A Titanium(IV)-based Metal-Organic Framework Featuring Defect-Rich Ti-O Sheets as Oxidative Desulfurization Catalyst

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Abstract: While titanium-based metal-organic frameworks (MOFs) have been widely studied for their (photo)catalytic potential, only a few Ti^{IV} MOFs have been reported due to the high reactivity of the employed titanium precursors. Here, we present the synthesis of COK-47, the first Ti carboxylate MOF based on sheets of $Ti^{IV}O_6$ octahedra, which can be synthesized with a range of different linkers. COK-47 can be synthesized as an inherently defective nanoparticulate material, rendering it a highly efficient catalyst for the oxidation of thiophenes. Its structure was determined by continuous rotation electron diffraction and studied in depth by X-ray total scattering, EXAFS and solid-state NMR. In addition, its photoactivity was investigated via electron paramagnetic resonance and demonstrated by catalytic photodegradation of rhodamine 6G.

Metal-organic frameworks (MOFs) are crystalline coordination polymers constructed through the directional bonding of metal ions and polydentate organic linkers, forming often porous networks. Over the last decade, MOFs have increasingly been investigated because of their highly tunable porosity and large density of accessible metal sites, making them suitable for catalytic applications, gas separation and storage.^[1–4] However, developing chemically and thermally robust materials remains challenging. This has fueled interest in using oxophilic group IV elements such as Zr^{IV} and Ti^{IV} , which tend to form stable structures based on their strong metal-carboxylate bonds. In this context, numerous Zr MOFs have been reported,^[5] but only 15 Ti^{IV} MOFs have been described to date, of which 5 in the last year, even though Ti precursors are cheap, non-toxic and Ti MOFs show good redox- and photoactivity.^[6–8] The much higher tendency of Ti^{IV} to form ill-defined oxyhydroxides lies at the basis of this discrepancy and makes the synthesis of Ti MOFs extremely challenging.^[9,10]

The majority of the to date reported Ti MOFs contain Ti-O clusters as secondary building unit (SBU), but very recently a few chain-based Ti MOFs were reported: DGIST-1, Ti-TBP and MIL-177-HT.^[7,11,12] The dimensionality of the SBU greatly influences the MOF properties, as was exemplified by photoconductivity measurements on the chain-based MIL-177-HT and its cluster-based counterpart, MIL-177-LT. The latter showed negligible conductivity whereas MIL-177-HT features similar conductivity as nano-sized TiO_2 , which demonstrates the benefit of increasing the SBU's dimensionality to achieve bulk oxide properties.

Herein, we report a new, photoactive, Ti^{IV} 4,4'-biphenyldicarboxylate (bpdc²⁻) MOF, termed COK-47, featuring a complex layer of TiO_6 octahedra as 2D SBU. Interestingly, a careful choice of synthetic conditions allows for control over particle morphology and defect content, making, COK-47_s (S = small particle) a highly active catalyst, e.g. towards the oxidation of dibenzothiophene. Several isorecticular analogues with for instance terephthalate or 2,2'-bipyridine-5,5'-dicarboxylate linkers were also synthesized (Figure S1).

The powder X-ray diffraction (PXRD) pattern of the obtained COK-47_s comprises only three broad diffraction peaks (Figure 1a, blue trace), which are typically associated with a high degree of disorder or very small crystallite domain size. While both can be desired from a standpoint of catalytic applications, the small number of broad reflections for COK-47_s strongly impedes indexing, structure elucidation and Rietveld refinement from conventional diffraction data. Therefore, a second synthetic procedure was developed to obtain particles of a sufficient quality to resolve COK-47's structure. The material, further referred to as COK-47_L (L = large particle), features the same three diffraction peaks as observed in COK-47_s, but of significantly decreased width (Figure 1a, red trace). Additionally, the PXRD pattern of COK-47_L contained some new, broad and overlapping peaks (e.g. at 15° and 26° 2 θ). It was unclear if these new peaks corresponded to those from the MOF structure or with impurities like titanium oxyhydroxides; so indexing and subsequent structure solution remained impossible. Given the small size of the crystallites, even in COK-47_L, and the ambiguity of the PXRD data, we opted to perform continuous rotation electron diffraction (cRED) to obtain a structural model for COK-47.^[13,14] Because electrons interact more strongly than X-rays, they are more suitable for single crystal diffraction experiments on nanocrystalline materials. Figure 1b shows the reconstructed 3D reciprocal lattice observed with cRED performed on a single COK-47_L crystallite. The collected data could be indexed in the monoclinic space group $C2/c$ (unit cell as refined to PXRD data: $a = 6.224 \text{ \AA}$; $b = 30.183 \text{ \AA}$; $c = 7.333 \text{ \AA}$, $\beta = 106.135^\circ$). Intensities were extracted from cRED data and the structure was solved and refined

