

Post-synthetic Modification of DUT-5-based Metal Organic Frameworks for the Generation of Single-site Catalysts and their Application in Selective Epoxidation Reactions

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New single-site catalysts based on mixed-linker metal-organic frameworks with DUT-5 structure, which contain immobilized Co^{2+} , Mn^{2+} and Mn^{3+} complexes, have successfully been synthesized *via* post-synthetic modification. 2,2'-Bipyridine-5,5'-dicarboxylate linkers were directly metalated, while 2-amino-4,4'-biphenyldicarboxylate linkers were post-synthetically modified by their conversion to Schiff-base ligands and a subsequent immobilization of the metal complexes. The resulting materials were used as catalysts in the selective epoxidation of *trans*-stilbene and the activities and selectivities of the different

catalysts were compared. The influence of various reaction parameters on conversion, yield and selectivity were investigated. Very low catalyst amounts of 0.02 mol% were sufficient to obtain a high conversion of *trans*-stilbene using molecular oxygen from air as the oxidant. For cobalt-containing MOF catalysts, conversions up to 90% were observed and, thus, they were more active than their manganese-containing counterparts. Recycling experiments and hot filtration tests proved that the reactions were mainly catalyzed *via* heterogeneous pathways.

Introduction

In recent years, metal-organic frameworks (MOFs) have gained high importance as highly crystalline and porous materials.^[1] Their chemical and structural diversity makes them potential candidates for specific applications, especially as heterogeneous catalysts in liquid phase reactions.^[2] Over the last decades, various MOF materials have been applied in oxidation reactions, for example, alcohol oxidation,^[3] epoxidation,^[4] or phenol

hydroxylation.^[5] Beside a variety of other oxidants, molecular oxygen is particularly interesting due to its environmentally friendly character, its abundance and its atom efficiency. However, highly active catalysts based on transition metals are necessary for the activation of molecular oxygen. Such molecular systems have been widely investigated in homogeneous catalysis.^[6] Therefore, metal-organic frameworks are perfectly suited to transfer these highly active single-site metal centers to solid structures, thus, combining the advantages of homogeneous and heterogeneous catalysis in one material. To elucidate the structure of active centers and the catalytic mechanisms, a detailed characterization of the metal centers is necessary. This is also relevant to get information about undesired metallic or oxidic nanoparticles inside the pores. For this purpose, many spectroscopic methods have already been used to identify the chemical environment, redox properties and reactivity of the single-site metal centers. Chen *et al.* confirmed the coordination interaction between the linkers and palladium *via* X-ray photoelectron spectroscopy (XPS) analysis.^[7] The group of Martín-Matute reported the synthesis of UiO-67 functionalized with iridium, palladium and rhodium complexes, which were characterized using X-ray absorption spectroscopy (XAS).^[8] Furthermore, Braglia *et al.* investigated a Cu-functionalized UiO-67-bpy MOF *via* XAS and FT-IR spectroscopy to prove the presence of the well-defined copper complex in the framework.^[9]

Various methods have been reported to introduce catalytically active centers into MOFs. Post-synthetic modification (PSM),^[10] i.e. the chemical modification of the material after framework synthesis, has received great interest and plays an important role for the design of well-defined single-site catalysts. Two different strategies are known for the preparation of catalysts, either the post-synthetic introduction of chelating side groups into the framework or the utilization of chelating

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linker molecules. Highly active metal ions can be introduced into the MOF structure by modifying amine functionalities with anhydrides or aldehydes. Tanabe and Cohen performed a PSM reaction of IRMOF-3 with succinic anhydride resulting in a carboxylate-bearing MOF, which was subsequently used to incorporate Cu^{2+} and Fe^{3+} ions. The iron-containing materials showed a high catalytic activity in Mukaiyama-type aldol reactions.^[11] In previous works, our group presented a mixed-linker MIL-53(Al)- NH_2 , which was post-synthetically modified with maleic anhydride. The resulting materials were transformed into single-site catalysts *via* the immobilization of Pd^{2+} and Mn^{3+} and used in C–C coupling reactions^[12,13] or the selective oxidation of α -pinene,^[14] respectively. Apart from post-synthetic modifications with anhydrides, reactions of primary amines and aldehydes resulting in Schiff-bases are well-suited for the incorporation of well-defined and highly active metal complexes into the MOF structure.^[15] Doonan *et al.* modified a UCMC-1- NH_2 framework with 2-pyridinecarboxaldehyde, which was used for a subsequent palladium immobilization.^[16] There are many examples of amine-functionalized UiO-66 and UiO-67 materials, which have been modified *via* PSM reactions with aldehydes and a subsequent metal immobilization to utilize them in catalytic applications.^[17]

Apart from that, the direct incorporation of chelating linker molecules during the framework synthesis allows the direct immobilization of metal ions.^[18] The well-known bidentate linker molecule 2,2'-bipyridine-5,5'-dicarboxylate has been used in various examples. For instance, MOF-253 containing 2,2'-bipyridine-5,5'-dicarboxylate linkers was used for post-synthetic metalation reactions with palladium, copper and ruthenium salts and applied in various liquid phase reactions.^[19] The group of Cohen synthesized a mixed-linker UiO-67 containing equal amounts of bipyridine- and biphenyldicarboxylate linkers, which was used for palladium immobilization and showed excellent catalytic activity in Suzuki-Miyaura cross-coupling reactions.^[20]

