Selective Growth and MOCVD Loading of Small Single Crystals of MOF-5 at Alumina and Silica Surfaces Modified with Organic Self-Assembled Monolayers[†]

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Thin polycrystalline films of phase-pure MOF-5 were grown directly from supersaturated MOF-5 mother solutions on suitably pretreated alumina and silica substrates. The surface acid/base properties characterized by the isoelectric point of the bare substrates controls the anchoring of MOF-5 nuclei. In addition to COOH-terminated SAMs on SiO_2, ALD-Al_2O_3 proved to be a very good adhesive for selective MOF-5 growth. The adsorption properties of the deposited MOF films on Al_2O_3 substrates were demonstrated by MOCVD loading with $[(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)]$ as Pd precursor to finally yield the palladium-loaded thin film material $\{Pd@MOF\text{-}5\}/Al_2O_3$ as a model of a variety of conceivable MOF-based functional chemical systems at surfaces.

Introduction

Functional microporous metal-organic coordination polymers (CPs) with zeolite-type structural and chemical properties are an emerging class of novel advanced materials.[1] Early reports on extraordinary gas-storage capacities for hydrogen and small hydrocarbons have attracted widespread interest, especially in the case of so-called metal-organic open framework coordination polymers (MOFs) based on chemically robust zinc carboxylate structural motifs pioneered by Yaghi and co-workers.[2] Related CPs with a certain lability or flexibility of the framework, namely, studied by Kitagawa and co-workers, exhibit very interesting responsive effects associated with the adsorption, desorption, shape and dynamics of guest molecules.[3] The MIL family of porous CPs, developed by Ferey and co-workers, allow the combination of magnetic features with host−guest chemistry.[4] The prospect of detailed property engineering at the molecular level render MOFs and congeners to be particularly useful for numerous catalytic applications.[5] The introduction of molecularly defined catalytically active metal sites into the framework has been demonstrated, bridging homogeneous and heterogeneous catalysis.[6] Recently, we have employed precursor chemistry originating from the metal-organic chemical vapor deposition of metal thin films (MOCVD)[7] to load microcrystalline powder samples of $[Zn_4O(bdc)_3]$, (MOF-5; bdc: 1,4-benezene-dicarboxylate = terephtalate) with very small catalytically active metal nanoparticles of Cu and Pd to yield the nanocomposites Cu@MOF-5 (methanol synthesis) and Pd@MOF-5 (hydrogenation).[8] Beyond this use as bulk (powder) materials it is obvious that the integration of the full potential of functional CPs as building blocks for bottom-up chemical nanosystems raises the challenge to direct and control the crystal growth of CPs, in particular at surfaces and at the nanoscale. However, not much is known about nanocrystals of coordination polymers in general (except Prussian Blue-type compounds).[9] For example, the effect of polyelectrolyte additives (poly(vinylsulfonic acid, sodium salt), on the homogeneous nucleation and crystal growth of $[\{Cu_2(pzdc)_2(pyz)\}_n]$ (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine) has been studied and crystallite-size dependent diffusion properties were characterized.[10] Our related interest is focused at the nucleation and growth of MOF crystallites at surfaces, for example, to contribute to the development of novel MOF-based membrane reactors similar to zeolite[11] mesoporous

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[†] Thin Films of Metal Organic Frameworks, II; for contribution I see ref 14.

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silica[12] and other metal oxide[13] based functional thin films and membranes and related chemical systems.