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using SHELXT and SHELXL respectively (for additional details see SI).

Figure 1. a) PXRD pattern of COK-47_s (blue) and COK-47_L (red) compared with the simulated COK-47 pattern for the structural model obtained from cRED data (black). b) Reciprocal lattice in the $hk0$ (left) and $hk2$ (right) plane from cRED data (b).

The structure of COK-47 consists of Ti-O sheets which are connected by bpd c^{2-} linkers to form a three-dimensional framework (Figure 2). The inorganic moiety contains double chains of edge-sharing TiO₆ octahedra which are interconnected by μ_2 -O bridges. Each linker molecule connects with one carboxylate to an edge sharing pair of octahedra, while the other carboxylate binds to a corner sharing TiO₆ pair in the next titanium-oxo sheet. The significant dihedral angle between the two linker carboxylates is probably the reason why the synthesis was most easily performed with the slightly twisted H₂bpd c linker.

Figure 2. Representation of the COK-47 structure along the a (left) and b (middle) direction. Red lines indicate the orientation of the carboxylates and orange lines show the phenyl ring alignment. The linker connects corner- and edge-sharing octahedron pairs from neighboring layers (right).

The theoretical powder pattern calculated from this structural model matches well with that of COK-47_L (Figure 1a), but containing much more reflections than COK-47_s. A closer look at the differences between both patterns revealed that the hkl reflections with $l \neq 0$ are very weak in the experimental pattern of COK-47_L and only the $0k0$ set of planes was observed for COK-47_s. This suggests preferred orientation of the powder bed,

disorder or smaller crystallite dimensions along specific axes.

To further rationalize these differences, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figure 3a) and a 3D tomographic reconstruction of a COK-47_s aggregate (Figure S11) were recorded. These revealed the presence of nanosized crystallites ($\approx 30 \text{ nm} \times 5 \text{ nm} \times 5 \text{ nm}$) made up of columns of bright contrast, corresponding to the inorganic sheets, separated by a distance of $15 \text{ \AA}$, matching the bpd c^{2-} linker. Remarkably, the crystallite dimensions are particularly small parallel to the Ti sheets (a and c axes), but relatively large perpendicular to this plane (b axis). This strong anisotropy explains why only the $0k0$ reflections can be observed in the PXRD pattern; all other peaks with $h \neq 0$ and/or $l \neq 0$ are too broadened to be detected. Compared to COK-47_s, the crystallites of COK-47_L are much larger ($\approx 30 \text{ nm} \times 100 \text{ nm} \times 100 \text{ nm}$) along the Ti plane axes (Figure 3b), giving sharper peaks in the PXRD pattern. The powder pattern shows low intensities for the reflections not belonging to the $hk0$ family, this is caused by disorder of the structure, which is seen as streaks along the b^* -axis in the cRED data (Figure 1b). We tentatively attribute this to stacking faults of the linker.

Figure 3. HAADF-STEM images of COK-47_s (a) and COK-47_L (b). Schematic overview of the crystal growth in COK-47_s (c) and COK-47_L (d). The size of the arrows indicates the growth rate perpendicular to (blue) and along with (red) the Ti-O layers in both cases.

