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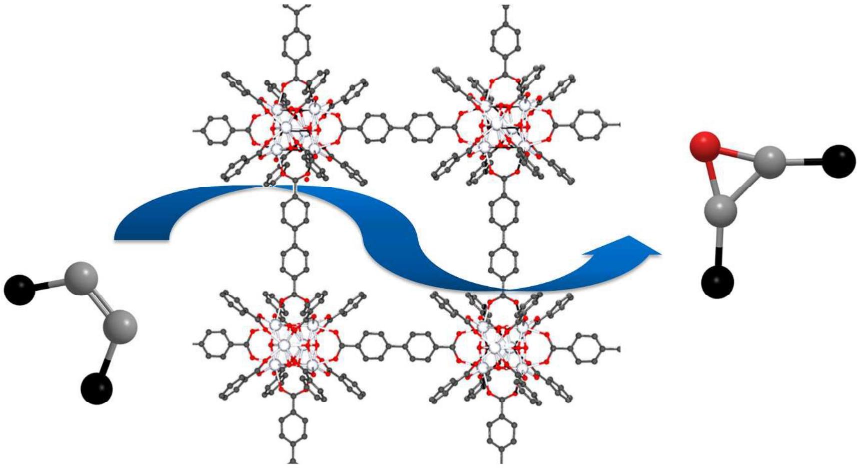

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ARTICLE

Immobilisation of a molecular epoxidation catalyst on UiO-66 and -67: effect of pore size on catalyst activity and recycling

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Amino-functionalised metal-organic frameworks UiO-66 and -67 were post-synthetically modified with salicylaldehyde. A molybdenum complex was immobilised on the resulting materials. They were characterised by ^{13}C-MAS-NMR, XPS and PXRD to confirm immobilisation and stability. The immobilised complex is an active and reusable catalyst for olefin epoxidation with *tert*-butyl hydroperoxide (TBHP) as oxidant. It is shown that the effective pore size, probed with Brunauer-Emmett-Teller (BET) surface areas, and the number of amino groups affect the diffusion of reactants and product, as well as catalyst recycling.

Introduction

The catalytic epoxidation of olefins is a very important reaction in chemical industry since epoxides are starting materials for a plethora of chemicals.[1,2] Although there are numerous highly active molecular catalysts of titanium, vanadium, manganese, rhenium, and more recently, iron,[3] most of them have been neglected so far in industrial epoxidations since they are usually too expensive and cannot be easily recycled for a large number of runs.

Molybdenum complexes have been used as catalysts for the industrial Halcon-ARCO, and more recently, the Sumitomo processes.[2] In the 1970s two mechanistic pathways for the Mo-catalysed epoxidation were proposed, both involving the formation of a Mo-peroxo intermediate, which is transferring an oxygen atom to the olefin.[4,5,6,7]

Molecular molybdenum epoxidation catalysts have been heterogenised to various supports over the last 15 years (silica, including MCM materials, polymers, carbon, etc.) to facilitate catalyst recycling.[8] However, in many cases the immobilisation is associated either with a loss of activity compared with the homogeneous congeners, or with a slow but significant catalyst leaching into the reaction slurry. Particularly the activity loss is a serious issue, originating from both diminishing accessibility of the metal centres and diffusion limitations.[9,10] For this reason, porous coordination polymers, and more specifically metal-organic frameworks (MOF) appear to be interesting supports for molecular catalysts, since they allow both a variation of pore size and introduction of functional groups by design of the organic linkers.[11] So far, some epoxidation catalysts have been immobilised on IRMOF-3,[12] paddle-wheel MOFs,[13] or MIL-101(Al)[14] and MIL-47.[15] To the best of our knowledge there are three reports of Mo(VI) species immobilised on MOFs, but either the conversions are lower compared to the homogeneous analogue,[16] the materials decompose over time in presence of an excess of oxidant[17] or comparability is not possible, because no catalyst loading is reported.[10] Hence, the molecular catalyst must be strongly bound to the MOF, the pore size must allow for a facile diffusion of both substrate and product, and the MOF must be stable to air, water and oxidants. Zr-based UiO frameworks 66 and -67 (UiO = Universitetet i Oslo) by Lillerud et al.[18,19] are exceptionally stable compounds, which have recently been used as support materials for epoxidation reactions.[10,17]

In this work, UiO-66 and -67 materials with varying contents of amino groups were fabricated and postsynthetically functionalised whereby the amino groups were employed for the immobilisation of a molecular molybdenum catalyst. The postsynthetic method used in this work has been applied in the immobilization of metals such as V(V)[12b], Au(III)[20], Ni(II)[21] and Ir(I)[22], however, the incorporation of Mo(VI) into an amino-containing MOF is reported for the first time. The obtained entities have been applied for the epoxidation of olefins, with special regard to material recycling and stability.