We have communicated the selective anchoring of 100−500 nm sized MOF-5 crystallites at patterned COOH/CF_3 terminated self-assembled organic monolayers (SAMs) on Au(111) model substrates[14] and have demonstrated the subsequent (reversible) adsorption of volatile $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)Pd]$ (**1**) to yield thin films of type $\{[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)Pd]@MOF\text{-}5\}/SAM$ and {Pd@MOF-5}/SAM after irradiation with UV light. Evidence of the selective nucleation and adhesion of MOF-5 crystals at the COOH sites was obtained. Studies toward a related layer by layer growth of MOFs, eventually allowing epitaxial growth of MOFs at suitable surfaces, are underway and first results will be published elsewhere.[15] Herein, we wish to present and discuss our results on the growth of MOF-5 crystals at bare alumina and silica surfaces in comparison with silica surfaces modified with COOH- or CF_3-terminated SAMs. The attachment of single MOF crystals or agglomerated crystals forming a polycrystalline layer to Si/SiO_2-type substrates may be potentially important for the fabrication of MOF-based microelectronic sensors and Al_2O_3 appears to be a general model of metal oxide surfaces with a high affinity for carboxylic groups. In addition, ultrathin (amorphous) Al_2O_3 adhesion layers can be grown by atomic layer deposition (ALD) at a broad variety of substrates,[16] including organic polymers, allowing MOF thin films to be combined with a variety of other materials.[17]

Experimental Section

All materials and chemicals were purchased commercially and used as received. The employed MOCVD precursor for palladium, $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$, was synthesized according to literature recipes.[18,19] The manipulation with air-sensitive compounds was performed employing standard Schlenk and vacuum line techniques under an inert gas atmosphere (dry argon or dinitrogen) and as well using gloveboxes (MBraun, Garching). All solvents were carefully dried and inter gas saturated (argon) by an automatically operated catalytic solvent purification system (SPS, MBraun, Garching).

Analytical Methods: ATR, PXRD, SEM, and Contact Angle Measurements. The following routine methods were employed: ATR spectra were measured with a Vector 22 spectrometer (Bruker) and powder XRD (PXRD) of the samples were recorded with a D8-Advance Bruker AXS diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) in $\Theta-2\Theta$ geometry and with a position-sensitive detector. Morphological investigations were carried out using a LEO 1530 Gemini scanning electron microscope (SEM). The contact angles of different SAMs were measured with a Phoenix 150 (Surface & Optics Co).

Substrate Preparation. Silica (Wacker Siltronig AG, 20 nm SiO_2 layer) and c-plane sapphire substrates (crystec) were cut into strips of 1.5 × 1.0 cm^2. These strips were immersed in boiling aqueous hydrogen peroxide (30%) for 30 min followed by soaking in boiling distilled water for 30 min to hydroxylate the surface. After drying at 363 K for 30 min, the samples were directly used for further manipulation. The ALD-Al_2O_3-coated silicon substrates were prepared using a ASM F120 ALD reactor system. On 5 × 5 cm^2 silicon (100) wafer (Wacker Siltronic AG) alumina was deposited in a standard process using trimethylaluminum and water as precursors.[16,17] The samples were highly uniform with standard deviations of less than 3.6 nm and average film thicknesses of approximately 100 nm. Results and parameters of the ALD experiments are listed in the Supporting Information.

SAM Preparation. Self-assembled monolayers of the different organosilanes were prepared by immersing the substrates in a solution (pentane) of 10% of 10-undecenyltrichlorosilane or 1*H*,1*H*,2*H*,2*H*-perfluorododecyltrichlorosilane, respectively. After 24 h the substrates were removed from the solution, thoroughly rinsed with pentane and dichloromethane, and dried in a stream of dry argon. According to literature recipes, the vinyl group of the 10-undecenyl-trichlorosilane SAM was oxidized by immersing the substrates into an aqueous solution (20 mL) of 2 mg of $KMnO_4$ and 84 mg of $NaIO_4$.[20] After 24 h the substrates were removed, rinsed with water, ethanol, and diethyl ether, and dried with argon. Evidence for the successful oxidation is the change of the contact angle from 95 ± 1° to 41 ± 3°, which nicely correlates with known values.[20]