The difference in growth rate along the inorganic plane between COK-47_s and COK-47_L (Figure 3c-d) can be explained by the diverse synthetic conditions (details in SI): COK-47_s is synthesized with a high reagent concentration at high temperature under microwave irradiation for short reaction times, which typically yields small particles.^[15] In addition, the low water content in the COK-47_s synthesis slows down the hydrolysis rate of the Ti precursor and thus the in-plane growth rate, whereas extension along the b -axis is increased by the high linker concentration. This results in a similar crystallite dimension along the b -axis for both synthetic procedures, while the COK-47_L crystallites are much bigger along the a - and c -axes. The distinct morphology

control is peculiar and could influence the macroscopic properties, for instance by preferentially exposing certain facets to tune the catalytic activity of the material.^[16]

PXRD and TEM confirmed the long range order of COK-47_L and COK-47_S but the influence of the synthetic method on the local structure remained unclear. Therefore, pair distribution functions (PDFs) were derived from X-ray total scattering measurements and compared to the simulated PDF (Figure 4a). In the low R-range ($R < 12$ Å), nearly all correlations are present in both COK-47_S and COK-47_L, demonstrating that they feature almost the same local structure. The PDF of COK-47_S is however more damped at higher R-values, likely due to disorder in this material. In addition, some peaks in the low R-range are slightly shifted (≈ 0.1 Å) compared to these of COK-47_L and the theoretical PDF, indicating minor differences in the COK-47_S structure. These differences are situated in the Ti layers so a detailed investigation on the local environment of Ti was performed via extended X-ray absorption fine structure (EXAFS) measurements of the Ti K-edge (Figure 4b). A good fit (R -factor = 0.03) was obtained for COK-47_L and there are indeed some distinct differences with the EXAFS spectrum of COK-47_S. The first maximum at 1-2 Å in the real part is split in two peaks for the latter material, indicating some rearrangement in the nearest Ti-O shell. The similar intensity of this maximum however demonstrates that Ti remains six fold coordinated. A second difference is the absence of a shoulder at 2.5 Å (phase uncorrected) in the COK-47_S spectrum. This peak is associated with a Ti-Ti pair on which a carboxylate is attached so the change is likely associated with missing linker defects.

Figure 4. a) PDF of COK-47_S (blue) and COK-47_L (red) compared with the simulated COK-47 PDF (black). b) Magnitude (left) and imaginary (right) part of the FT EXAFS of COK-47_S (blue), COK-47_L (red) and the fit of COK-47_L (black dots). The EXAFS fitting range is indicated by vertical dashed lines.

Missing linker defects are widely studied in MOFs and often deliberately introduced because they are associated with open metal sites, which are potentially catalytically active, and a change in porosity. In the case

of COK-47, the structural model does not contain micropores, and indeed the measured BET surface area of COK-47_L is only 60 m²/g. COK-47_S however displays a stunning BET surface area of 573 m²/g, of which 100 m²/g was fitted to be external surface area (Figure S15); its pore size calculated from the nitrogen isotherm is 6 Å, which is in agreement with the theoretical pore size of the COK-47 structure featuring a missing linker (Figure S17).

The presence of other molecules on these linker defects of COK-47_S was investigated via ¹H liquid NMR after digestion with HF (Figure S18). Both modulator and cyclopentadiene were completely absent from the ¹H NMR spectrum, but besides the H₂bpdC linker, a large amount of methanol was present for COK-47_S, which was almost completely absent in COK-47_L's solution. Since the materials were evacuated under vacuum at 200°C prior to digestion, physisorbed methanol in the pores could be excluded and the lack of methanol in COK-47_L was attributed to its pristine nature. ¹³C and ¹H MAS NMR of COK-47_S revealed the presence of methoxides, which have been widely observed as capping agents both on discrete Ti^{IV} clusters, on the Ti^{IV} cluster in MOF-901 and on Zr-MOFs like UiO-66 (Figure S20).^[10,17,18] As in the latter example, the methoxides in COK-47_S stem from reversible post-synthetic exchange with hydroxyl groups during washing (Figure S21).