Results and Discussion

Synthesis and characterisation

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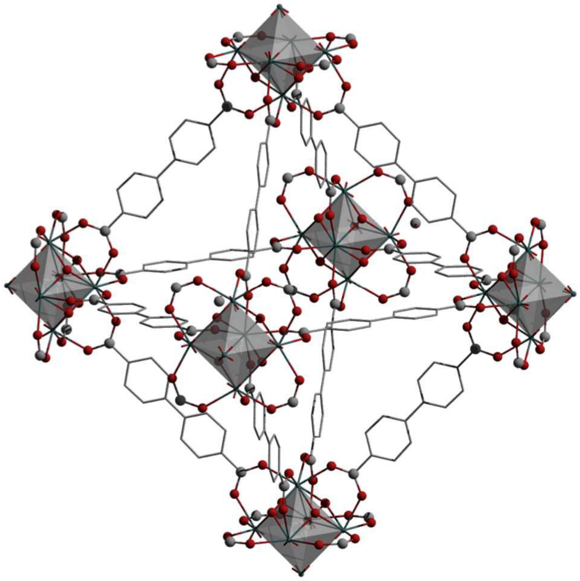

Fig. 1 X-ray single crystal structure of UiO-67-NH_2 (Amino groups are disordered due to the statistical distribution of the NH_2-groups within the pores and are therefore omitted for clarity, see the Supporting Information (SI) for details).

A set of four carrier materials was synthesised, including the fully amino-functionalised UiOs,[18] as well as mixed UiOs, where only 1/6 of the linkers contain –NH_2 groups.[23] Already the functionalisation – full or partial – reduces the effective pore size. The structure of UiO-67-NH_2 was confirmed by single crystal X-ray diffraction (see Fig. 1) using a crystal obtained via modulated synthesis with benzoic acid.[24] Despite all efforts, single crystals of the Mo complex immobilised on UiO materials could not be obtained due to the statistical distribution of the NH_2-groups within the pores.

The amino groups in the functionalised MOFs UiO-66-NH_2 (**1**), UiO-66 mixed (**2**), UiO-67-NH_2 (**3**) and UiO-67 mixed (**4**) were transformed with salicylaldehyde to a salicylidene (SI) substituent via a previously reported vapour diffusion reaction.[25] The washed and dried materials were then treated with a solution of $[MoO_2(acac)_2]$ (acac = acetylacetonate) in methylene chloride, washed and dried again prior to characterisation and catalysis tests (for details see the Experimental Section). The steps of the modification are shown in Scheme 1. The obtained MOFs are denoted as UiO-SI and Mo@UiO respectively. Their molybdenum content after modification was determined by elemental analysis. The values for carbon, hydrogen and nitrogen deviate from the expected ones and were different for every batch of MOF, because different amounts of solvent remained in the pores. Even extensive drying could not completely remove the solvents. This is in particular the case for the UiO-66 materials, which exhibit smaller pores than the UiO-67 type composites. In the experimental part the values for the MOFs used in catalysis are given. Different amounts of H_2O and dimethylformamide (for the unmodified MOFs) and additionally CH_2Cl_2 for the Mo@UiOs had to be added to the calculation to fit the experimental values. Furthermore the degree of functionalisation of Mo@UiO MOFs can vary and therefore has to be considered. The solvents most presumably interact with either the SBU or the amino group (in the case of the functionalised MOFs) via hydrogen bonds, and therefore a complete removal of all solvent molecules is difficult. It also has to be noted that for the functionalised Mo@UiO-67 and Mo@UiO-67 mixed the content of residual solvents is significantly lower than for the Mo@UiO-66 and Mo@UiO-66 mixed MOF composites (see the Experimental Section), which have smaller quantities. Therefore, it can be concluded that in dependence of the pore size solvent removal is hindered and thus can also negatively affect the diffusion of substrates in catalysis (see below).

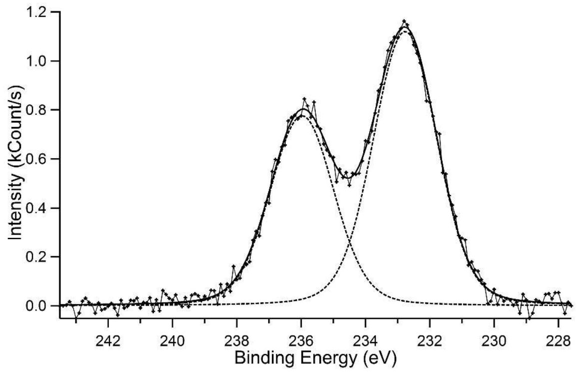

Fig. 2 Mo 3d XPS line with binding energies of 232.8 and 236.0 eV for the Mo 3d5/2 and 3d3/2 levels, respectively.

Fig. 2 shows the powder X-ray diffraction (PXRD) patterns of UiO-67-mixed (**4**) before and after functionalisation (Fig. 3a-c), ^{13}C MAS-NMR spectra of the same structure are shown in Fig. 4. The patterns are similar to previous reports, showing that the UiO-type structure is formed.[18,24] After modification with the Mo compound ^{13}C MAS-NMR show an additional peak at 24-25 ppm corresponding to the methyl groups of acetylacetonate. In the ^{95}Mo-NMR spectrum no signal was observed due to both low natural abundance of the ^{95}Mo isotope (ca. 15 %), the quadrupolar moment of the ^{95}Mo nucleus (I = 5/2), leading to broad signals and the low concentration of immobilised Mo.

