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Design of Highly Porous Single-Site Catalysts through Two-Step Postsynthetic Modification of Mixed-Linker MIL-53(AI)

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Defined mixed-linker metal-organic frameworks based on MIL-53-NH₂(AI) were successfully synthesized under ambient pressure, thus, enabling easy scaling up of the synthesis. The twostep postsynthetic modification reaction of these materials with, first, maleic anhydride and, second, palladium(II) acetate resulted in immobilized palladium(II) complexes at the side chain of the linker molecules. The high porosity of the mixed-

Introduction

Owing to their defined crystalline structure and high porosity, metal–organic frameworks (MOFs) have emerged as interesting materials for postsynthetic modifications (PSMs)^[1] and catalytic applications.^[2] MOFs consist of metal ions or clusters that are connected by organic linker molecules with two or more functional groups which can bind to the metal atoms.^[3] A multitude of linker molecules can be utilized as building blocks in MOFs (e.g., di- or tricarboxylic acids,^[4] diphosphonates^[5]), resulting in a high variety of structures and properties of the materials. Furthermore, linker molecules with additional functional groups that do not bind to the metal ions themselves can be used. The most prominent example for this approach are the isoreticular metal–organic framework (IRMOF) series based on MOF-5^[6] and isoreticular frameworks with various functional

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linker materials was retained throughout the modification process, which was in contrast to a previous study with pure MIL-53-NH₂(AI). The novel palladium-containing materials were applied in Heck-type C–C coupling reactions of bromo- or chlorobenzene with styrene, in which they exhibited high catalytic activity and selectivity.

groups based on the structure of MIL-53(AI),^[4a,7] which have been utilized in various applications, including gas adsorption,^[8] separation,^[9] and catalysis.^[10] Such functional groups (e.g., amine groups, formyl groups) can also be seen as potential binding sites for more complex organic functionalities, which can be introduced using the PSM approach.^[1b,c] Through this approach, it is also possible to insert more complex functionalities that cannot be introduced during MOF synthesis because they would hinder the framework formation or result in different crystalline or amorphous structures. If chelating functionalities are incorporated, the modified side chains can be employed to bind catalytically active metal centers, thus, facilitating the immobilization of highly active and defined metal complexes in the framework materials.^[1d, 11] The MOF-based catalyst materials should combine the beneficial characteristics of both homo- and heterogeneous catalyst systems. On one hand, they contain defined metal complexes that should result in high catalytic activity, whereas, on the other hand, the separation and reuse of the solids should be feasible.

We have previously shown that MIL-53-NH₂(Al), which consists of Al–OH– chains connected by 2-aminoterephthalate (ABDC) linkers,^[4a] can be synthesized at ambient pressure,^[12] thus, facilitating easy scaling up of the synthesis. The amine groups of the linker molecules were successfully modified in a two-step postsynthetic reaction and the resulting catalyst material exhibited high activity in the Heck-type C–C coupling reaction of bromo- (BrBz) or chlorobenzene (CIBz) and styrene.^[12] Although the structure was retained throughout the modification process, a drastic decrease of the specific surface area and pore volume was observed. This observation was explained by the fact that modification of the amine groups preferentially took place on the outer surface, thus leading to blocking of the pore entrances. Because of this finding, we decided to tune the number and distribution of amine groups

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Scheme 1. Schematic representation of the two-step PSM of mixed-linker MIL-53-NH₂(AI); yellow: AI, red: O, gray: C, blue: N, white: H, green: Pd, dark red: ligands (acetate or H₂O).

inside the framework using the mixed-linker metal–organic framework (MIXMOF) concept,^[13] in which both functionalized and nonfunctionalized linker molecules are incorporated in a MOF in defined ratios. Previously, MIXMOFs based on MIL-53(AI) were synthesized under hydrothermal conditions by using terephthalic acid (H₂BDC) and aminoterephthalic acid (H₂ABDC) in different ratios.^[13d] Herein, we synthesized defined MIXMOFs based on MIL-53-NH₂(AI) under ambient pressure. We also report a strategy for the design of Pd/MIXMOF catalysts through a two-step PSM by using, first, maleic anhydride and, second, palladium(II) acetate (Scheme 1).