Preparation of MOF-5 Mother Liquor and Formation of MOF-5/Substrate Thin Films. Samples of 3.14 g of $Zn(NO_3)_2 \cdot 4H_2O$ and 0.67 g of terephthalic acid were dissolved in 100 mL of high-purity diethylformamide (DEF, Merck). The solution was first heated to 65 °C. After 72 h the temperature was increased to 105 °C and the solution was kept at this temperature until the beginning of crystallization. The mother liquor was filtered (0.2 μm syringe pre-filter) and cooled down to 20 °C (water bath). Into this MOF-5 mother liquor the pretreated substrates were mounted in a perpendicular fashion to avoid the growth of a coating by sedimentation. After 24 h the MOF-5 film growth was stopped by removing the substrates from the solution. The wafers were rinsed with pure DEF and immersed into chloroform (24 h) to exchange the low volatile solvent and finally dried in vacuum (RT, 24 h). ATR υmax/cm^{-1}: 1604 s, 1570 w, 1505 m, 1431 w, 1394 s, 1316 w, 1230 w, 1156 w, 1106 w, 1017 m, 977 vw, 932 vw, 882 w, 864 vw, 824 m, 745 s, 606 m, 575 w, 520 s.

Gas-Phase Loading of MOF-5/Substrate Thin Films and Subsequent Photo Reduction. The dried and emptied MOF-5/substrate samples were placed under inert conditions (Ar, H_2O, below 1 ppm) in a Schlemk tube together with a vial containing 100 mg of the Pd precursor $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$. In static vacuum (1 Pa, 20 °C) the loading was carried out for 4 h. The process was finished by opening the tube under argon. Subsequently, the loaded MOF-5 thin films of the type $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5]_n@MOF\text{-}5$/substrate were photolyzed in an inert gas stream (Ar, He) for 120 min at 30 °C (Hg high-pressure lamp, 500 W, Normag TQ 718). Traces of remaining ligand fragments were removed in vacuum (24 h, 100 °C).

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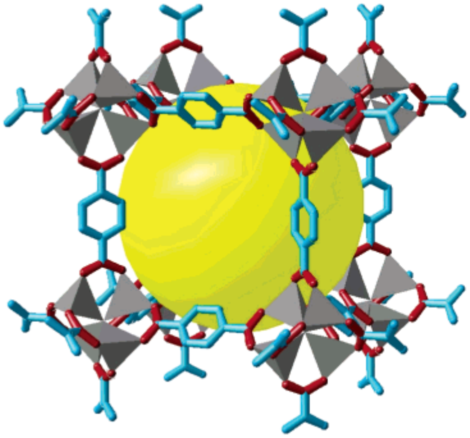

Figure 1. Structures of MOF-5 illustrated for a single cube fragment of their respective cubic three-dimensional extended structure. The large yellow spheres represent the largest sphere that would fit in the cavities based on the van der Waals contacts of the frameworks. Hydrogen atoms have been omitted.

Results and Discussion

General Procedure of MOF-5 Growth and Substrate Pretreatment. According to our previous and preliminary work on MOF thin films,[14] we again selected MOF-5 as representative example of a microporous CP based on carboxylic linkers (Figure 1). Zeolite thin films grown from defined colloidal solutions of ideally monodisperse nanosized zeolite crystals are of superior quality compared to zeolite films grown on substrates being directly immersed into the mother liquor of the zeolite synthesis under hydrothermal conditions.[21] However, until now, there is no reliable protocol for the preparation of *stable* colloidal MOF-5 solutions with tailored crystallite sizes being useful for the assembly of MOF crystallites at surfaces, despite our ongoing efforts to achieve that. The study below thus follows the straightforward strategy already outlined previously.[14] Supersaturated MOF-5 mother solutions were prepared following a detailed temperature program and MOF crystal growth from those solutions was allowed contact with suitably pretreated substrates over certain periods of time after cool down of the mother liquor to room temperature and filtration prior to contact with the substrates. A detailed characterization and evaluation of the substrates obtained is given in the next section, referring to MOF-5 crystal growth at bare and SAM-modified SiO_2 and bare Al_2O_3 substrates.