Additionally, XPS measurements were performed to confirm the valence of the immobilised molybdenum. The Mo3d

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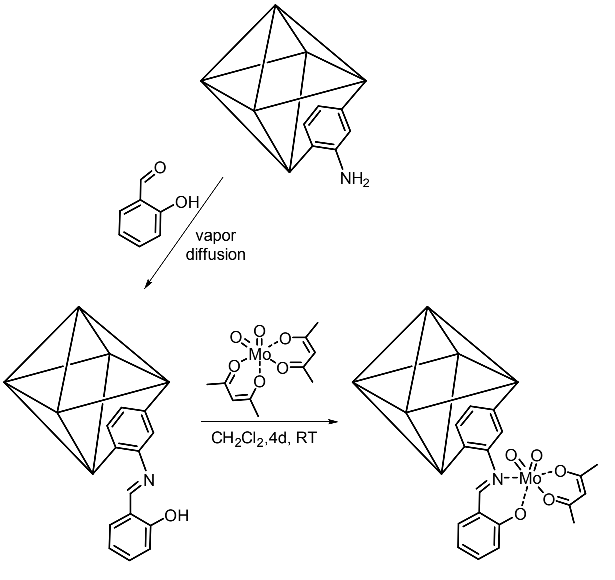

Scheme 1 Post-functionalisation route of UiO-MOFs with salicylaldehyde and [$MoO_2(acac)_2$].

spectrum exhibits two clear peaks, one at 232.8 eV and one at 236.0 eV (see Fig. 2). Both the binding energy splitting (3.2 eV) and the relative peak intensities (59:41) agree well with expected values for the spin-orbit coupled Mo3d line (3.13 eV and 3:2, respectively).[26,16] Accordingly, the XPS signature evidences the presence of a single Mo species with an oxidation state of 6+ as concluded from the measured binding energies.

For UiO-67-mixed a specific surface area of 2200 m^2g^{-1} was found using BET measurements (Fig. 5), while the surface of fully functionalised UiO-67-NH_2 is reported as 1800 m^2g^{-1},[27] which is clearly showing the effect of reducing the number of amino groups in the porous material. Furthermore for Mo@UiO-67-mixed BET measurements showed a specific surface area of 2000 m^2g^{-1}. Therefore it can be stated that the pores are not obstructed by the immobilised complex (Fig. 5).

Catalytic tests and recycling

All four Mo@UiO composites (wt.% Mo: 8.48% for UiO-66, 5.69% for UiO-66 mixed, 3.23% for UiO-67 and 2.43% for UiO-67 mixed) were examined as catalysts for the epoxidation of cyclooctene in neat TBHP (5.5 M in decane) at 50 °C.

After catalysis the Mo@UiO-67-mixed material remainsunchanged (see Fig. 3d), suggesting that the framework is still intact and stable towards TBHP.

While in all cases the selectivity of cyclooctene oxide is very high, the conversion shows a strong dependence on the degree of functionalisation (Table 1). Note that the epoxidation does not take place in the case of UiO-66 and -67 without immobilised Mo catalyst (not shown in Table 1). Additionally, in all cases a reduction of the reaction temperature has a detrimental effect on the conversion. Kinetic studies have been performed (Figure 6) and TOF was calculated to be 130 h^{-1} (after 15 min). With the homogeneous

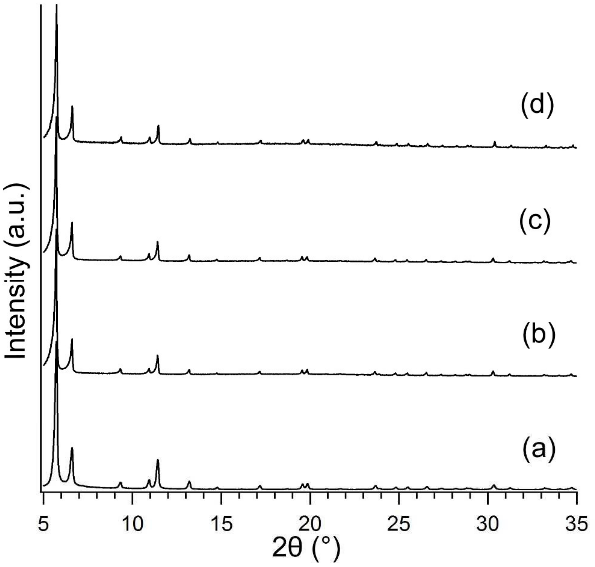

Fig. 3 PXRD patterns of (a) UiO-67-mixed, (b) UiO-67-SI-mixed, (c) Mo@UiO-67-mixed and (d) Mo@UiO-67-mixed after catalysis.

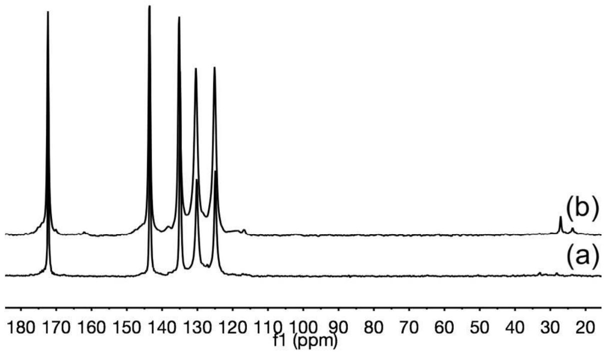

Fig. 4 ^{13}C-MAS-NMR spectra of (a) UiO-67-mixed and (b) Mo@UiO-67-mixed.