In the present work, post-synthetic modifications have been applied using DUT-5, which consists of $[\text{Al}(\text{OH})]_n$ chains that are connected by 4,4'-biphenyldicarboxylate linker molecules.^[21] The mixed-linker concept (MIXMOFs, MTV-MOFs)^[22] was applied, which guaranteed a better framework porosity and a good distribution of catalytically active sites within the framework structure. Previously, functionalized DUT-5 materials with sulfone, amine and nitro groups have been published, which were used in the gas phase adsorption of alkanes, alkenes and aromatics.^[23] Furthermore, DUT-5 and mixed-linker DUT-5 bearing amine, alkyne, azide and nitro groups with various degree of functionalization have been synthesized by our group.^[24] These amine-functionalized MIXDUT-5 materials were used for post-synthetic modification reactions with maleic anhydride, salicylaldehyde and 2-pyridinecarboxaldehyde. However, none of these materials has been used for metal immobilization and subsequent heterogeneous catalytic applications yet.

Therefore, in the present work, mixed-linker DUT-5 catalyst materials containing Co^{2+} , Mn^{2+} and Mn^{3+} complexes have been synthesized *via* post-synthetic modification and subsequent metal immobilization. The obtained materials were

thoroughly characterized and tested in the aerobic epoxidation of *trans*-stilbene using air as the oxidant. Different reaction parameters were optimized and the activities and selectivities of the different catalysts were compared. Hot filtration and recycling tests were performed to investigate the heterogeneity of the reaction.

Results and Discussion

The starting materials for this study were mixed-linker DUT-5 materials containing a defined percentage (10%) of functionalized linker molecules. Based on literature procedures,^[21,24] the framework syntheses were performed in a closed vessel under solvothermal conditions (see ESI). In addition to 4,4'-biphenyldicarboxylic acid (H_2BPDC), 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2BPyDC) or 2-amino-4,4'-biphenyldicarboxylic acid (H_2ABPDC) have been used as linker molecules. The BPyDC linkers were used to facilitate a direct and easy immobilization of cobalt and manganese ions, which resulted in metal complexes close to the pore walls (Figure 1a). The amine-functionalized DUT-5 materials were post-synthetically modified with salicylaldehyde to generate chelating side groups *via* Schiff-base reactions, which were subsequently used for the immobilization of cobalt and manganese ions resulting in metal complexes located farther inside the pores (Figure 1b).

Powder X-ray diffraction (PXRD) measurements showed that the DUT-5 structure was retained during the catalyst preparation for all materials. Thus, the insertion of the chelating side groups and/or the metal ions did not affect the framework structure (Figure 2).

Attenuated total reflectance (ATR) IR spectra proved that no residual linker (characteristic absorption bands corresponding to the C=O stretching expected at around 1685 cm^{-1}) or solvent molecules (DMF; characteristic absorption bands corresponding to the C=O stretching expected at around 1650 cm^{-1}) were found within the pores of all frameworks (Figure S2). Thus, the pores of the functionalized frameworks were not blocked and an easy access for the post-synthetic modifications and the subsequent catalytic reaction was provided.

N_2 physisorption measurements revealed that all materials were obtained with large specific surface areas and accessible micropore volumes. The surface areas of the post-synthetically modified DUT-5 materials did not change significantly due to the low modification degree (Table 1 and Table S3). Note that

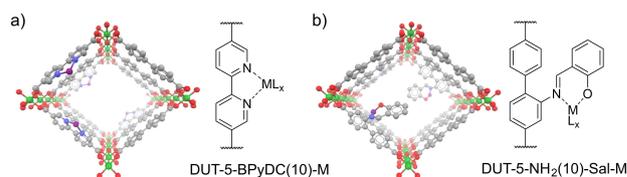


Figure 1. Schematic representation of metal-containing a) DUT-5-BPyDC(10) and b) DUT-5- NH_2 (10)-Sal materials obtained *via* post-synthetic modification. $\text{M}=\text{Co}^{2+}$, Mn^{2+} or Mn^{3+} . Green: Al; blue: N; red: O; grey: C; purple: Co^{2+} , Mn^{2+} or Mn^{3+} .

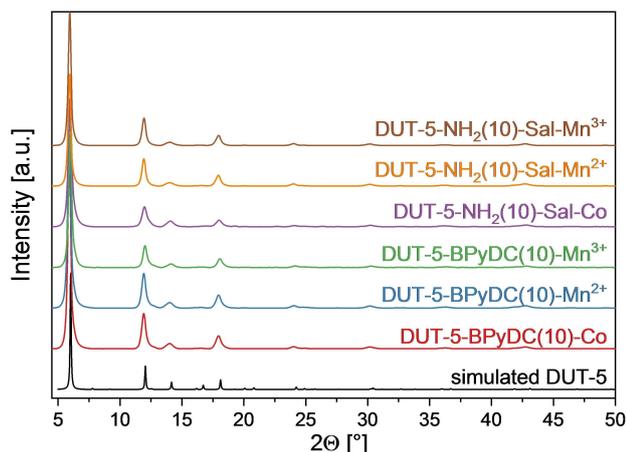


Figure 2. PXRD patterns of mixed-linker DUT-5 materials after PSM with salicylaldehyde and metal immobilization.

Table 1. Specific surface areas (S_{BET}), total pore volumes (tpv) and micropore volumes (mpv) derived from N_2 physisorption measurements and metal contents determined via ICP-OES of metal-containing DUT-5 materials.