The aim of this study was the introduction of targeted amounts of well-defined anchored palladium complexes into MIXMOFs with a tuned number of amine groups. Using this new approach, the undesired pore blocking that was observed for MIL-53-NH₂(AI) should be prevented. Therefore, not only the active palladium(II) centers on the outer surface, but also those inside the pores should be accessible during catalysis. To examine the catalytic activity of the palladium(II)-containing MIXMOFs, we have chosen a Heck-type C–C coupling reaction of bromobenzene or chlorobenzene and styrene as a suitable test reaction. Furthermore, the properties and catalytic activity of the new materials were compared with those of modified MIL-53-NH₂(AI), which was previously studied in our group.^[12]

Results and Discussion

Owing to the observed loss of pore volume throughout the modification process of pure MIL-53-NH₂(AI),^[12] we decided to use MIXMOFs based on MIL-53-NH₂(Al), with a reduced number of amine groups, as the starting materials. The dilution of the amine groups should promote the distribution of immobilized complexes inside the framework, and therefore, prevent pore blocking. MIXMOFs containing 2-aminoterephthalate (ABDC) and terephthalate (BDC) in defined ratios (4:1, 3:2, 2:3; see the Experimental Section) were successfully synthesized under ambient pressure at elevated temperature. In contrast to the hydrothermal conditions previously used for the synthesis of those MIXMOFs,^[13d] the new route facilitates easy scaling up. To confirm the isoreticular structures for the mixed-linker materials and MIL-53-NH₂(Al), powder X-ray diffraction (PXRD) measurements were taken. The patterns shown in Figure 1 prove the successful synthesis of crystalline MIXMOFs.

Attenuated total reflectance (ATR) IR spectra were recorded to confirm the different linker ratios qualitatively. In the spectra, a decrease in intensity of the N–H stretching vibrations was observed when the amount of the 2-aminoterephtalate



Figure 1. XRD patterns of MIL-53-NH $_2$ (Al) and MIXMOFs based on MIL-53-NH $_2$; the number given in parentheses represents the percentage of ABDC in the MIXMOF material.

linker in the MIXMOFs was reduced (Figure S2, left, in the Supporting Information). Furthermore, the aromatic C–H bending vibrations of ABDC and BDC could be distinguished by their different substitution patterns at the aromatic ring (Figure S2, right, in the Supporting Information). Therefore, the IR spectra clearly prove the successful incorporation of both linker molecules into the MIXMOFs. The IR spectra did not show a band at $\tilde{\nu} \approx 1680 \text{ cm}^{-1}$ (C=O stretching vibration of protonated linker molecules), which led to the conclusion that there were no residual acid molecules present in the pores (Figure 2); this would be the case for hydrothermally synthesized MIXMOFs without further activation.



Figure 2. IR spectra of MIL-53-NH₂(40) (black) and modified MIL-53-NH₂(40)-Mal (dark gray). For comparison the spectrum of MIL-53-NH₂(AI)_as containing free acid molecules is shown (light gray).

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NMR spectroscopy of digested samples was used to quantify the ratio of ABDC and BDC incorporated in the mixed frameworks. Because the IR spectra revealed that there were no residual free acid molecules in the pore system, the ABDC/BDC ratio determined by NMR spectroscopy could be directly related to the composition of the MIXMOFs. The linker ratios determined by NMR spectroscopy (Table 1 and Figures S3–S6 in the

Table 1. Theoretical and measured linker ratios.						
	ABD Applied	C/BDC Determined				
MIL-53-NH ₂ (80) MIL-53-NH ₂ (60) MIL-53-NH ₂ (40)	4:1 3:2 2:3	3.7:1.0 2.8:2.0 2.0:3.0				

Supporting Information) matched very well with the ratios applied during synthesis, which proved that both linker molecules were built into the framework with the same preference.