MOFs@SAMs. Homogeneous nucleation of MOFs is likely to proceed via the formation of the so-called secondary building units (SBUs) which in the case of MOF-5 is a tetrahedral $[Zn_4O]^{6+}$ cluster ion with the six Zn−Zn edges bridged by terephtalate. These octahedral connectors then fuse together via Zn^{2+}/carboxylate coordination and form the network and eventually cubic macrocrystals. However, direct evidence of the persistence of the (postulated) SBUs during the actual crystal growth from the mother solution is rather shallow. Only recently, EXAFS data measured from amorphous intermediates and mother solutions were presented, giving evidence that trimeric iron oxide secondary building units remain intact during crystallization of the metal-organic framework MIL-89 from starting materials to products.[22] Directed growth on solid substrates should thus be possible if solvated or polynuclear Zn^{2+} complexes, e.g., SBUs, or larger MOF-5 nuclei strongly adsorb to the surface. The anchoring of linkers (e.g., terephthalic acid), $Zn^{2+}{}_{(solv)}$, SBUs, and/or MOF nuclei to the substrate surface obviously depends on the surface chemistry. As we presented earlier on alkanethiol-modified Au(111) substrates, MOF-5 will not grow on alkyl- or CF_3-terminated SAMs while it nicely attaches to COOH-terminated areas.[14] SAMs or LB films with carboxylic acid surface groups are well-known to coordinatively bind metal cations $M_{(solv)}{}^{n+}$ from solution phase.[23] Tailored surfaces of that kind and/or certain surfactants as additives have been used to model the influence of soft surfaces or interfaces to direct nucleation and crystal growth of inorganic solid-state materials, particularly within the frame of the elucidation of the biomineralization processes.[24]

Selection of Substrates and Substrate Pretreatment. The surface chemistry of the selected metal oxides SiO_2 and Al_2O_3 are quite different. Alumina belongs to a class of oxides that are known to form strong bonds to carboxylic acids similar to the analogous surface chemistry of alkane- and aryl-thiols on gold substrates.[25−27] The binding strength of carboxylates on these type of surfaces depends on different basicities of oxides characterized by the isolectric point (IEP) which is a measure of the pH at which the surface will be electrically neutral.[28] For alumina the IEP is 9.1[29] and thus greater than the pK_a of typical carboxylic acids. Therefore, the MOF-5 linker molecule terephthalic acid ($pK_{a1} = 3.52$; $pK_{a2} = 4.46$) is likely to attach to the surface and thus we expect that MOF-5 crystals should adhere very nicely to Al_2O_3. In the case of SiO_2 type of surfaces the isoelectric point is between pH 2 and pH 2.5.[30] Certainly, these data refer to the solid/aqueous interface and are not directly transferable from the aqueous to the nonaqueous solvent system. However, the actual protic and polar DEF/water combination appears to be not too far away from the conditions the referred IEPs correspond to. Thus, we anticipate a different behavior of the more acidic silica surfaces toward MOF-5 crystals compared to the more basic alumina. In the study presented here we selected Si(100) wafers with a well-defined 20 nm layer of SiO_2 next to bare Al_2O_3(0006) wafers (sapphire) as well as amorphous ALD-grown Al_2O_3 adhesion layers on the same (oxidized) Si(100) wafers as primary substrates for the growth studies. The self-terminated layer by layer growth of alumina from trimethylaluminum and water vapor using the technique of atomic

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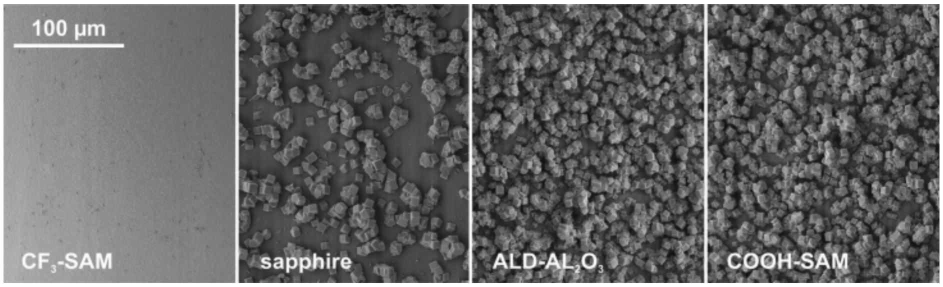

Figure 2. Scanning electron microscopy images of MOF-5 thin films on different pretreated alumina substrates. No crystal growth can be observed on CF_3-terminated surfaces whereas densely packed MOF-5 thin films occur for ALD-Al_2O_3 or COOH-terminated surfaces.

layer deposition (ALD) is well-known and allows the deposition of Al_2O_3 on many other surfaces with high precision.[16,17] According to literature procedures, we further modified these range of substrate surfaces with ω-functionalized alkyltrichlorosilanes to fabricate $-COOH$ and $-CF_3$ terminated surfaces on the primary SiO_2 substrates (see Experimental Section). This option allows the direct comparison of MOF-5 growth of these different types of surfaces.