Entry	Sample	S_{BET} [m ² /g]	Tpv [cm ³ /g]	mpv [cm ³ /g]	Metal Loading [wt%]
1	DUT-5	1880	0.81	0.61	-
2	DUT-5-BPyDC(10)-Co	1870	0.80	0.68	0.10
3	DUT-5-BPyDC(10)-Mn ²⁺	1810	0.82	0.71	0.10
4	DUT-5-BPyDC(10)-Mn ³⁺	1530	0.67	0.55	0.47
5	DUT-5-NH ₂ (10)-Sal-Co	1480	0.75	0.53	0.10
6	DUT-5-NH ₂ (10)-Sal-Mn ²⁺	1760	0.79	0.65	0.10
7	DUT-5-NH ₂ (10)-Sal-Mn ³⁺	1750	0.80	0.63	0.14

these obtained results provide only qualitative information about the successful formation of the framework structure.

However, by using ¹H NMR spectroscopy, the quantitative amount of the functionalized linker molecules could be determined (Figure S3–S4). For both, the bipyridine- and the amine-containing DUT-5 materials, 8% of functionalized linkers have been incorporated in the materials. Further NMR studies were employed to determine the modification degree with salicylaldehyde relative to amine functionalization. A modification degree of 30% could be calculated from the integration of the peaks in the spectra (Figure S5).

The metal contents of the DUT-5 catalysts were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) and the values are listed in Table 1. The obtained results showed that the chelating moieties were partially occupied by the metal complexes. Electron microscopy images in combination with EDX mapping taking the DUT-5-NH₂(10)-Sal-Co material as an example showed that the active metal is homogeneously distributed within the framework structure (Figure S6). Since only metal loadings of 0.1 wt% could be achieved with Co and Mn²⁺ precursors (Table 1, entries 2, 3, 5–7), we also tried Mn³⁺ precursor and achieved a higher metal loading of 0.47 wt% (Table 1, entry 4).

X-ray absorption spectroscopy (XAS) was used to characterize the introduced metal complexes and to differentiate them from undesired metal clusters or particles inside the pore systems, which might have been additionally formed. Previous studies on palladium containing MIL-53(Al) structure showed that the introduced palladium species in the framework strongly depended on the amount of the palladium precursor used during the modification process. To facilitate the desired formation of the metal complexes, only 0.9 equivalents of the metal precursor relative to the number of chelating groups were used, since larger amounts of the metal precursor led to the formation of undesired metal nanoparticles.^[12,13] Hence, the metal immobilization in this work was also performed with 0.9 equivalents of metal precursor with regard to the chelating group. The Co K-edge XANES spectrum of DUT-5-BPyDC(10)-Co (Figure 3a) and the Mn K-edge XANES spectra of the manganese-containing DUT-5 materials (Figure 3b) revealed that the oxidation states of the incorporated metals in the MOF structure were the same as in the precursor salts, which were used for metal immobilization.

Figure 4 shows the Fourier-transformed spectra for DUT-5-BPyDC(10)-Co, DUT-5-BPyDC(10)-Mn²⁺ and DUT-5-BPyDC(10)-Mn³⁺. The spectra revealed that the first complex shell showed a high intensity in contrast to the higher shells indicating that

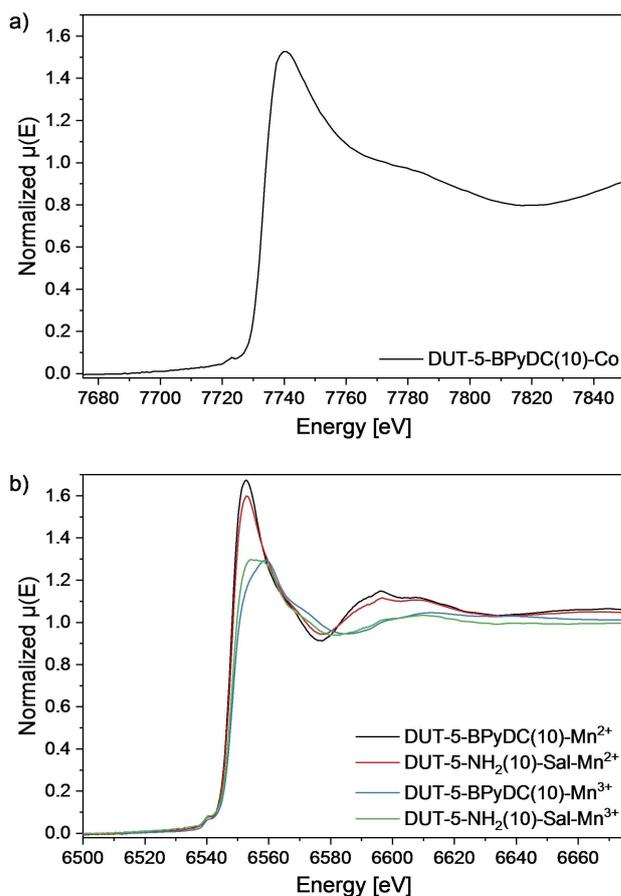


Figure 3. XANES spectra of the metal-containing DUT-5 catalysts at the Co K-edge (a) and the Mn K-edge (b).