To exclude the formation of core-shell particles and to prove a mostly homogeneous distribution of the two linkers, three additional samples with an initial linker ratio of 1:1 were synthesized for 8, 24, and 72 h. The crystallinity of the resulting frameworks increased with the reaction time (for XRD patterns, see Figure S14 in the Supporting Information), whereas NMR spectra (Figures S11–S13 in the Supporting Information) of all three samples showed that both linker molecules were present in the desired ratio. Those findings support the formation of frameworks with homogeneously distributed linkers, rather than the formation of core-shell structures. A detailed study on the distribution of the individual linker molecules in mixedlinker MIL-53(AI) materials was previously reported by Lescouet et al.^[14]

Nitrogen physisorption measurements revealed that the micropore volumes of the mixed-linker materials were lower than that of pure MIL-53-NH₂(Al) (Table 2). Whereas the micropore volume of MIL-53-NH₂(Al) was 0.39 cm³ g⁻¹, the micropore volumes of the MIXMOFs were between 0.17 and 0.30 cm³ g⁻¹.

After thorough characterization of the starting materials, catalytically active palladium(II) centers were immobilized in the frameworks through a two-step PSM reaction. First, the reaction of maleic anhydride with the amine groups in the mixed materials led to the formation of functionalized side chains, which could then in the second step be used as chelating ligands for the immobilization of palladium(II) ions (Scheme 1).

Table 2. Micropore volumes of MIXMOFs and modified materials obtained from nitrogen physisorption measurements.					
	MIL-53- NH ₂ (100) [cm ³ g ⁻¹]	MIL-53- NH ₂ (80) [cm ³ g ⁻¹]	MIL-53- NH ₂ (60) [cm ³ g ⁻¹]	MIL-53- $NH_2(40)$ $[cm^3 g^{-1}]$	
unmodified maleic anhydride palladium(II) acetate	0.39 0.03 0.01	0.17 0.08 0.08	0.22 0.20 0.10	0.30 0.12 0.11	

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We previously used this two-step reaction with MIL-53-NH₂(100) as a starting material. In that case, we observed a significant decrease of the micropore volume throughout the modification process from 0.39 to only $0.01 \text{ cm}^3 \text{g}^{-1}$ (Table 2 and Figure 3, top).^[12] Owing to this discovery, we decided to



Figure 3. Adsorption (filled symbols) and desorption (open symbols) isotherms of MIL-53-NH₂(100) (top) and MIL-53-NH₂(40) (bottom) before and after modification.

use MIXMOFs with a reduced number of amine groups to prevent blocking of the pores during the immobilization of the palladium(II) complexes.

To test our hypothesis, we performed nitrogen physisorption measurements of the modified MIXMOFs (Table 2). Whereas MIL-53-NH₂(100) lost most of its micropore volume throughout the modification process (Figure 3, top), the MIXMOFs remained highly porous with a micropore volume of up to 0.11 cm³g⁻¹ (Figure 3, bottom and Figure S1 in the Supporting Information). The adsorption and desorption isotherms for MIL-53-NH₂(40) before and after modification are also shown in Figure 3, bottom. Clearly, the dilution and distribution of the amine functionalities inside the MIXMOFs minimized blocking of the pores during modification, thus, proving the benefit of the MIXMOF approach.

The XRD patterns affirmed that the structure and crystallinity of the MIXMOFs were retained throughout the modification process. The reflections representing distances perpendicular to the pore system ((*hkl*) = (200) and (400)) remained at the same position (2θ = 9.28 and 18.62°, respectively), whereas a small shift was observed for all other reflections (Figure 4). This shift can be explained by the so-called "breathing effect"^(4a,15) of MIL-53(AI), which describes the ability of the frame-

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Figure 4. XRD patterns of MIL-53-NH₂(80), MIL-53-NH₂(80)-Mal, and MIL-53-NH₂(80)-Mal-Pd. The dotted lines illustrate the shift of the reflections that are not perpendicular to the pores.

work to change its geometry, depending on the substrates inside the pores. Thus, the shift also confirmed the successful modification of the amine groups. The position of the second reflection ((hkl) = (110); Table 3) might also be a qualitative indication of the degree of modification.

Table 3. Position of the reflection $(hkl) = (110)$ in the XRD patternthroughout the modification process.						
x	MIL-53-NH ₂ (X) [°]	MIL-53-NH ₂ (X)-Mal [°]	MIL-53-NH ₂ (X)-Mal-Pd [°]			
100	12.32	12.13	12.12			
80	12.33	12.22 12.10				
60	12.33	12.27	12.21			
40	12.31	12.28 12.23				

The decreasing intensity of the N–H stretching vibrations ($\tilde{\nu} = 3498$ and 3387 cm^{-1}) in the IR spectra further indicated the formation of the amide. The additional band at $\tilde{\nu} \approx 1700 \text{ cm}^{-1}$, which appeared for the samples modified with maleic anhydride (Figure 2) could be ascribed to the additional C=O vibration of the inserted carbonyl functionalities.