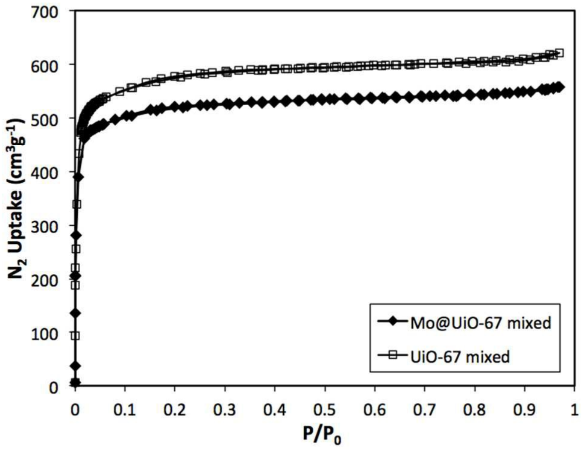

Fig. 5 Nitrogen adsorption isotherms of mixed UiO-67-NH_2 and Mo@UiO-67 mixed.

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analogue a TOF of 870 h^{-1} is reached. The reduced TOF for the MOF catalyst can be attributed to the intrinsic diffusion limitation of heterogeneous systems. A leaching experiment was performed with Mo@UiO-67 by separating the reaction mixture from the solid catalyst after 50 % conversion (30 min). The remaining solution showed an increase in conversion to 62 % over the next 4 h. However, it has to be noted that substrate and oxidant without catalyst yielded in a conversion of 8 % after 4 h.Therefore it can be concluded that no leaching occurred. The catalysts were used for ten cycles to investigate the stability and recyclability of the materials. After each cycle the MOFs were separated from the reaction products by decantation, washed with dichloromethane and dried in vacuum overnight either at room temperature (run 1-3) or at 150 °C (run 4-10). Powder X-ray diffraction (PXRD) measurements after the reactions confirmed that the frameworks stay intact during catalysis and recycling (Fig. 3 for Mo@UiO-67 mixed, Fig. S1-S3 in the SI for the others). In a parallel study by Valente et al. recycling was not possible since the network decomposed.[17]

Best recycling results were achieved with Mo@UiO-67 mixed (Fig. 7). This fact can be attributed to the larger pore size of the mixed MOF compared to Mo@UiO-67 and the UiO-66 series. Therefore the pores are not as easily obstructed and the remaining educts, products and by-products can be removed in vacuum even at room temperature. However, for an efficient recycling of the unmixed MOF it is necessary to heat the system to 150 °C to remove all remaining substrate, solvent and product molecules.

After several runs even heating could not clear the pores of the unmixed Mo@UiO-67 and the UiO-66 MOFs completely, leading to a drop in activity. This was most prominently observed for Mo@UiO-66, which is exhibiting the smallest pores. A comparison of the catalytic results with those reported previously[10] is not possible since in this work the Mo content in the catalyst has not been given.

Furthermore, Mo@UiO-67 mixed was tested for epoxidation of 1-octene and styrene (see Table 1, entries 5 and 6). In contrast to cyclooctene, here the conversions are lower, which can be attributed to the fact that additionally to its Lewis acid character the MOF contains OH groups coordinated to the zirconium clusters. Therefore diols are formed from less stable epoxides. To eliminate the OH groups the MOF was heated in vacuum to 300 °C for 48 h prior to modification and catalysis.[28] By using this method the selectivity is increased to 100 %, whereas the conversion for 1-octene drops to 13 % after 24 h. This effect is most presumably due to *tert*-butanol coordinating to the free coordination sites at the zirconium cluster, which blocks the pores and inhibits further reaction. To prove this hypothesis, we added *tert*-butanol to the dehydrated Mo@UiO-67-mixed material prior to addition of cyclooctene and TBHP solution. Indeed, the conversion drastically reduces, corroborating the hypothesis that the ^{t}BuO groups coordinate to Zr centres and decrease the pore size of the material, thus limiting substrate diffusion and hence the conversion.

Table 1. Epoxidation of cyclooctene with different catalysts at 50 °C[a]

Catalyst	Substrate	Conv. (%)	Sel.[b] (%)
Mo@UiO-66	Cyclooctene	63	100
Mo@UiO-66 mixed	Cyclooctene	94	100
Mo@UiO-67	Cyclooctene	100	100
Mo@UiO-67 mixed	Cyclooctene	100	100
Mo@UiO-67 mixed	1-Octene	62	70
Mo@UiO-67 mixed	Styrene	38	68

a Reaction conditions: 1 mol % catalyst, 150 mol % TBHP, 50 °C, 4h,
b Selectivity to cyclooctene oxide