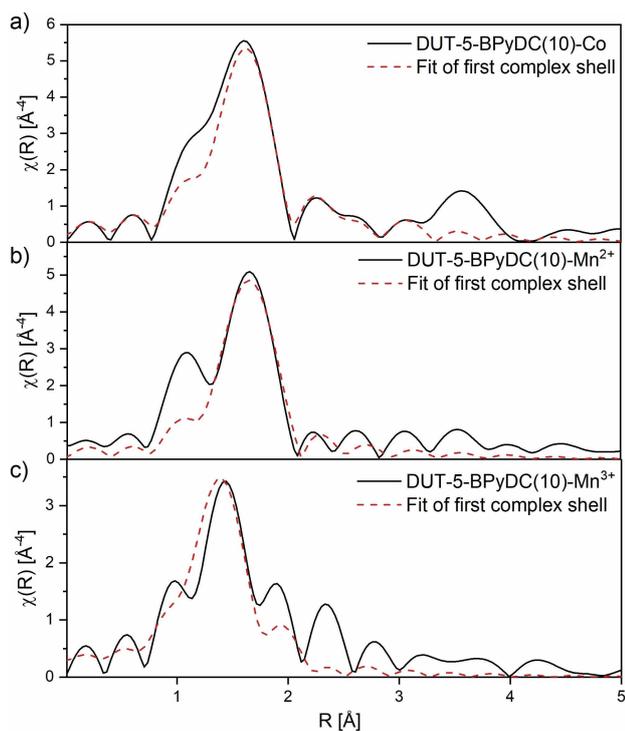
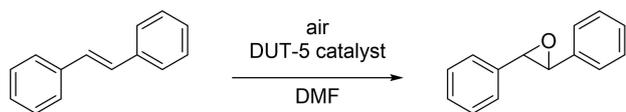


Figure 4. Fourier-transformed experimental EXAFS spectra and the fitting results of the first complex shell of DUT-5-BPyDC(10)-Co (a), DUT-5-BPyDC(10)-Mn²⁺ (b) and DUT-5-BPyDC(10)-Mn³⁺ (c).

the metals are exclusively present in the form of the desired complexes. The corresponding fitting parameters and the results of the EXAFS analysis are listed in Table S5. In the first shell, two different distances with two and four neighbor atoms, respectively, could be fitted, which are assigned to two nitrogen atoms of the bipyridine linker and four oxygen neighbor atoms belonging to the ligands of the complex and, thus, these values are in good agreement with the expected structure. To exclude the presence of oxidic phases in the material, fits of the metal complexes with an additional metal shell from the corresponding metal oxides were performed (Figure S6). These fits did not result in a significant contribution of metal backscatters from an oxide. Consequently, other metal containing species could be excluded.

The resulting catalysts were subsequently used in the aerobic epoxidation of *trans*-stilbene. In a typical reaction, *trans*-stilbene oxide was obtained as the main product and benzaldehyde as a side product in the oxidation of *trans*-stilbene using air as the oxidant in *N,N*-dimethylformamide (DMF) (Scheme 1). DMF was chosen as the solvent for the



Scheme 1. Aerobic epoxidation of *trans*-stilbene catalyzed by metal-containing DUT-5 resulting in *trans*-stilbene oxide (main product).

epoxidation reactions due to a solvent co-oxidation mechanism, which has been reported before.^[25,26] Various reaction parameters such as temperature, oxidant flow rate, catalyst concentration and substrate concentration were screened by using the catalysts DUT-5-BPyDC(10)-Co and DUT-5-BPyDC(10)-Mn²⁺. The remaining catalysts (DUT-5-BPyDC(10)-Mn³⁺, DUT-5-NH₂(10)-Sal-Co, DUT-5-NH₂(10)-Sal-Mn²⁺ and DUT-5-NH₂(10)-Sal-Mn³⁺) were then tested under optimized reaction conditions and the activities of the different catalyst systems were compared. Conversions, yields and selectivities were evaluated by variation of one reaction parameter at a time and quantified by GC analysis using biphenyl as an internal standard.

Blank tests at 150 °C for 24 h with continuous air flow through the solution (200 ml/min) were carried out to ensure that the catalytic activity originated from the metal-containing DUT-5 materials and not from the framework itself. The blank test without MOF catalyst after 24 hours resulted in 12% conversion with only 10% product formation (Table S6, Entry 1). Also a blank test using a bipyridine-containing DUT-5 material without further metal immobilization resulted in only 9% conversion and 6% yield (Table S6, Entry 2), whereas much higher conversion of 93% with DUT-5-BPyDC(10)-Co and 32% with DUT-5-BPyDC(10)-Mn²⁺ was obtained. A time-dependent study of conversion and yield of *trans*-stilbene oxide with DUT-5-BPyDC(10)-Co and DUT-5-BPyDC(10)-Mn²⁺ as catalyst under the same conditions is shown in Figure 5. These results proved that the successful formation of *trans*-stilbene oxide was truly induced by the cobalt- or manganese-containing DUT-5.

Next, we have studied the influence of different reaction parameters on the performance of the oxidation. First of all, the influence of the reaction temperature was investigated. For this purpose, temperatures of 90, 110, 130 and 150 °C were applied. The conversion of *trans*-stilbene increased at higher temperatures due to an increased reaction rate (Table 2 and 3). Higher temperatures using DUT-5-BPyDC(10)-Co led to the additional formation of benzaldehyde (up to 10%) as a side product resulting in a decreased selectivity. For the catalyst DUT-5-

Table 2. Influence of the temperature on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Co. Reaction conditions: 24 h, catalyst amount (0.02 mol% of cobalt), air flow (200 ml/min), *trans*-stilbene (1 mmol), DMF (60 ml).