To quantify the degree of modification with maleic anhydride, we again used NMR spectroscopy of digested samples (Table 4 and Figures S7–S10 in the Supporting Information). Although the overall degree of modification, that is, the total number of functional groups, was identical for all materials, the degree of modification per amine group increased for the mixed-linker frameworks. At the same time, a comparatively

Table 4. Degree of modification of the frameworks, as determined by NMR spectroscopy.							
Degree of modification Degree of modification of amine groups [%] of the framework [%]							
MIL-53-NH ₂ (100)-Mal	5	5					
MIL-53-NH ₂ (80)-Mal 5 4							
MIL-53-NH ₂ (60)-Mal	6	4					
MIL-53-NH ₂ (40)-Mal 11 5							

large micropore volume was retained for the MIXMOFs, thus proving that pore blocking was successfully minimized, despite the higher degree of modification. This observation again illustrates the beneficial effects of the diluted amine groups in the MIXMOFs. Notably, in the literature, a higher degree of modification of approximately 40% was reported for MIL-53-NH₂(100), which could be explained by the fact that, in this study, a 15 times higher amount of maleic anhydride was used relative to that used herein.^[16] In addition, no pore volume or specific surface area was reported for the materials after PSM.

To determine the palladium loading of the modified frameworks, atomic absorption spectroscopy (AAS) was used. The measurements revealed that the palladium loading of the modified MIXMOFs increased with a decreasing number of amine groups inside the framework. Whereas MIL-53-NH₂(100)-Mal-Pd contained only 2.1 wt% of Pd, the metal loading could be increased to 3.1 wt% for MIL-53-NH₂(40)-Mal-Pd (Table 5).

Table 5. Results of the AAS measurements of the modified MIXMOFs.						
MIL-53-NH ₂ (100)- Mal-Pd	MIL-53-NH ₂ (80)- Mal-Pd	MIL-53-NH ₂ (60)- Mal-Pd	MIL-53-NH ₂ (40)- Mal-Pd			
2.1 wt% Pd	2.8 wt % Pd	2.9 wt% Pd	3.1 wt% Pd			

Despite their higher Pd content, the micropore volume of all MIXMOFs was significantly larger after the second modification step than that of MIL-53-NH₂(100)-Mal-Pd.

Although the degree of modification per amine group could be increased in the mixed materials compared with that of MIL-53-NH₂(100), the overall degree of modification was identical. Therefore, the increasing palladium loading of the modified MIXMOFs may be explained by the increased accessibility of the chelating ligands inside the pores owing to the higher micropore volume of the modified mixed-linker frameworks. It is also possible that undesired palladium nanoparticles were formed, thus increasing the palladium content.

X-ray absorption spectroscopy (XAS) is a useful method to gain information about the short-range coordination structure and oxidation state of the metal centers.^[17] Therefore, XAS measurements were performed to confirm the successful immobilization of palladium(II) complexes and to exclude the possible formation of nanoparticles. For MIL-53-NH₂(100)-Mal-Pd, the nature of the palladium species immobilized in the framework strongly depended on the amount of the palladium precursor used during the modification process. The desired immobilization of palladium(II) acetate were used, whereas higher concentrations of the precursor led to the additional formation of undesired palladium nanoparticles.^[12] Thus, we again used small amounts of the palladium(II) precursor for the modification of the MIXMOFs to prevent particle formation.

The X-ray absorption near-edge structure (XANES) spectra (Figure 5) of all modified MIXMOFs showed a double-peak structure, which is characteristic of palladium(II).^[18] The extended X-ray absorption fine structure (EXAFS) spectra of the three

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Figure 5. Normalized and self-absorption-corrected X-ray absorption spectra of MIL-53-NH $_2(80)$ -Mal-Pd (bottom), MIL-53-NH $_2(60)$ -Mal-Pd (middle), and MIL-53-NH $_3(40)$ -Mal-Pd (top).