Growth of MOF-5 at Bare Al_2O_3 Surfaces. C-plane sapphire wafers, $-CF_3$, and $-COOH$ surface functionalized samples as well as ALD-Al_2O_3-coated silicon substrates were prepared as described in the Experimental Section. As mentioned above, these substrates were immersed in pretreated MOF-5 mother liquor. To exclude sedimentation-induced film growth, the different substrates were mounted perpendicular to the bottom of the vessel and were immersed completely in the solution. After a reaction time of 24 h, all substrates were worked up as described above. The cleaned and dried samples were characterized by scanning electron microscopy (SEM). It is obvious and completely anticipated that the fluorinated surface proved to undergo complete nucleation and/or to be adhesion passive, while cubic MOF-5 crystallites of 5−10 μm grew on bare sapphire, ALD-Al_2O_3, and the COOH-terminated sapphire surface (Figure 2). The thickness of the obtained, rather rough, coatings were around 30 μm (by SEM cross section; estimated growth rate of about 0.5−1 μm/h). However, the growth of the MOF-5 particles seams to depend on the different types of surfaces. COOH-functionalized and amorphous ALD-Al_2O_3-covered silicon substrates show a dense MOF-5 film growth whereas single-crystalline Al_2O_3 (c-plane sapphire) surfaces are just partially covered. The ability to anchor MOF-5 crystals obviously correlates with the density of structural defects or vacancies (amorphous ALD-AL_2O_3) or the surface concentration of flexible binding positions (COOH-SAM).

In addition to the SEM characterization all MOF-5 thin films were analyzed by powder X-ray diffraction (PXRD) and attenuated total reflection infrared spectroscopy (ATR). The ATR spectra match well with a freshly synthesized MOF-5 powder sample (see Supporting Information). Unambiguous evidence of the retained cubic structural motif of the MOF-5 crystallites composed of the thin film is given by PXRD characterization. The PXRD patterns shown in Figure 3 compare well with an authentic polycrystalline sample of MOF-5 (Figure 3b) and with the calculated pattern derived from single-crystal X-ray diffraction data[7] and are apparently independent of the type of surface (sapphire or ALD-Al_2O_3). The deposited crystallites were without preferential orientation. These observations correlate with the results of our previous work about MOF-5 thin films on functionalized Au(111) surfaces.[14]

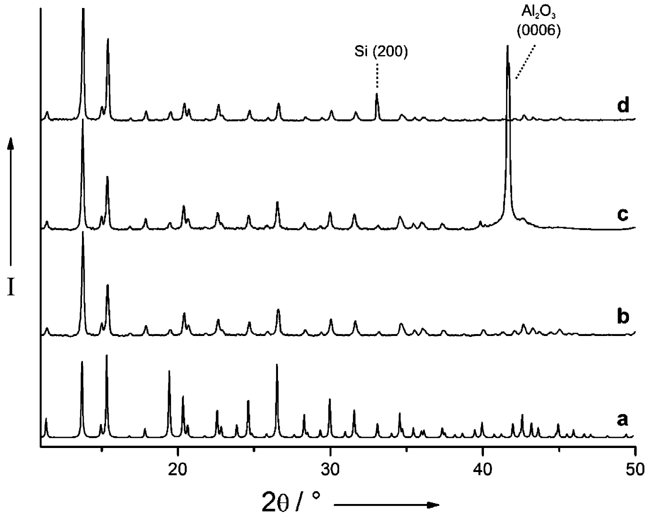

Figure 3. XRD patterns of the systems: (a) calculated MOF-5 diffraction pattern; (b) MOF-5 reference sample (microcrystalline powder); (c) MOF-5/sapphire; (d) MOF-5/ALD-Al_2O_3/Si(100). The substrate-specific reflexes are marked for Al_2O_3(0006), $2\theta = 41.6°$, and Si(200), $2\theta = 32.96°$.