Entry	Temperature [°C]	Conversion [%]	Yield [%]	Selectivity [%]
1	90	51	46	89
2	110	80	71	88
3	130	89	72	81
4	150	93	70	75

Table 3. Influence of the temperature on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Mn²⁺. Reaction conditions: 24 h, catalyst amount (0.02 mol% of manganese), air flow (200 ml/min), *trans*-stilbene (1 mmol), DMF (60 ml).

Entry	Temperature [°C]	Conversion [%]	Yield [%]	Selectivity [%]
1	90	5	4	76
2	110	11	9	78
3	130	16	14	90
4	150	32	28	87

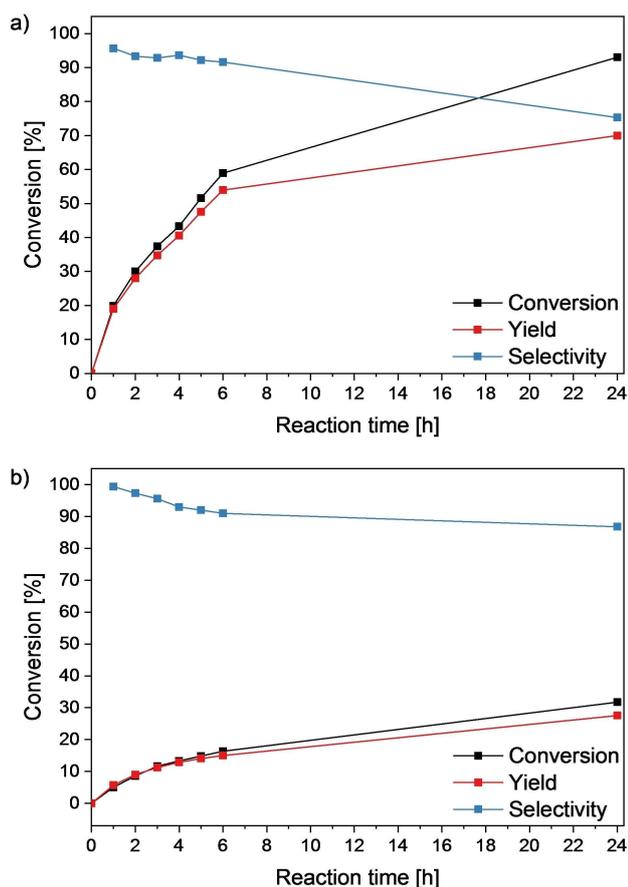


Figure 5. Conversion, yield and selectivity for the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Co (a) and DUT-5-BPyDC(10)-Mn²⁺ (b). Reaction conditions: 24 h, 150 °C, catalyst amount (0.02 mol% of metals), air flow (200 ml/min), *trans*-stilbene (1 mmol), DMF (60 ml).

BPyDC(10)-Mn²⁺, the formation of benzaldehyde was not observed in detectable amounts.

The air flow was varied using 100, 200 and 300 ml/min. Conversion of *trans*-stilbene with the catalyst DUT-5-BPyDC(10)-Co was evaluated after 6 hours reaction time, since the conversion was almost complete after 24 hours (Figure 6a). The analysis showed that the increase from 100 to 200 ml/min led to an increased conversion from 31 to 50% and to an increased yield from 28 to 44%. However, an increase of the flow rate from 200 to 300 ml/min did not further enhance the conversion as well as the yield. For DUT-5-BPyDC(10)-Mn²⁺, only a slight difference in conversion and yield was observed after 24 hours. The best result was also obtained at 200 ml/min with 32% conversion and 28% yield (Figure 6b).

In the following, the dependency of conversion and yield on the catalyst amount was investigated. The catalyst concentration was varied from 0.05 to 0.01 mol% based on the determined metal content (cf. Table 1). The results were compared after 6 hours for DUT-5-BPyDC(10)-Co (Table 4) and after 24 hours for DUT-5-BPyDC(10)-Mn²⁺ (Table 5). Decreasing the amount of DUT-5-BPyDC(10)-Co from 0.05 to 0.02 mol% caused a drop of the *trans*-stilbene conversion from 73 to 58%.

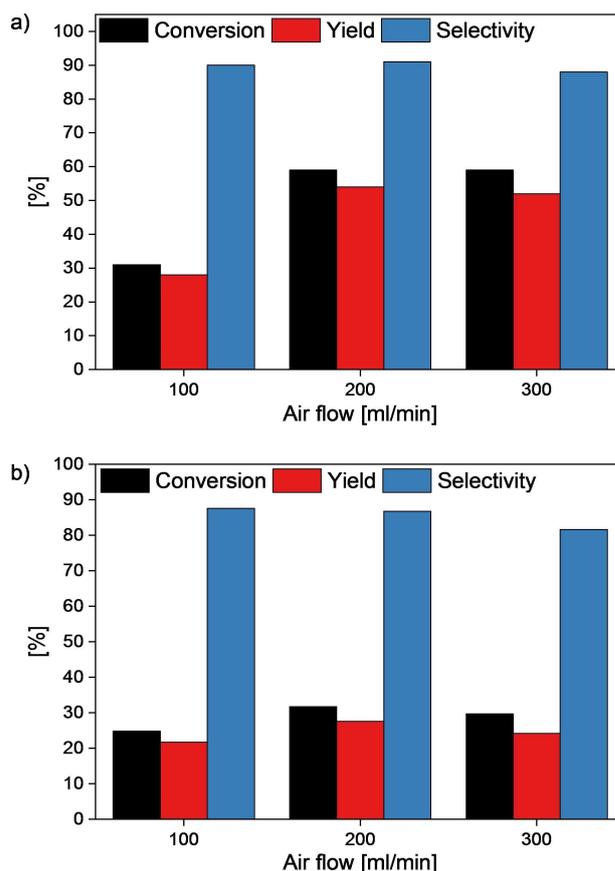


Figure 6. Influence of the air flow rate on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Co after 6 h (a) and DUT-5-BPyDC(10)-Mn²⁺ after 24 h (b). Reaction conditions: 150 °C, catalyst amount (0.02 mol% of metals), *trans*-stilbene (1 mmol), DMF (60 ml).