Figure 6. Fourier-filtered EXAFS spectra (left) and corresponding Fourier-transformed functions (right) of the samples MIL-53- $NH_2(80)$ -Mal-Pd (bottom), MIL-53- $NH_2(60)$ -Mal-Pd (middle), and MIL-53- $NH_2(40)$ -Mal-Pd (top).

 Table 6.
 Number, type, and distances of backscatterers of palladium in MIL-53-NH₂(80)-Mal-Pd, MIL-53-NH₂(60)-Mal-Pd, and MIL-53-NH₂(40)-Mal-Pd obtained by EXAFS analysis.

	Abs-Bs ^[a]	N(Bs) ^[b]	<i>R</i> (Abs-Bs) [Å] ^[c]	σ [Å] $^{-1[d]}$	R [%] ^[e] E _f [eV] ^[f] Afac ^[g]
	Pd–O	1.7±0.08	1.908±0.0190	0.050 ± 0.005	
	Pd–O	2.0 ± 0.2	2.072 ± 0.0207	0.032 ± 0.003	
MIL-53-NH ₂ (80)-	Pd–Pd	0.3 ± 0.03	2.640 ± 0.0264	0.032 ± 0.003	9.168
Mal-Pd	Pd–C	2.0 ± 0.2	2.914 ± 0.0291	0.112 ± 0.011	-6.113
	Pd–Pd	0.7 ± 0.07	3.605 ± 0.0360	0.032 ± 0.003	0.4346
	Pd–C	2.0 ± 0.2	3.963 ± 0.0396	0.039 ± 0.003	
	Pd–O	1.7±0.08	1.891±0.0189	0.032 ± 0.003	
	Pd–O	2.7 ± 0.2	2.048 ± 0.0204	0.032 ± 0.003	
MIL-53-NH ₂ (60)-	Pd–Pd	0.7 ± 0.07	2.658 ± 0.0265	0.087 ± 0.008	12.77
Mal-Pd	Pd–C	1.5 ± 0.1	2.852 ± 0.0285	0.112 ± 0.011	-8.871
	Pd–Pd	1.0 ± 0.1	3.587 ± 0.0358	0.045 ± 0.004	0.3633
	Pd–C	3.1 ± 0.3	3.956 ± 0.0395	0.045 ± 0.004	
	Pd–O	2.0±0.1	1.929±0.0192	0.067 ± 0.006	
	Pd–O	1.8 ± 0.1	2.077 ± 0.0207	0.032 ± 0.003	
MIL-53-NH ₂ (40)-	Pd–Pd	0.2 ± 0.02	2.670 ± 0.0267	0.055 ± 0.005	9.957
Mal-Pd	Pd–C	2.0 ± 0.2	2.894 ± 0.0289	0.110 ± 0.011	-5.034
	Pd–Pd	0.5 ± 0.05	3.592 ± 0.0359	0.032 ± 0.003	0.4222
	Pd–C	2.0 ± 0.2	3.941 ± 0.0394	0.050 ± 0.005	

tween the absorbing and backscattering atom. [d] Debye–Waller-like factor. [e] Fit index. [f] Fermi energy that accounts for the shift between theory and experiment. [g] Amplitude reducing factor.

3.6 Å (Table 6) were found, which indicate a minor contribution of very small particles that cannot be detected by XRD. The presence of small palladium nanoparticles was also confirmed by the observed Pd—Pd distances, which were contracted compared with those in bulk palladium.

Palladium-based catalysts exhibit high activity in C–C coupling reactions, for example, Heck reactions of aryl halides and olefins. MOFs containing palladium nanoparticles^[19] or immobilized palladium species^[20] have previously been used in Heck reactions. The material with immobilized species was tested with iodobenzene, which is a very reactive substrate for C–C coupling reactions. Moreover, even negligible concentrations of active palladium species (10^{-5} mol%) can be sufficient to catalyze Heck-type reactions of aryl iodides.^[21] Previously, we optimized the reaction parameters (reaction temperature, base, additives) for a Heck-type reaction of less-activated bromobenzene or chlorobenzene with styrene with MIL-53-NH₂(100)-Mal-Pd as a heterogeneous catalyst.^[12] Therefore, the novel catalyst materials were investigated in the same reaction (Scheme 2) under optimized conditions to evaluate and compare the catalytic activity of the palladium-containing MIX-MOFs to that of MIL-53-NH₂(100)-Mal-Pd.

