarity and kinetic diameter d_{kin}) for the adsorption of styrene was examined in detail for MIL-101 (Fig. 5). The concentration of styrene used for adsorption experiments was 0.1 mol l^{-1}.

By changing the polarity of the solvent the selectivity and efficiency of the substrate adsorption may be tuned. Essentially, compared to nonpolar solvents used (ε from 1.9 up to 2.4), styrene uptake is largely suppressed when adsorption occurs from polar ethylacetate ($\varepsilon = 6.0$) or DCM ($\varepsilon = 8.9$) (Fig. 5). For these polar solvents, the amount of styrene detected is very low and fluctuates around zero-point over the whole time range. Thus, ethylacetate and DCM are evaluated as unsuitable solvents for the adsorption of styrene in MIL-101.

Additionally, the size of the solvent has significant influence on the adsorption, what could be demonstrated for nonpolar solvents.

In case of small solvent molecules, *e.g.* *n*-heptane ($d_{kin} = 4.3$ Å), *i*-octane ($d_{kin} = 6.2$ Å) or toluene ($d_{kin} = 5.9$ Å), the adsorption of the solvent seems to be in strong competition to the adsorption of substrate molecule styrene. Additionally, the utilisation of solvents with a kinetic diameter similar to the substrate molecule like *i*-octane ($d_{kin} = 6.2$ Å)

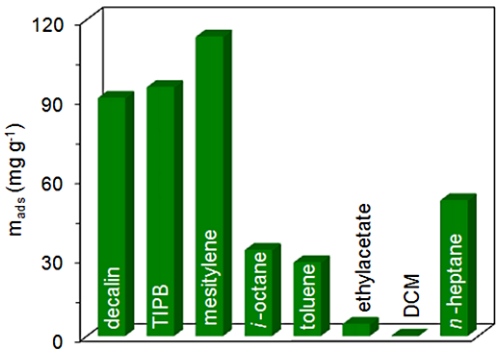

Fig. 5 Adsorption of styrene in different solvents on MIL-101 (initial concentration of 0.1 mol l^{-1})

or toluene ($d_{kin} = 5.9$ Å), leads to a decrease of the amount adsorbed in comparison to *n*-heptane. Higher loadings were detected if larger solvents, like mesitylene ($d_{kin} = 7.5$ Å), triisopropyl benzene ($d_{kin} = 8.5$ Å), and a *cis*/*trans*-decalin mixture ($d_{kin} \sim 9.0$ Å), were used. However the evaluation of the data *via* GC/MS analysis is difficult when high-boiling liquids are used. The peaks of solvent and standard (hexadecane) overlap in the chromatogram leading to uncertainness in the determination of the amount adsorbed.

The next pronounced example for the influence of the solvent on the adsorption behaviour is the adsorption of ethylcinnamate on ZIF-8 from *n*-heptane or *i*-octane. Branched alkanes (*i*-octane included) cannot enter the pores of the ZIF material as demonstrated by Luebbers et al. (2010). Consequently, the ethylcinnamate adsorption capacity in *i*-octane solution (282 mg g^{-1}) are remarkable larger than in *n*-heptane solution (11 mg g^{-1}) (Fig. 3). Bearing in mind the hydrophobic nature of ZIF-8 framework and that *n*-heptane ($\varepsilon = 1.9$) is more hydrophobic than ethylcinnamate ($\varepsilon = 6.0$), this result is in good agreement with the expectation, that solvent in this case should be adsorbed in favour.

3.4 Adsorption isotherms

From the collected data it was possible to plot ethylcinnamate adsorption isotherms for MIL-101 and DUT-9 in