Table 4. Influence of the catalyst concentration on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Co. Reaction conditions: 6 h, 150 °C, air flow (200 ml/min), *trans*-stilbene (1 mmol), DMF (60 ml).

Entry	Catalyst amount [mol%]	Conversion [%]	Yield [%]	Selectivity [%]	TON
1	0.05	73	64	87	1300
2	0.02	59	54	91	2700
3	0.01	34	29	85	3000

Table 5. Influence of the catalyst concentration on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Mn²⁺. Reaction conditions: 24 h, 150 °C, air flow (200 ml/min), *trans*-stilbene (1 mmol), DMF (60 ml).

Entry	Catalyst amount [mol%]	Conversion [%]	Yield [%]	Selectivity [%]	TON
1	0.05	54	45	83	500
2	0.02	32	28	87	1400
3	0.01	19	17	90	1700

Further decrease of the cobalt concentration to 0.01 mol% led to a decrease of the conversion to 34%. The highest selectivity (91%) was achieved using 0.02 mol% cobalt. When the amount of DUT-5-BPyDC(10)-Mn²⁺ was reduced, the conversion of *trans*-stilbene decreased from 54 to 19% and the selectivity

Table 6. Influence of the substrate concentration on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Co. Reaction conditions: 6 h, 150 °C, catalyst (6.4 mg), air flow (200 ml/min), DMF (60 ml).

Entry	Molar amount of <i>trans</i> -stilbene [mmol]	Catalyst amount [mol %]	Conversion [%]	Yield [%]	Selectivity [%]	TON	TOF [h ⁻¹]
1	1	0.02	59	54	91	2700	420
2	2	0.01	57	52	91	5200	870
3	3	0.0067	58	49	85	7400	1230
4	4	0.005	48	41	85	8100	1350
5	5	0.004	45	42	94	11000	1770

increased from 83 to 90%. Turnover numbers (TON) were calculated to compare the activity of the catalysts. Despite the small catalyst amount, high yields were obtained resulting in very high turnover numbers. For DUT-5-BPyDC(10)-Co, an increase from 1300 for 0.05 mol% to 3000 for 0.01 mol% was observed. The lowest TON was achieved by using 0.05 mol% of DUT-5-BPyDC(10)-Mn²⁺ (TON ≈ 500). Nevertheless, these values are significantly higher than for other MOF-based catalysts previously used for epoxidation reactions.^[14,27]

The influence of the substrate concentration was also tested. The molar amount of *trans*-stilbene was increased from 1 to 10 mmol, whereas the amounts of the catalyst and solvent were not varied. With increasing amount of *trans*-stilbene, the catalyst/substrate ratio decreased from 0.02 mol% to 0.002 mol% of cobalt and manganese, respectively. For DUT-5-BPyDC(10)-Co, nearly full conversion was found after 24 hours regardless of the substrate concentration. After 6 hours, a decrease of the conversion from 55% for 1 mmol *trans*-stilbene amount to 22% for 10 mmol *trans*-stilbene amount was observed (Table 6). Considering the time-dependent progress in Figure 7a, the conversion increased slower with increased substrate concentration. Despite the marginally decreasing conversion, the absolute amount of formed product increased for DUT-5-BPyDC(10)-Co from 0.50 to 3.84 mmol (Figure 7b). Consequently, an increase of the turnover numbers was observed. Using DUT-5-BPyDC(10)-Mn²⁺, the conversion dropped from 32 to 13%, whereas the productivity of the catalyst increased from a TON of 1400 to 2800 (Table 7). The determined turnover frequencies (TOF) after 6 hours showed increased values from 420 to 1770 h⁻¹ with higher substrate concentrations for the cobalt-containing catalyst, whereas the turnover frequencies using the manganese-containing catalyst were similar.