samples (Figure 6) were similar and the structural parameters obtained from EXAFS analysis were identical, within experimental error. In addition to the type and number of fitted shells, the distances of adjusted backscatterers were also very similar (Table 6). Fitting of the spectra resulted in four oxygen atoms between 1.9 and 2.0 Å, which could be assigned to the carboxyl groups of the modified linker and acetate or H₂O ligands. Two carbon shells at distances of 2.9 and 3.9 Å could be attributed to the carbon scaffold of the modified linker. Therefore, XAS measurements back up the desired immobilization of palladium(II) complexes in the MIXMOFs. However, palladium contributions at distances of 2.6 and 3.6 Å indicated the additional presence of a low amount of palladium clusters. Regarding the coordination numbers, approximately 0.3 atoms in the shell at 2.6 Å and 0.6 atoms at

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Scheme 2. Heck-type C–C coupling reaction of aryl halides and styrene with palladium-containing MIXMOFs as the catalyst materials.

We discovered that all catalyst materials exhibited similar activities (conversion and turnover numbers (TONs)) in the investigated C–C coupling reactions (Table 7). In the reaction of BrBz with styrene, the selectivity towards *trans*-stilbene was the same for all investigated catalyst materials (92–93%). In

Table 7. Results of the catalytic tests.					
	Substrate	Conversion [%]	Yield [%]	Selectivity [%]	TON
MIL-53-NH ₂ (100)-Mal-Pd	BrBz ^[a]	96	88	92	8236
MIL-53-NH ₂ (80)-Mal-Pd	BrBz ^[a]	94	86	92	8710
MIL-53-NH ₂ (60)-Mal-Pd	BrBz ^[a]	93	86	93	8369
MIL-53-NH ₂ (40)-Mal-Pd	BrBz ^[a]	91	84	93	8625
MIL-53-NH ₂ (100)-Mal-Pd	CIBz ^[b]	22	17	78	1740
MIL-53-NH ₂ (80)-Mal-Pd	CIBz ^[b]	21	18	84	1975
MIL-53-NH ₂ (60)-Mal-Pd	CIBz ^[b]	19	16	84	1730
MIL-53-NH ₂ (40)-Mal-Pd	CIBz ^[b]	18	15	83	1685
[a] Reaction conditions: BrBz (10 mmol), styrene (15 mmol), sodium ace- tate (12 mmol), Pd (0.01 mol%), <i>N</i> -methyl-2-pyrrolidone (NMP; 10 mL), 140°C, 3 h. [b] Reaction conditions: ClBz (10 mmol), styrene (15 mmol), calcium hydroxide (12 mmol), tetrabutylammonium bromide (TBAB; 6 mmol), Pd (0.01 mol%), NMP (10 mL), 160°C, 6 h.					

the coupling of CIBz and styrene, the palladium-containing MIXMOFs exhibited a slightly higher selectivity of 84% compared with 78% for MIL-53-NH₂(100)-Mal-Pd. The low micropore volume of MIL-53-NH₂(100)-Mal-Pd suggests that the palladium(II) complexes are located mainly on the outer surface of the material. The modified MIXMOFs exhibited a significantly higher micropore volume, which indicates a good distribution of the immobilized palladium complexes inside the porous framework structure. However, the same TONs were observed for the palladium-containing mixed-linker frameworks and MIL-53-NH₂(100)-Mal-Pd, which led to the conclusion that, for the MIXMOFs, not only the immobilized palladium complexes on the outer surface, but also those inside the pores could be reached and were catalytically active. Additional catalytic studies involving substrates of different sizes might be suitable to further corroborate this claim in future studies.