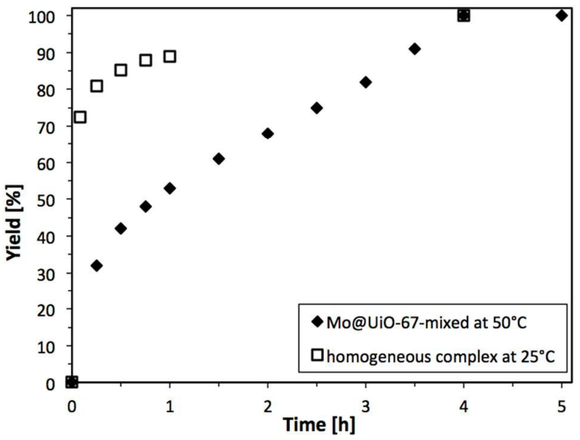

Fig. 6 Plot of yield versus time in the oxidation of cyclooctene with TBHP and 1 mol % of Mo@UiO-67-mixed at 50 °C and [MoO_2(acac)(PhN=C-PhO)] at room temperature.

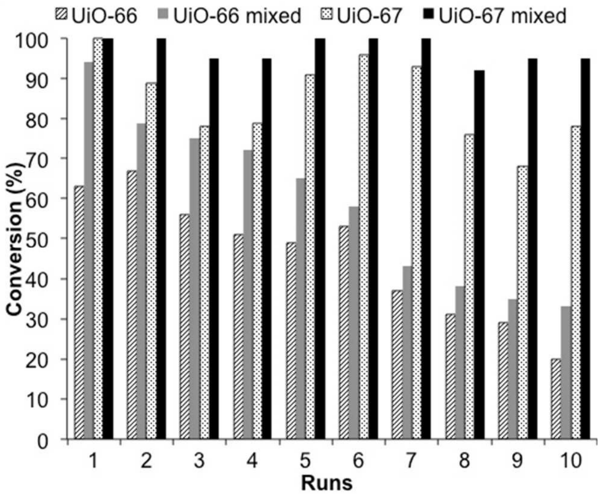

Fig. 7 Recycling of the different modified MOF catalysts in epoxidation reaction with cyclooctene.

Conclusions

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In summary, a series of chemically robust composite materials containing molecular molybdenum complexes anchored to UiO-type MOFs has been synthesised. Both the catalyst anchor and the porous host network are very stable towards oxidative conditions and leaching was not observed. It could be shown that the catalytic activity depends strongly on the effective pore size of the carrier material, owing to diffusion limitations of substrate, product and oxidant. This can be easily modulated by changing the content of amino functionalities at the organic linker. The Mo@UiO catalyst with the highest effective pore size can be reused for several times without a notable loss of activity, rendering this material viable for two-phase epoxidation of various olefins.

Experimental

General Remarks

All chemicals were obtained commercially (Aldrich, Acros) and used without further purification.

Liquid NMR spectra were recorded on a Bruker Avance DPX 400 and a Bruker DRX 400. Chemical shifts are given in parts per million (ppm) and the spectra were referenced by using the residual solvent shifts as internal standards (dimethylsulfoxide-*d*$_6$, ^{1}H NMR: 2.50 ppm, ^{13}C NMR: 39.52 ppm). Solid-state ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer equipped with a 4 mm BBMAS probe head and referenced to adamantane as an external standard at 298 K.

Specific surface area, pore diameters and pore size distributions were determined by physisorption of N_2. Measurements were carried out using a PMI automatic BET-Sorptometer operating at liquid nitrogen temperature (77 K), after outgassing under vacuum. The results were calculated using the weight after outgassing. Prior to analysis the samples were outgassed to 20 microns vacuum at 250 °C.

XPS measurements were performed in a UHV chamber at a pressure of $5 \cdot 10^{-10}$ mbar and approximately 77 K sample temperature with a non-monochromatic Mg anode source ($\hbar\omega$ = 1253.6 eV) at magic angle incidence and normal emission. Data were obtained with a hemispherical electron energy analyser (100 mm radius) set at a pass energy of 20 eV. To the Mo3d raw data a Shirley-type background subtraction was applied and the energy binding scale was calibrated against the C1s line at 284.8 eV. For peak fitting a Voigt line slope was employed; no constraints were utilized for relative peak energies or intensities.

Elemental analysis was obtained from the microanalytical laboratory of the Technische Universität München.

X-ray powder diffraction was carried out using a Stoe Stadi P diffractometer operated with CuKα_1 radiation (λ = 1.5406 Å) and a Ge(111) monochromator in transmission mode. X-ray single crystal diffraction data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ-CCD), a rotating anode FR591 equipped with a Montel mirror optic (UiO-67-NH_2) or a fine focused sealed tube equipped with a graphite monochromator ([MoO_2(acac)(PhN=C-PhO)]) by using the APEXII software package.[29] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals were frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarisation effects, scan speed, and background using SAINT.[30] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[30] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps,[31] and were refined against all data using the APEX 2 software[29] in conjunction with SHELXL-97[32] and SHELXLE.[33] Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Hydrogen atoms bond to nitrogen were not refined. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97 weighting scheme.[32] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography*.[34] Images of the UiO-67-NH_2 crystal structures were generated by Diamond,[35] for [MoO_2(acac)(PhN=C-PhO)] by PLATON.[36]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.'s CCDC-1026989 ([MoO_2(acac)(PhN=C-PhO)]) and CCDC-1026990 (UiO-67-NH_2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Linker preparation