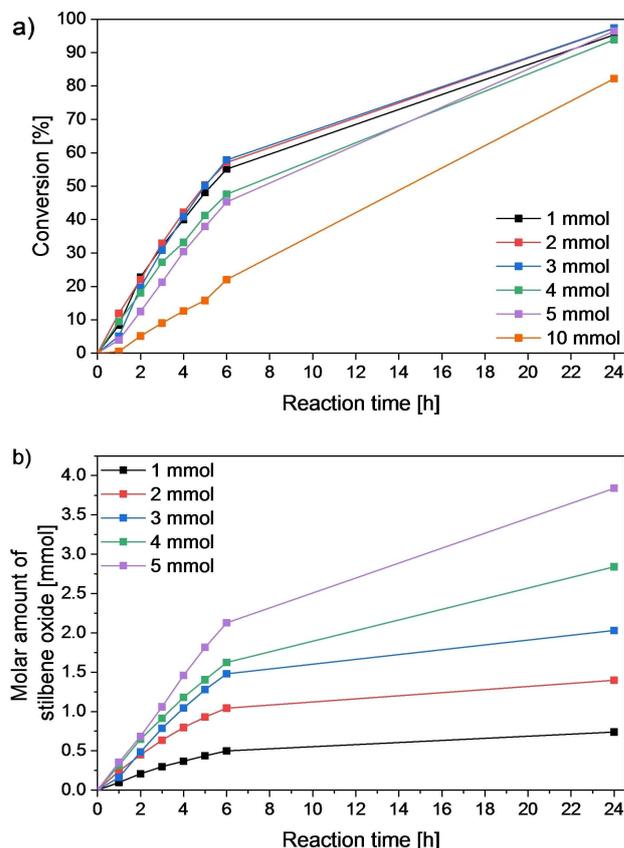

Figure 7. Conversion of *trans*-stilbene (a) and molar amount of stilbene oxide (b) with increasing molar amount of *trans*-stilbene by using DUT-5-BPyDC(10)-Co. Reaction conditions: 24 h, 150 °C, DUT-5-BPyDC(10)-Co (6.4 mg), air flow (200 ml/min), DMF (60 ml).

Table 7. Influence of the substrate concentration on the epoxidation of *trans*-stilbene catalyzed by DUT-5-BPyDC(10)-Mn²⁺. Reaction conditions: 24 h, 150 °C, catalyst (6.4 mg), air flow (200 ml/min), DMF (60 ml).

Entry	Molar amount of <i>trans</i> -stilbene [mmol]	Catalyst amount [mol %]	Conversion [%]	Yield [%]	Selectivity [%]	TON	TOF [h ⁻¹] ^[a]
1	1	0.02	32	28	87	1400	125
2	2	0.01	25	23	92	2300	120
3	3	0.0067	17	15	86	2200	130
4	4	0.005	20	17	86	3400	230
5	5	0.004	13	11	87	2800	200

[a] Determined after 6 hours.

Finally, the optimized reaction conditions (24 h, 150 °C, 0.02 mol% catalyst amount, 200 ml/min air flow and 1 mmol *trans*-stilbene) were applied to test the catalytic performance of DUT-5-BPyDC(10)-Mn³⁺, DUT-5-NH₂(10)-Sal-Mn²⁺, DUT-5-NH₂(10)-Sal-Mn³⁺ and DUT-5-NH₂(10)-Sal-Co. The cobalt-containing DUT-5 catalysts showed a significantly higher catalytic activity than their manganese counterparts (Figure 8), which is in accordance with earlier studies in our group on liquid phase oxidation reactions using cobalt^[26]- and manganese^[28]-based single-site catalysts under similar conditions. Conversions, yields and selectivities that were obtained with DUT-5-BPyDC(10)-Co and DUT-5-NH₂(10)-Sal-Co after 24 h were comparable. Note, however, that DUT-5-NH₂(10)-Sal-Mn²⁺ gave a higher conversion (44%) than DUT-5-BPyDC(10)-Mn³⁺ (32%), while both reached the same selectivity (86%). DUT-5-BPyDC(10)-Mn³⁺ and DUT-5-NH₂(10)-Sal-Mn³⁺ did not differ significantly from the Mn²⁺ materials.

Heterogeneity tests were performed using a hot filtration experiment, which was carried out for DUT-5-BPyDC(10)-Co. The catalyst was removed after 2.5 h reaction time and the reaction was continued without the solid catalyst. At the same time, a control experiment was performed, in which the catalyst remained in the reaction mixture. After catalyst removal, the results showed that the conversion and the yield of *trans*-stilbene oxide increased only slightly (Figure 9a). The reaction rate was much lower than the reaction rate of the control experiment, which indicated that the reaction was mainly catalyzed *via* a heterogeneous pathway. A conversion of 49% and a yield of 45% were obtained *via* the hot filtration experiment, whereas the control experiment provided a conversion of 90% and a yield of 69%. Additionally, it should be noted that the particle size of the DUT-5 catalysts after the synthesis was very small (< 1.6 μm) and the particles had to be granulated before use to obtain particles sizes of 200–500 μm. Even though the hot filtration test and the control experiment were conducted without stirring, a grinding of the DUT-5 particles during the catalytic tests could not be excluded. Thus,

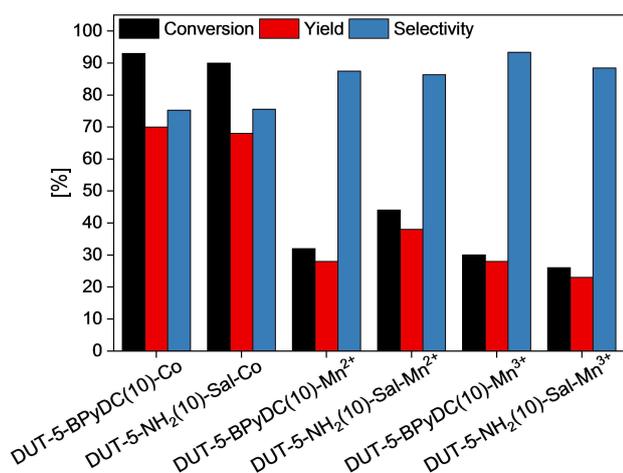


Figure 8. Comparison of conversion, yield and selectivity for the different DUT-5 catalysts. Reaction conditions: 24 h, 150 °C, catalyst (0.02 mol% of metals), air flow (200 ml/min), *trans*-stilbene (1.0 mmol), DMF (60 ml).