The nature of these methoxides was investigated by constructing and DFT optimizing four different defective models (Figure 5a). Inclusion of the CH₃-moieties most likely occurs on missing linker defects so the first two models comprised the replacement of a linker by a bridging (model 1) or terminal (model 2) methoxide. The latter model also contains an open site on the neighboring Ti atom. Model 3 and 4 were included to check whether methoxides could replace respectively μ_2 or μ_3 framework oxygens. After DFT optimization, GIPAW (Gauge-Including Projector Augmented Waves) calculations were performed and the calculated chemical shifts were compared with the experimental ¹³C NMR spectra (Figure 5b). The shifts of the linker carbons in all models agreed well with the experimental data but there were large differences in the calculated methoxide-carbon shifts. Interestingly, the measured methoxide peak of COK-47_S also shifts (from 63 ppm to 77 ppm) when increasing the activation temperature from 150°C to 200°C. The shift of the bridging methoxide in model 1 (62 ppm) coincided perfectly with the measured spectrum after activation at 150°C whereas the calculated shift of the terminal methoxide in model 2 (74 ppm) aligned with the CH₃-peak after activation at 200°C. The ¹³C-shifts of the methoxides in model 3 (87 and 94 ppm) were much higher so replacement of a μ_2 -O is deemed unlikely. Similarly, the terminal methoxide in model 4 (84 ppm) was shifted too high and missing μ_3 -O defects can therefore be excluded. We can thus conclude that the missing linker defects of COK-47_S are capped by bridging methoxides after evacuation at 150°C and that high temperature activation at 200°C results in the formation of terminal methoxides with neighboring open sites.

Figure 5. a) Schematic representation of the basic motifs within pristine COK-47 and the different defect models. b) Measured ^{13}C MAS NMR spectrum with indicated GIPAW-calculated isotropic methoxide shifts for COK-47 models 1 (blue), 2 (red), 3 (green) and 4 (purple) and the linker shifts (grey). c) Spin-diffusion curve describing the transfer of ^1H polarization between the methoxide and linker molecules in COK-47_s activated at 150°C (blue dots) and 200°C (red dots) compared to the calculated spin-diffusion curves in model 1 and 2 (black lines). d) ^{13}C -detected 2D proton spin-diffusion NMR spectrum of COK-47_s activated at 150°C recorded with spin-diffusion mixing time of 10 ms. The cross-peaks, indicated by red lines, between linker and methoxide indicate that they are in close proximity.

The spatial distribution of the methoxides was studied in depth via ^1H spin-diffusion NMR, a technique which probes the proximity of organic moieties (Figure 5c-d).^[19,20] The intense cross-peaks between the methoxide protons (resonating at 4.2 ppm) and the linker carbon nuclei (resonating between 120 and 180 ppm) in the spectrum demonstrate that the methoxides and linkers are in close proximity. The measured spin-diffusion rate of the sample activated at 150°C resembles well the calculated one of model 1, whereas the simulation for model 2 fits the experimental diffusion kinetics of the sample activated at 200°C (Figure 5c). This provides additional evidence for the temperature induced transition from bridging to terminal methoxides and also demonstrates that the defects are homogeneously distributed through the material.^[19] The experimentally determined number of methoxides ($\text{MeO}/\text{bpdc} = 1.3$) in COK-47_s corresponds with 39% missing linkers, an exceptionally high number that is only possible because the 2D inorganic moieties are theoretically linked by an infinite number of dicarboxylates. The chemical composition ($[\text{Ti}_2(\mu_3\text{-O})_2(\mu_2\text{-O})(\text{bpdc})_{0.61}(\text{MeO})_{0.78}]$) matches well with the loss of organic matter (50%) during decomposition at 440°C, as determined by thermogravimetric analysis (Figure S24).

The presence of large numbers of methoxide groups and open sites in COK-47_s suggests the availability of Lewis acidity (LA), especially since the former can easily be replaced by reactive species.^[17] LA sites would imbue

the material with catalytic activity, and for COK-47_s this was explored using the oxidation of dibenzothiophene (DBT) (Figure 6a). Oxidative desulfurization (ODS) is a mild, industrially relevant alternative for hydrodesulfurization since the latter requires high hydrogen pressures to remove thiophenes in order to meet the ever more stringent requirements for combustion fuels.^[21] The reaction is known to be catalyzed by a range of Ti-containing materials including hierarchical titanium silicates and MIL-125, but also by other MOFs such as the vanadium-based MIL-47 and the zirconium-based UiO-66.^[22–24]