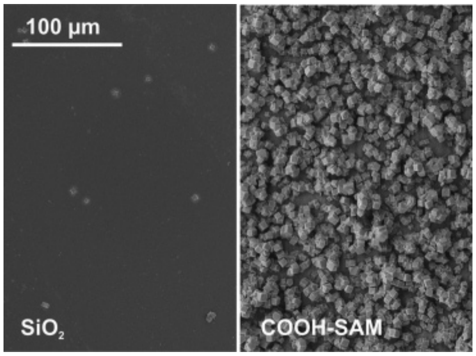

Figure 4. Scanning electron microscopy images of MOF-5 thin films on bare and SAM-modified silica substrates. No crystal growth can be observed on bare SiO_2 surfaces. On COOH-functionalized silica a densely packed MOF-5 thin film is formed.

Growth of MOF-5 at SiO_2 Surfaces. Furthermore, the growth of MOF-5 on well-defined bare SiO_2 layers on Si-(100) wafers was investigated. For comparison we also immersed a COOH-functionalized SiO_2/Si(100) substrate into the MOF-5 mother liquor. In following the already presented procedure, the substrates were worked up and analyzed by SEM. It is obvious that on bare SiO_2 surfaces almost no deposition of MOF-5 crystals occurs (Figure 4). This behavior of silica surfaces toward MOF-5 crystals can be explained by the low isoelectric point of SiO_2 (IEP = 2−2.5)

Figure 5. Optical images (digital photographs) of an empty 5 μm thick MOF-5 thin film on sapphire substrates before (left) and after (middle) the exposition to the vapor of the deep red MOCVD precursor [(η^5-C_5H_5)Pd(η^3-C_3H_5)]. Subsequent treatment of the loaded film with UV light converts [(η^5-C_5H_5)Pd-(η^3-C_3H_5)]@MOF-5 into Pd@MOF-5, visible by the color change to deep black (right).

as suggested above. At a pH value significantly above pH = 7, which we assume for the MOF-5 mother liquor (tested by simple organic pH indicators), the wafer surface will have a net negative charge. This seems to result in an electrostatic repulsion barrier between the surface and probably the carboxylate-terminated and thus also negatively charged MOF-5 particles in the solution. The supposed barrier impedes nuclei deposition from the solution onto the wafer surface during immersion. In the case of the silica substrates we have modified the surfaces by SAM techniques. As visible in Figure 4, the COOH-terminated surfaces again allow the growth of a dense MOF-5 film with a quite similar morphology to the MOF-5 thin films on COOH-functionalized alumina. ATR and PXRD characterization attest to a pure phase of MOF-5 crystallites composed of the thin film (see Experimental Section and Supporting Information). We speculate that the surface carboxylates effectively bind Zn^{2+} from the solution and/or surface-exposed Zn^{2+} sites of the MOF-5 nuclei. However, the growth mechanism of MOF-5 on COOH-terminated SAMs is still under investigation and results will be published elsewhere.

MOCVD Loading of MOF-5/Al_2O_3 with Pd. Cleaned and emptied MOF-5 powder can be conveniently loaded with metal organic precursor molecules as we described earlier.[7,8] To transfer this concept to the new class of MOF-5 thin films on metal oxides, the following experiment was carried out: A MOF-5/Al_2O_3 film (Figure 5 left) was prepared and dried in vacuo to allow desorption of all included solvent residues. Then, the MOF-coated substrate was exposed to the vapor of [(η^5-C_5H_5)Pd(η^3-C_3H_5)], which is a red-colored, volatile metal-organic compound well-known as a clean precursor for MOCVD of palladium.[18,19] The bright red color of the resulting film indicates the loading of the MOF-5 cavities with [(η^5-C_5H_5)Pd(η^3-C_3H_5)] (Figure 5, middle). We suggest that each cavity is loaded with exactly four molecules of [(η^5-C_5H_5)Pd(η^3-C_3H_5)], similar to the stoichiometric intercalation compound [(η^5-C_5H_5)Pd(η^3-C_3H_5)]$_4$@MOF-5, characterization of which we have reported earlier.[8]