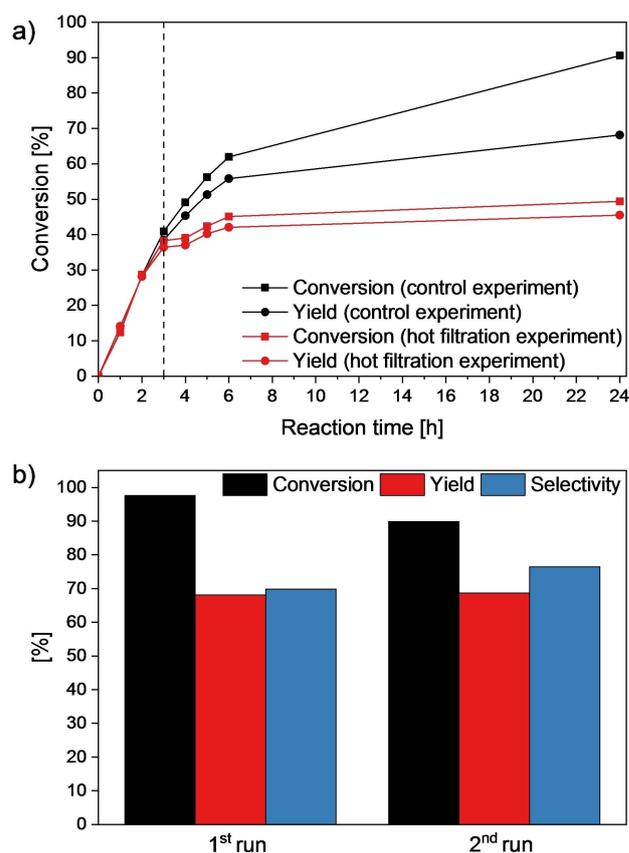


Figure 9. a) Comparison of conversion and yield of the *trans*-stilbene epoxidation with and without catalyst removal after 2.5 h (as indicated by vertical line). b) Conversion and yield in two cycles of *trans*-stilbene epoxidation. Reaction conditions: 24 h, 150 °C, granulated DUT-5-BPyDC(10)-Co (0.02 mol% of cobalt), air flow (200 ml/min), *trans*-stilbene (1.0 mmol), DMF (60 ml).

the observed activity after filtration might also originate from DUT-5-BPyDC(10)-Co particles, which were too small to be removed from the reaction mixture.

Furthermore, the reusability of the DUT-5-BPyDC(10)-Co catalyst was studied. After the first catalytic reaction, the catalyst was filtered off, washed and dried at room temperature and reused in a second epoxidation reaction under the same conditions. Although granulated powder material (200–500 μm) was used to facilitate an easy recovery of the catalyst, a grinding of the granules was observed and, thus, the amount of recovered catalyst was not sufficient for a third run. Nevertheless, the results shown in Figure 9b proved that the catalyst was active for more than one reaction cycle without a significant loss of activity. In summary, the epoxidation reaction of *trans*-stilbene proceeded mainly *via* a heterogeneous pathway using the obtained catalyst materials, although minor amounts of catalytically active homogeneous species could not be ruled out completely.

Conclusions

Novel single-site MOF-based catalysts with defined metal complexes at different positions of the framework have been synthesized. For this purpose, mixed-linker metal-organic frameworks with DUT-5 structure containing 10% of 2,2'-bipyridine-5,5'-dicarboxylate or 2-amino-4,4'-biphenyldicarboxylate linker molecules were successfully synthesized. The amine-functionalized material was post-synthetically modified with salicylaldehyde resulting in a chelating side group. ¹H NMR spectroscopy confirmed the incorporation of the functionalized linker molecules in the desired amount (8%) and revealed a modification degree of 30% of the amine groups with salicylaldehyde. Both chelating units, the 2,2'-bipyridine and the salicylideneimine, were modified by immobilizing Co²⁺, Mn²⁺ and Mn³⁺ ions. The resulting materials showed high crystallinity and were obtained with high surface areas throughout the post-synthetic modification process. X-ray absorption spectroscopy analysis proved the successful immobilization of cobalt and manganese ions in the form of well-defined complexes for all materials and the absence of other undesired metal-containing species like clusters or nanoparticles.

The selective epoxidation of *trans*-stilbene in liquid phase was chosen as the catalytic test reaction. Different reaction parameters were varied to test their effect on conversion, yield and selectivity. The cobalt-containing catalysts featured significantly higher activity than their manganese counterparts. Under optimized conditions, 93% conversion of *trans*-stilbene and 75% yield of *trans*-stilbene oxide was achieved using DUT-5-BPyDC(10)-Co and 32% conversion and 28% yield using DUT-5-BPyDC(10)-Mn²⁺, both with a low catalyst loading of 0.02 mol% using molecular oxygen as the oxidant. Concerning on the different positioning of the metal ions, the cobalt- and Mn³⁺-containing catalysts showed no effect on the catalytic activity. Only differences for the Mn²⁺-containing catalysts were observed, where DUT-5-NH₂(10)-Sal-Mn²⁺ gave a significantly higher conversion than its counterpart DUT-5-BPyDC(10)-Mn²⁺. Hot filtration and recycling tests revealed that the reaction proceeded mainly *via* a heterogeneous pathway. The results obtained in this study evidenced that the synthesized catalysts can be considered as promising solid catalyst materials for other fine chemical syntheses in the liquid phase.

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Conflict of Interest

The authors declare no conflict of interest.

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