Dimethyl-2-nitrobiphenyl-4,4'-dicarboxylate (1). The compound was prepared similar to literature-known procedure.[37] A mixture of nitric acid (56%, 1.3 mL, 74 mmol) and concentrated sulfuric acid (1.6 mL) was added dropwise to a solution of dimethylbiphenyl-4,4'-dicarboxylate (5 g, 74 mmol) in 50 mL of concentrated sulfuric acid at 0 °C under intense stirring. The reaction mixture was maintained at 0-5 °C for 1 h and at 10-15 °C for 4 h before being poured on crushed ice. The precipitated solids were separated by filtration, washed with water and recrystallised from isopropanol. Yield: 4.12 g (71 %) of colorless powder. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ = 3.89 (s, 3H, -CH_3), 3.94 (s, 3H, -CH_3), 7.56 (d, 2H, *J* = 8.4 Hz, 3',5'/2',6'-Ar), 7.76 (d, *J* = 8.0 Hz, 6-Ar(NO_2)), 8.06 (d, 2H, *J* = 8.4 Hz, 3',5'/2',6'-Ar), 8.31 (dd, 1H, *J* = 1.65, 8.01 Hz, 5-Ar(NO_2)), 8.51 (d, 1H, *J* = 1.55 Hz, 3-Ar(NO_2)); ^{13}C NMR (101 MHz, DMSO-d$_6$, ppm) δ = 52.8, 53.4, 125.4, 128.8, 130.0, 130.3, 130.9, 133.2, 133.7, 138.9, 141.4, 148.9, 164.8, 166.2.

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Other data matched those previously reported for this compound.

Dimethyl-2-aminobiphenyl-4,4'-dicarboxylate[38] (2). To a stirred solution of dimethyl-2-nitrobiphenyl-4,4'-dicarboxylate (2.9 g, 9.19 mmol) in 115 mL of methanol tin powder (6.45 g) and 40 mL of an aqueous 1 M HCl solution were added. The suspension was heated to reflux for 2 h under intense stirring before being poured on to crushed ice. The solution was then basified with aq. 1 M NaOH solution and the precipitated solids were separated by filtration. The crude product was extracted with warm ethyl acetate. Any remaining insoluble byproducts were removed by filtration over Celite. The solvent was removed under vacuum and crude product was purified by flash chromatography (ethyl acetate/dichloromethane: 10 %). Yield: 2.18 g (92 %) of light yellow powder. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ = 3.83 (s, 3H, -CH$_3$), 3.88 (s, 3H, -CH$_3$), 5.23 (s, 2H, -NH$_2$), 7.14 (d, 1H, J = 8.0 Hz, 6-Ar(NH$_2$)), 7.22 (dd, 1H, J = 1.8, 7.8 Hz, 5-Ar(NH$_2$)), 7.44 (d, 1H, J = 1.6 Hz, 3-Ar(NH$_2$)), 7.61 (d, 2H, J = 8.4 Hz, 3',5'/2',6'-Ar), 8.04 (d, 2H, J = 8.4 Hz, 3',5'/2',6'-Ar); ^{13}C NMR (101 MHz, DMSO-d$_6$, ppm) δ = 52.0, 52.2, 116.0, 117.1, 128.3, 128.5, 128.9, 129.7, 129.9, 130.4, 143.7, 145.6, 166.1, 166.5. Other data matched those previously reported for this compound.

2-Aminobiphenyl-4,4'-dicarboxylic acid (BPDC-NH$_2$)[38]. A mixture of dimethyl-2-aminobiphenyl-4,4'-dicarboxylate (0.68 g, 2.39 mmol, 1 equiv.) in 13 mL of THF and 13.2 mL of an aqueous 1M KOH solution was heated to reflux for 16 h. After cooling to room temperature in air, the THF was removed under vacuum and the solution was acidified with aq. 1M HCl. The resulting precipitate was separated by filtration, washed with water, then methanol and air-dried. Yield: 0.585 g (95 %) of yellow powder. ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ = 5.15 (s, 2H, -NH$_2$), 7.12 (d, 1H, J = 8.0 Hz, 6-Ar(NH$_2$)), 7.21 (dd, 1H, J = 1.4, 7.8 Hz, 5-Ar(NH$_2$)), 7.41 (d, 1H, J = 1.6 Hz, 3-Ar(NH$_2$)), 7.58 (d, 2H, J = 8.4 Hz, 3',5'/2',6'-Ar), 8.02 (d, 2H, J = 8.4Hz, 3',5'/2',6'-Ar), 12.83 (bs, 2H, -CO$_2$H); ^{13}C NMR (101 MHz, DMSO-d$_6$, ppm) δ = 116.7, 117.8, 128.8, 129.2, 129.9, 130.3, 130.7, 131.4, 143.8, 145.9, 167.6, 168.0. Other data matched those previously reported for this compound.