Reaction was performed with 15 mol% catalyst and 2.5 eq. *tert*-butylhydroperoxide (TBHP) as oxidant in toluene at 60 °C. Without catalyst, only 2% conversion was obtained after 24 h while COK-47_s converted 99% of DBT within two hours (Figure 6b). GC/MS confirmed full selectivity to the corresponding sulfone. No conversion occurred when TBHP was omitted. The reaction follows pseudo-first order kinetics and the apparent rate constant for COK-47_s ($41.1 \times 10^{-3} \text{ min}^{-1}$) exceeds that of all other tested catalysts. COK-47_L ($3.6 \times 10^{-3} \text{ min}^{-1}$) is eleven times less active because it contains almost no open sites and has a much lower surface area. Similarly, MIL-125 ($0.8 \times 10^{-3} \text{ min}^{-1}$) displays very limited activity because it lacks defective sites and the low activity of Degussa P25 TiO_2 ($<0.1 \times 10^{-3} \text{ min}^{-1}$) can be explained by the limited surface area of the latter. UiO-66 with two missing-linker defects per Zr_6 cluster ($2.7 \times 10^{-3} \text{ min}^{-1}$) and MOF-808 (4.3

$\times 10^{-3} \text{ min}^{-1}$) which contains six open sites per cluster, showed reaction rates still an order of magnitude lower than for COK-47_s. MIL-47 ($11.9 \times 10^{-3} \text{ min}^{-1}$) lacks open sites but likely acts as a homogeneous catalyst since it was observed to degrade during reaction.^[25] Oxidation of other thiophenes such as benzothiophene (BT) was also performed but the reaction is slower because BT is a less electron rich substrate, making it an inherently less reactive substrate (Figure S29).^[26] ICP analysis indicated less than 1 ppm Ti in solution after DBT oxidation, which together with a hot filtration test confirmed the heterogeneity of the COK-47_s. Its stability was furthermore established via PXRD and a recycling test (Figure S30-31). The reaction mechanism is believed to proceed through the coordination of TBHP to the LA open sites, thereby replacing the capping methoxides, which was demonstrated by the detection of methanol in the solution after reaction.

Figure 6. a) Reaction scheme of the DBT oxidation and b) DBT conversion vs. time with different catalysts.

Development of new Ti MOFs is often driven by expectations about their redox properties and photoactivity.^[27] Irradiation of COK-47_s or COK-47_L with UV-A in ethanol under inert atmosphere resulted in a color change from a white to a dark blue powder, indicating a valence change from Ti^{IV} to Ti^{III}, while maintaining its structural integrity (Figure S34). In addition, a strong signal with g -values ($g_{\perp} = 1.932$ and $g_{\parallel} = 1.899$) corresponding to octahedrally coordinated Ti^{III} appears in the electron paramagnetic (EPR) spectrum (Figure 7).^[28,29]

Figure 7. EPR spectrum of photoreduced COK-47_s (black) indicating the presence of Ti^{III} with $g_{\perp} = 1.932$ and $g_{\parallel} = 1.899$. Simulated spectrum is shown in red.

When the photoreduced COK-47_s is exposed to air, the EPR signal and blue color disappear within minutes, thus confirming the reversibility of the reduction. The change in valence state of Ti^{IV} to Ti^{III} is expected to be compensated by replacement of oxo through hydroxo bridges in the inorganic moiety, as has been previously demonstrated for COK-69.^[28] The photocatalytic activity of COK-47_s was studied via the degradation of a fluorescent dye, rhodamine 6G (Rh6G) (Figure S35). COK-47_s fully decomposes Rh6G upon UV exposure, while maintaining its structural stability (Figure S36). The degradation rate is similar as in a reaction catalyzed by a conventional TiO₂ photocatalyst and higher than for MIL-125. This demonstrates the photocatalytic potential of COK-47_s and paves the way for further applications.

In conclusion, we synthesized the first titanium carboxylate MOF exhibiting a sheet-based structure, COK-47, and by selecting appropriate synthesis conditions, a highly defective material was obtained. The resulting COK-47_s is porous, featuring bridging or terminal methoxides, and shows excellent catalytic activity for the oxidation of dibenzothiophene. COK-47_s can reversibly be reduced and degrades Rh6G upon UV irradiation indicating its potential in (photo)catalytic applications.

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