For conventional supported palladium catalysts, it is well known in the literature that the Heck reaction is exclusively catalyzed by leached species in the form of defined palladium complexes and not by the bulk material. The reaction mechanism is "quasi-homogeneous".^[21b,22] In our case, defined palladium(II) complexes are already immobilized in the framework materials and, consequently, leaching from the solid catalyst might not be necessary. To answer the question of whether the reaction pathway was homogeneous owing to leached species or truly heterogeneous, we conducted hot filtration experiments. To enable fast separation of the catalyst, it was placed in a paper filter that was removed after 30 min. The reaction was then resumed under the same reaction conditions for

another 2.5 h. To exclude external diffusion limitations, a control experiment was performed, for which the catalyst was also put in a filter, but remained in the reaction mixture for 3 h. For MIL-53-NH₂(100)-Mal-Pd, we found that the reaction was partly heterogeneous,^[12] which was in contrast to the quasi-homogeneous mechanism widely accepted for conventional supported catalyst systems.^[21b,22] During the hot filtration tests with the palladium-containing MIXMOFs, the conversion and yield further increased, although the catalyst had been removed. However, after 3 h, the conversion of the hot filtration test was significantly lower than that of the experiment without catalyst removal (Figure 7). Hence, contributions from a truly heterogeneous pathway were found. The observed activity after removal of the catalyst might originate from leached species or very small catalyst particles, which could not be retained by the filter.



Figure 7. Conversion of the hot filtration test after 0.5 and (0.5 + 2.5) h and of the control experiment after 3 h. Reaction conditions: BrBz (10 mmol), styrene (15 mmol), sodium acetate (12 mmol), Pd (0.01 mol%), NMP (10 mL), 140 °C.

Conclusion

Isoreticular MIXMOFs based on MIL-53-NH₂ were successfully synthesized with defined ratios of 2-aminoterephthalate (ABDC) and terephthalate (BDC) under ambient pressure. The linker ratios found by NMR spectroscopy matched the applied ratios very well; this confirmed that both linker molecules were built into the framework with the same preference under the applied reaction conditions. Furthermore, we could prove that using MIXMOFs for the immobilization of defined palladium(II) complexes led to catalyst materials with high micropore volumes of up to 0.11 cm³g⁻¹. Clearly, blocking of the pore structure observed for MIL-53-NH₂(100)-Mal-Pd could successfully be minimized by dilution of the amine groups in the mixed frameworks. All new materials showed similar high ac-

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tivity and selectivity in the Heck-type C–C coupling reaction of bromobenzene or chlorobenzene and styrene. Owing to the high micropore volume of the modified MIXMOFs, the palladium complexes immobilized inside the pores could be reached, whereas for MIL-53-NH₂(100)-Mal-Pd only the complexes on the outer surface were catalytically active. Therefore, MIXMOFs turned out to be interesting materials for further immobilization of different metal complexes and might also be promising for size- or shape-selective catalytic reactions.

Experimental Section

Synthesis of MIXMOFs

Based on the synthesis of MIL-53-NH₂(Al) under ambient pressure,^[12] MIXMOFs containing 80, 60, and 40% ABDC were synthesized. The linker molecules (5.33 mmol; H₂ABDC and H₂BDC, ratios are listed in Table 8) were dissolved in H₂O (25 mL) and DMF (50 mL) at 90 °C. A solution of Al(NO₃)₃·9H₂O (2.0 g, 5.33 mmol) in H₂O (5 mL) was added and the reaction mixtures were stirred at 90 °C for 24 h. After filtration, the materials were washed with DMF (3×25 mL) and H₂O (1×25 mL). The samples were dried overnight at room temperature and then for 3 days at 130 °C in air.

Table 8. Ratios of H_2ABDC and H_2BDC that were applied in the synthesis of MIXMOFs.						
	H ₂ ABDC [%]	H₂ABDC [g]	H ₂ BDC [%]	H ₂ BDC [g]		
MIL-53-NH ₂ (80)	80	0.7730	20	0.1900		
MIL-53-NH ₂ (60)	60	0.5800	40	0.3800		
MIL-53-NH ₂ (40)	40	0.3860	60	0.5690		

PSM of MIXMOFs

The MIXMOFs were modified in a two-step PSM reaction. First step: modification with maleic anhydride: maleic anhydride (4 equiv, based on the number of amine groups) was dissolved in acetonitrile (50 mL). MIXMOFs (2 mmol) were suspended in the solution and the reaction mixtures were heated to 80 °C for 24 h. After filtration, the resulting materials were washed with acetonitrile (5×20 mL), DMF (1×20 mL), and H₂O (1×20 mL). The samples were dried overnight at room temperature and then for 3 days at 130 °C in air.