Catalyst preparation

Preparation of UiO-MOFs[18]. All preparations were performed in a 100 mL screw thread glass vials. ZrCl$_4$ (650 mg, 2.73 mmol,) and the linker (500 mg (2.73 mmol) 2-aminotherephthalic acid for UiO-66-NH$_2$; 83 mg (0.45 mmol) 2-aminoterephthalic acid and 382 mg (2.28 mmol) terephthalic acid for UiO-66 mixed; 703 mg (2.73 mmol) BPDC-NH$_2$ for UiO-67-NH$_2$; 117 mg (0.45 mmol) BPDC-NH$_2$ and 569 mg (2.28 mmol) biphenyl-4,4'-dicarboxylic acid for UiO-67 mixed) were dissolved in 64 mL DMF and water (0.2 mL, 11.1 mmol). The resulting mixture was placed in a preheated oven at 80 °C for 12 h and then held at 100 °C for 24 h. After cooling to room temperature in air, the liquid was decanted and the resulting solid was washed with 30 mL of absolute ethanol three times for 24 h at 60 °C. The resulting powder was dried under vacuum for 16 h.

UiO-66: ^{13}C MAS-NMR: δ = 116.2, 132.5, 138.6, 152.4, 170.7, 172.5; elemental analysis (%): calcd. for $C_{48}H_{34}N_6O_{32}Zr_6$·(9 DMF + 3 H_2O): C 36.53, H 4.21, N 8.52; found: C 32.40, H 4.53, N 8.16.

UiO-66 mixed: ^{13}C MAS-NMR: δ = 118.0, 129.4, 138.1, 148.0, 170.9; elemental analysis (%): calcd. for $C_{48}H_{29}NO_{32}Zr_6$·(15 H_2O): C 29.58, H 3.05, N 0.72; found: C 29.65, H 3.42, N 0.65.

UiO-67: ^{13}C MAS-NMR: δ = 119.6, 127.2, 128.6, 130.3, 136.2, 137.9, 142.8, 144.2, 171.9, 172.5; elemental analysis (%): calcd. for $C_{84}H_{58}N_6O_{32}Zr_6$·(8 H_2O): C 42.84, H 3.17, N 3.57; found: C 42.65, H 2.96, N 3.60.

UiO-67 mixed: ^{13}C MAS-NMR: δ = 124.9, 130.1, 134.9, 143.4, 172.3; elemental analysis (%):calcd. for $C_{84}H_{53}NO_{32}Zr_6$·(1 DMF + 7 H_2O): C 44.75, H 3.19, N 1.20; found: C 44.74, H 2.75, N 1.2.

Single-crystals of UiO-67-NH$_2$ were obtained when ZrCl$_4$ (108 mg, 0.42 mmol), BPDC-NH$_2$ (100 mg, 0.42 mmol) and benzoic acid (1.54 g, 12.6 mmol) were dissolved in 12 mL DMF. The resulting mixture was placed in a preheated oven at 35 °C and slowly heated to 120 °C over a time period of five days and left at that temperature for 12 days.[24]

Modification with salicylaldehyde. UiO-SI MOFs were prepared using a previously reported vapor diffusion method.[25] Salicylaldehyde (50 µL, 0.48 mmol, 2 equiv.) was introduced into a Schlenk tube and the MOFs (1 equiv. of amino groups; 70 mg, 0.04 mmol UiO-66-NH$_2$; 400 mg, 0.24 mmol UiO-66 mixed; 88 mg, 0.04 mmol UiO-67-NH$_2$; 508 mg, 0.24 mmol UiO-67 mixed) were weight into a conical filter paper and fixed in the Schlenk tube not touching the liquid. The system was evacuated and heated overnight at 100 °C under static vacuum. The products were washed with dichloromethane three times for 24 h and dried under vacuum for 16 h. UiO-66-SI: ^{13}C MAS-NMR: δ = 116.8, 132.3, 138.8, 151.9, 171.5, 172.9; UiO-66-SI mixed: ^{13}C MAS-NMR: δ = 115.9, 133.0, 138.3, 152.0, 170.4; UiO-67-SI: ^{13}C MAS-NMR: δ = 117.0, 119.8, 127.7, 128.8, 129.6, 134.3, 135.9, 143.3, 173.1, 173.7; elemental analysis (%): C 53.37, H 2.92, N 2.96; found: C 45.78, H 2.74, N 2.69; UiO-67-SI mixed: ^{13}C MAS-NMR: δ = 119.7, 130.4, 134.1, 143.3, 172.2; elemental analysis (%):C 48.80, H 2.57, N 0.63; found: C 47.81, H 3.22, N 0.72.

Modification with [MoO$_2$(acac)$_2$]. Dried MOFs (1 equiv. of imide groups; 61 mg, 0.03 mmol UiO-66-NH$_2$-SI; 182 mg, 0.1 mmol UiO-66-SI mixed; 72 mg, 0.03 mmol UiO-67-NH$_2$-SI; 229 mg, 0.1 mmol UiO-67-SI mixed) were reacted with bis(acetylacetonato)dioxomolybdenum(VI) (100 g, 0.31 mmol) in dichloromethane over four days under inert atmosphere. The products were washed with dichloromethane three times for 24h and dried under vacuum for 16 h.