Subsequent UV irradiation of the loaded film at room temperature with a mercury lamp (500 W, Normag TQ 718) converts [(η^5-C_5H_5)Pd(η^3-C_3H_5)]@MOF-5 rapidly into Pd@MOF-5, visible by the color change to deep black. Afterward, the organic fragments were removed under reduced pressure (10 Pa) at 100 °C (24 h). The resulting powder XRD pattern is shown in Figure 6. It displays a broad reflection (fwhm = 5.4°) at 40.16° 2θ, which indicates Pd nanocrystallites of the dimension 1.4 (±0.1) nm (profile analysis with Topas P 1.0, pseudoVoigt). However, the characteristic reflections of the MOF-5 framework in the XRD of the {Pd@MOF-5}/sapphire sample are still clearly visible; thus, it appears obvious that the lattice of MOF-5 is still intact. Previously, we have communicated a similar MOCVD preparation and characterization of Pd@MOF-5 as a powder material and some further examples of the type of precursor@MOF-5[7] and metal@MOF-5.[8] The PXRD features of the thin film material {Pd@MOF-5}/sapphire match the data reported for Pd@MOF-5 reference material which we also characterized by TEM. In the latter case, the Pd nanoparticles are trapped inside the intact metal-organic framework of the 100−500 nm sized MOF-5 crystallites.[8]

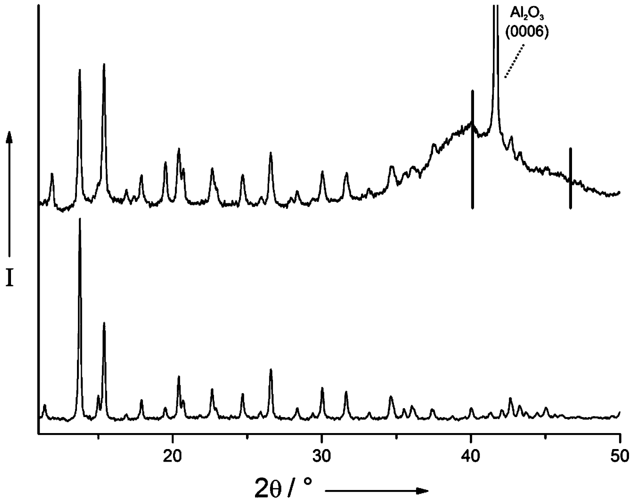

Figure 6. XRD patterns of the systems (below) MOF-5 (powder) and (above) {Pd@MOF-5}/sapphire. The 2θ values characteristic for palladium are highlighted. The substrate-specific Al_2O_3(0006) (2θ = 41.6°) reflex is marked too.

Conclusion

In summary, our study provides evidence that thin polycrystalline films of phase-pure MOF-5 can be grown directly from supersaturated mother solutions on suitably pretreated substrates. The deposited crystallites adhere well and the size and density of the crystallites in the micrometer range can be adjusted by the conditions and the type of the substrate. The surface acid/base properties characterized by the isoelectric point of the substrate control the anchoring of MOF-5 nuclei. ALD-Al_2O_3 proved to be a very good adhesive for the selective MOF-5 growth. This is particularly important because ultrathin amorphous Al_2O_3 layers can be deposited by ALD techniques on many substrates including organic polymers.[17] Thin MOF-5 films are likely to be grown on any type of substrate which can be previously modified either by application of a suitably functionalized SAM (e.g., COOH-terminated) or by a few nanometers of ALD-Al_2O_3.

Last but not least we demonstrated the adsorption properties of the deposited MOF-5 coatings on Al_2O_3 by MOCVD loading with $[(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)]$ as Pd precursor to finally yield the material {Pd@MOF-5}/Al_2O_3 as a model of a variety of conceivable MOF-based functional chemical systems, for example, catalytically active electrodes or sensors. Future investigations are directed to obtain such devices.

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Supporting Information Available: ATR spectra and tables of results and parameters of ALD process. This material is available free of charge via the Internet at http://pubs.acs.org.

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