Second step: modification with palladium acetate: palladium(II) acetate (0.15 mmol) was dissolved in DMF (20 mL). The modified MIXMOFs (1.5 mmol) were suspended in the solution and the reaction mixtures were heated to 60 °C for 4 h. After filtration, the resulting materials were washed with DMF (3×20 mL) and H₂O (1× 20 mL). The samples were dried overnight at room temperature and then for 3 days at 130 °C in air.

Powder X-ray diffraction (PXRD)

The measurements were performed using a Bruker D8 Advance diffractometer. The samples were analyzed in the range of $2\theta = 6-50^{\circ}$ using $Cu_{k\alpha}$ radiation. The step width was $2\theta = 0.0082^{\circ}$ with a dwell time of 2 s.

Nitrogen physisorption

The samples were activated for 20 h at 130 $^\circ\text{C}$ under vacuum and analyzed using a Belsorp mini II instrument from BEL Japan.

FTIR spectroscopy

IR data were acquired using a Vertex 70 FTIR spectrometer from Bruker Optics equipped with a Golden Gate Single Reflection ATR sample cell from Specac. The data were collected from $\tilde{\nu} = 4500$ to 600 cm⁻¹ and for each spectrum the arithmetic average of 400 measurements was taken.

NMR spectroscopy

Samples (10 mg) were digested in NaOH/D₂O (0.5 mL). Spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer. Chemical shifts were referenced to internal solvent resonances and reported relative to tetramethylsilane (TMS).

Atomic absorption spectroscopy (AAS)

For AAS measurements, a Z-6100 Polarized Zeeman atomic absorption spectrometer from Hitachi was used. The palladium-containing solid frameworks were digested in aqua regia (7 mL) and diluted with distilled water to 100 mL.

X-ray absorption spectroscopy (XAS)

XAS experiments were performed at beamline BM25A at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The measurements were performed at the palladium K-edge at 24350 keV with a Si(311) double-crystal monochromator and a maximum synchrotron beam current of 200 mA. Spectra of undiluted powder between two Kapton windows were recorded in fluorescence mode at ambient temperature.

Gas chromatography (GC)

For GC measurements, a GC-2010 Plus instrument from Shimadzu with a nonpolar column (Rxi-5Sil MS, length: 30 m, diameter: 0.25 mm, film thickness: 0.25 μ m) and a flame-ionization detector (FID) was used. The sample (1 μ L) was injected and vaporized at 250 °C. The column was heated from 50 to 280 °C at a rate of 10 Kmin⁻¹.

Heck reaction of bromobenzene and styrene

In a typical experiment, bromobenzene (BrBz; 10 mmol), styrene (15 mmol), sodium acetate (12 mmol), and diethylene glycol dibutyl ether (2.3 mmol as an internal GC standard) were dissolved in NMP (10 mL) in a sealed glass tube. The catalyst (0.01 mol%, based on Pd in regard to BrBz) was suspended in the reaction mixture and the mixture was then heated to 140 °C for 3 h. For the hot filtration test, the catalyst was put into a paper filter bag, which was removed from the reaction mixture after 0.5 h. The reaction was then resumed for another 2.5 h. Samples for GC analysis were taken after 0.5 and (0.5 + 2.5) h.

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In a typical experiment, chlorobenzene (ClBz) (10 mmol), styrene (15 mmol), calcium hydroxide (12 mmol), TBAB (6 mmol), and diethylene glycol dibutyl ether (2.3 mmol as an internal GC standard) were dissolved in NMP (10 mL) in a sealed glass tube. The catalyst (0.01 mol%, based on Pd in regard to ClBz) was suspended in the reaction mixture and the mixture was heated to 160 °C for 6 h.

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FULL PAPERS



Holey MOFs! Defined single-site palladium catalysts have been synthesized through postsynthetic modification (PSM) of mixed-linker metal-organic frameworks (MIXMOFs). The high porosity of the MIXMOF catalysts was retained throughout the modification process. This resulted in accessible and highly active catalytic sites for Hecktype C–C coupling reactions. M. A. Gotthardt, R. Schoch, T. S. Brunner, M. Bauer,* W. Kleist*

Design of Highly Porous Single-Site Catalysts through Two-Step Postsynthetic Modification of Mixed-Linker MIL-53(AI)