Mo@UiO-66: ^{13}C MAS-NMR: δ = 25.0, 118.5, 133.1, 138.8, 150.9, 171.8; elemental analysis (%): calcd. for $C_{108}H_{84}Mo_5N_6O_{57}Zr_6$·(9 DMF + 20 H_2O + 15 CH_2Cl_2): C 31.62, H 3.84, N 3.69, Mo 8.42; found: C 32.06, H 3.93, N 3.78, Mo 8.48.

Mo@UiO-66 mixed: ^{13}C MAS-NMR: δ = 25.9, 118.2, 129.6, 137.4, 163.3, 171.6; elemental analysis (%): calcd. for $C_{72}H_{54}Mo_2N_2O_{42}Zr_6$·(2 DMF + 30 H_2O + 8 CH_2Cl_2): C 27.73, H 3.90, N 1.50, Mo 5.15; found: C 26.74, H 3.10, N 1.38, Mo 5.69.

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Mo@UiO-67: ^{13}C MAS-NMR: δ = 24.4, 116.8, 119.4, 128.7, 129.8, 134.3, 137.9, 143.1, 172.2; elemental analysis (%): calcd. for $C_{103}H_{72}MoN_6O_{38}Zr_6$·(1 DMF + 2 H_2O): C 46.23, H 3.04, N 3.56, Mo 3.48; found: 46.27, H 2.85, N 3.02, Mo 3.23.

Mo@UiO-67 mixed: ^{13}C MAS-NMR: δ = 24.6, 125.0, 130.3, 135.0, 143.4, 172.2; elemental analysis (%):calcd. for $C_{92}H_{59.7}Mo_{0.7}NO_{35.3}Zr_6$·(2 CH_2Cl_2): C 44.70, H 2.54, N 0.55, Mo 2.53; found: C 44.20, H 2.59, N 0.58, Mo 2.43.

Preparation of [MoO_2(acac)(PhN=C-PhO)][39] **(4).** A CH_2Cl_2 (5 mL) solution of previously prepared PhN=C-PhOH[40] (292 mg, 1.48 mmol) was added to a solution of [$MoO_2(acac)_2$] (483 mg, 1.48 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature overnight, and the resulting yellow mixture was filtered via a cannula. The solvent was removed under vacuum and the yellow oily residue suspended in Et_2O (10 mL). The solution was filtered and left overnight to give yellow crystals. ^{1}H NMR (400 MHz, CD_2Cl_2, ppm) δ = 8.25 (1H, s, N=CH), 7.58 (1H, m, 5-Ar), 7.47 (1H, m, 3-Ar), 7.35 (2H, m, 3,5-Ar(-N)), 7.27 (1H, m, 4-Ar(-N)), 7.16 (2H, m, 2,6-Ar(-N)), 7.10 (1H, m, 9-Ar), 7.07 (1H, m, 11-Ar), 5.46 (1H, s, acac), 2.00 (3H, s, Me), 1.47 (3H, s, Me). ^{13}C NMR (101 MHz, CD_2Cl_2, ppm) δ = 196.5, 186.5, 166.4, 161.6, 151.9, 136.1, 135.2, 129.1, 127.2, 123.7, 122.3, 121.7, 120.2, 104.5, 28.0, 25.4. ^{95}Mo NMR (26 MHz, CD_2Cl_2, ppm): -25.2.

Catalytic tests

All catalytic tests were performed under argon using Schlenk techniques.

Epoxidation of olefins with MOF catalysts. All four Mo@UiO composites (0.03 mmol; 34 mg for UiO-66, 51 mg for UiO-66 mixed, 89 mg for UiO-67 and 119 mg for UiO-67 mixed) were examined as catalysts for the epoxidation of olefins (3 mmol; 414 µL cyclooctene, 344 µL styrene, 471 µL 1-octene) in neat *tert*-butyl hydroperoxide (4.5 mmol; 818 µL, 5.5 M solution in decane) at 50 °C. Samples were taken after 4 h and analysed by NMR spectroscopy in $CDCl_3$.

Kinetic study for Mo@UiO-67 mixed. The reaction for the kinetic study was performed as described above. The resulting graph is displayed in Figure 5. TOF was determined for the sample taken after 15 min.

Kinetic study of the homogeneous catalyst [MoO_2(acac)(PhN=C-PhO)]. Complex **4** (0.012 mmol, 5 mg) was examined as catalyst for the epoxidation of cyclooctene (1.18 mmol, 154 µL) in neat *tert*-butyl hydroperoxide (2.36 mmol, 430 µL, 5.5 M solution in decane) at room temperature. The resulting graph is displayed in Figure 5. TOF was determined for the sample taken after 5 min.

Leaching test for Mo@UiO-67. Mo@UiO-67 (0.01 mmol) was examined for leaching by performing a catalytic reaction with cyclooctene (1 mmol; 130 µL) in neat *tert*-butyl hydroperoxide (1.5 mmol; 273 µL, 5.5 M solution in decane) at 50 °C. Samples were taken after 5 and 30 min. After that the solid catalyst was removed by filtration, the reaction mixture was kept at 50° for four more hours, a last sample was taken and analysed by NMR spectroscopy in $CDCl_3$.

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