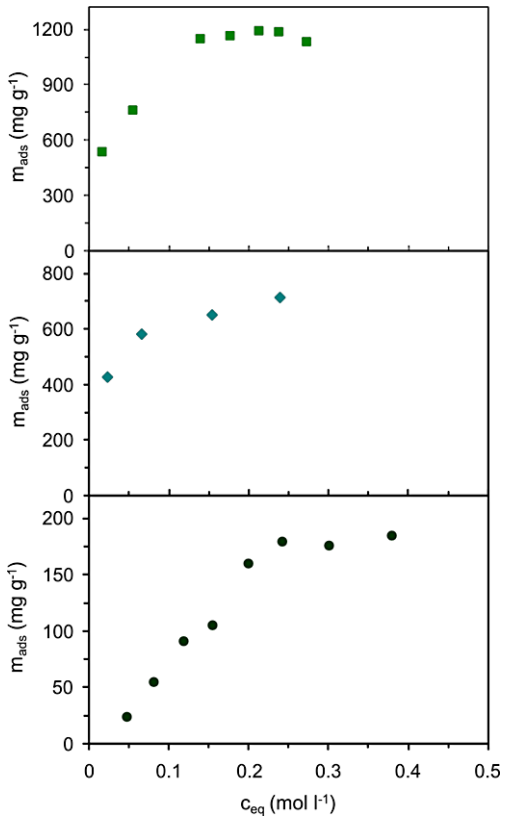

Fig. 6 Adsorption isotherm of ethylcinnamate in *n*-heptane on MIL-101 (*top*), DUT-9 (*middle*) and of styrene in *n*-heptane on Pd/MIL-101 (*bottom*) at 295 K

n-heptane and styrene adsorption isotherm for Pd/MIL-101 in *n*-heptane (Fig. 6). When choosing MIL-101 as adsorbent, the curve reaches a maximum at around 1200 mg ethylcinnamate per gram MOF at an equilibrium concentration of nearly 0.2 mol l^{-1} (Fig. 6 top). In comparison, the adsorption isotherm for DUT-9 is increasing over the whole measured concentration range without reaching saturation (Fig. 6 middle).

The adsorption isotherm of styrene on palladium loaded MIL-101 shows a slope not as steep as the adsorption isotherm of ethylcinnamate and a lower maximum uptake (Fig. 6 bottom).

3.5 Hydrogenation reaction

Styrene is a common substrate for heterogeneous catalytic hydrogenation reaction. In previous works we show the good performance of palladium supported MOFs in the hydrogenation of styrene without any additional solvents (Sabo et al. 2007; Henschel et al. 2008).

The hydrogenation reaction can be simplified viewed as consisting of three steps: adsorption of substrate, reaction on the surface of the catalyst, and desorption of the product. The solvent can influence all of these processes. The

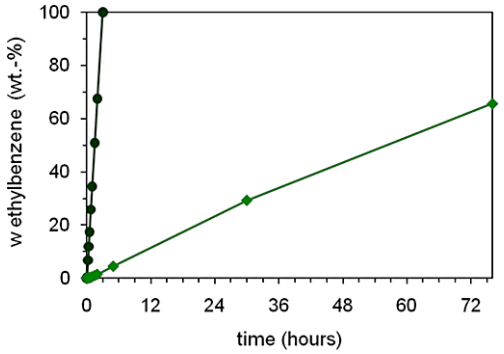

Fig. 7 Hydrogenation of styrene in *n*-heptane (*circle*) and DCM (*diamond*) on Pd/MIL-101 at 308 K with an initial concentration of 1 mol l^{-1}

study of the adsorption equilibrium is helpful to evaluate the appropriate solvent for the first step. A further factor, influencing the reaction performance in addition to adsorption/desorption rate, is the solubility of hydrogen in the given solvent.

To consider all additional factors, the hydrogenation of styrene with Pd/MIL-101 as catalyst was carried out in two solvents selected based on adsorption experiments (Fig. 7). On the one hand *n*-heptane was chosen due to its good performance in our adsorption tests. Otherwise DCM was employed because no adsorption of styrene was detectable. Interestingly, DCM is up to now one of the most often used solvents for catalytic reactions with MOFs reported in the literature.

Figure 7 depicts the results of the hydrogenation reaction. Using *n*-heptane as solvent, the conversion of styrene to ethylbenzene is already completed after three hours. By using DCM the complete conversion is not reached even after 76 hours of hydrogenation. This observation is in good agreement with the adsorption experiment, and shows that the solvent plays an important role not only in adsorption process, but also govern the catalytic reaction.

4 Conclusion

Metal-organic frameworks are able to adsorb large amounts of substrate molecules from the liquid phase. However, the adsorption capacity strongly depends on surface chemistry, pore size and shape, as well as total pore volume of the studied MOFs. More important is the solvent used and the differences in polarity of the solvent and substrate causing co-adsorption. The understanding of interaction between the solvent, substrate and framework is certainly the most important point for the optimisation of adsorption process and the use of MOFs in catalytic reactions. DCM and ethylacetate turn out to be disadvantageous as solvents for the adsorption on the most prominent metal-organic framework

MIL-101. The influence of the solvent used could also be shown for the hydrogenation reaction using a palladium loaded MIL-101 as catalyst.

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