

Heterogeneous Catalysis

Drastic Enhancement of Catalytic Activity via Post-oxidation of a Porous Mn^{II} Triazolate Framework

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Abstract: Mn^{III} is a powerful active site for catalytic oxidation of alkyl aromatics, but it can be only stabilized by macrocyclic chelating ligands such porphyrinates. Herein, by using benzobistriazolate as a rigid bridging ligand, a porous Mn^{II} azolate framework with a nitrogen-rich coordinated environment similar to that of metalloporphyrins was synthesized, in which the Mn^{II} ions can be post-oxidized to Mn^{III} to achieve drastic increase of catalytic (aerobic) oxidation performance.

Because pore size, shape and functionality can be tailored over a wide range, porous coordination polymers (PCPs) are very attractive as heterogeneous catalysts.^[1] The Mn^{III} ion is an efficient active site for catalytic oxidation of alkyl aromatics to corresponding ketones.^[2] Catalytic active Mn^{III} centers are generally chelated by macrocyclic (such as porphyrinates) or quasimacrocyclic (such as Salen) ligands.^[3] Without protection of the macrocyclic or polydentate chelating ligand, Mn^{III} is usually unstable in solution and easily disproportionate to Mn^{III} and Mn^{IV,[4]} which makes it difficult to directly synthesize a PCP with Mn^{III} active sites.

In very stable/robust mesoporous organosilicas and zeolites, unstable metal ions such as Mn^{III} , Cu^{I} , and Zn^{I} with high catalytic activities are usually obtained by redox treatment of the more stable precursors $Mn^{II,[5]}$ $Cu^{II,[5]}$ and $Zn^{0,[6]}$ respectively. However, this strategy can be hardly applied in PCPs because they are less robust than the covalent adsorbents.^[7] In this work, we report a porous metal azolate framework (MAF) based on Mn^{II} and a rigid bridging bis-triazolate ligand, in which the Mn^{II} ions can be post-oxidized to Mn^{III} to drastically enhance the catalytic activity for (aerobic) oxidation of alkyl aromatics. The triazolate donors are beneficial for stabilization of not only the Mn^{III} ions but also the porous coordination network during the harsh oxidation reaction conditions, while sim-

ilar PCP structures easily decompose during activation and/or oxidation. $\ensuremath{^{[8]}}$

Solvothermal reaction of MnCl₂ and 1H,5H-benzo(1,2-d:4,5d')bistriazole (H₂bbta) at 210 °C gave single crystals of [Mn₂Cl₂-(bbta)(H₂O)₂]·guest (MAF-X25, 1g). The bulk microcrystalline sample of 1 g can be obtained at 75 °C. Single-crystal X-ray diffraction analysis revealed that 1 g possesses a three-dimensional (3D) coordination framework with a honeycomb-like structure (Figure 1 a). The asymmetric unit of **1 g** (space group $R\bar{3}m$) contains $\frac{1}{2}$ Mn^{II} atom, $\frac{1}{4}$ deprotonated bbta²⁻ ligand, $\frac{1}{2}$ Cl⁻ ligand, and $\frac{1}{2}$ coordinated H₂O molecule (Figure 1 b). Each Mn^{II} is coordinated in a distorted octahedral fashion by three nitrogen atoms from three $bbta^{2-}$ ligands, two μ -Cl⁻ anions and a terminal H₂O molecule, and each bbta²⁻ ligand coordinates to six Mn^{\parallel} ions. The Mn^{\parallel} ions are bridged by μ_3 -triazolate ring and μ -Cl⁻ (Mn···Mn 3.6885(7) Å) to form a 3₁ helical chain (Figure S1 in the Supporting Information), which are connected by the phenyl backbone of bbta²⁻ to generate a pillared-rod structure with large 1D channels ($d \approx 11$ Å if all guest and the coordinating water are removed) parallel to the helical chains. Similar structures have been observed in [M₂(dobdc)(H₂O)₂] (MOF-74/CPO-27; H_4 dobdc = 2,5-dihydroxyl-1,4-benzenedicarboxylic acid; M = Mg, Mn, Fe, Co, Ni, Zn)^[8a-d] and [Mn₂Cl₂(bdt)- $(DMF)_2$] $(H_2bdt = 1,4$ -benzeneditetrazole, DMF = N,N-dimethylformamide).^[8e] Because of the lower symmetries of dobdc⁴⁻ and bdt²⁻, these compounds crystallize in a slightly lower-symmetry space group $R\bar{3}$. According to the bridging lengths of the ligands, the pore size of [Mn₂Cl₂(bbta)] is similar to those of [M₂(dobdc)] but much smaller than that of [Mn₂Cl₂(bdt)]. Preliminary synthetic experiments showed that, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} analogues of **1 g** can be also synthesized under similar reaction conditions (Figure S2 in the Supporting Information), although their purity still needs to be improved. On the other hand, Zn^{II} always led to a known cubic structure [Zn₅Cl₄-(bbta)₃].^[9]

Thermogravimetry (TG) and powder X-ray diffraction (PXRD) analysis showed that **1g** releases all guest and coordinated water molecules below 200 °C and retains high crystallinity up to at least 250 °C (Figure S3 in the Supporting Information), which is similar to $[M_2(dobdc)(H_2O)_2]$.^[10] Additionally, **1g** is stable in hot acidic/basic (80 °C, $4 \le pH \le 12$) solution for at least 48 h (Figure S3). On the other hand, $[Mn_2Cl_2(bdt)(DMF)_2]$ transforms to a less porous, amorphous structure after guest removal,^[Be] which might be ascribed to the high acidity and flexibility of the long bistetrazolate ligand. Single-crystal structure of guest-free **1** was measured to confirm the retention of

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Figure 1. a) The 3D network of 1, and coordination environments of: b) 1 g, c) 1, and d) 1' (thermal ellipsoids are drawn with probability 30%; symmetric codes: A: 4/3-y, -1/3+x-y, -1/3+z; B: 1/3+x-y, 2/3-y, 2/3-z; C: 5/ 3-x+y, 4/3-x, 1/3+z; D: 2/3+y, -2/3+x, 4/3-z; E: 5/3-x, 1/3-y, 2/3-z; F: 1-y, 1-x, z).

host framework and complete removal of guest and coordinated molecules (Table S1 in the Supporting Information). After removing the coordinated H_2O molecules, the coordination fashion of Mn^{II} was changed from octahedral geometry to tetragonal-pyramid geometry with an open coordination site (Figure 1c). To confirm the porosity of activated 1, N₂ sorption isotherm was measured at 77 K (Figure 2a), which showed a type-I characteristic with saturated uptake of 358 cm³g⁻¹, giving an apparent Langmuir surface area of 1566 m²g⁻¹ and a pore volume of 0.56 cm³g⁻¹. For comparison, the crystallography pore volume of 1 can be calculated as 0.55 cm³g⁻¹ (void = 59.2%, $\rho_{calcd} = 1.074$ g cm⁻³).

Considering the coordination environment of **1** is similar to that of metalloporphyrin and hydrogen peroxide can oxidize Mn^{II} to Mn^{III} in small molecular complexes,^[11] we treated **1** with H_2O_2 under alkaline condition to obtain the oxidation product



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Figure 2. a) N₂ isotherms, and b) IR spectra of 1 and 1'.

Chem. Eur. J. **2014**, 20, 1–6

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(MAF-X25ox or 1'). Scanning electron microscopy (SEM) images of 1 and 1' showed that the crystals crashed but remained well crystalline after treatment with H₂O₂ (Figure S4 in the Supporting Information). The oxidation states of the metal ions in 1 and 1' were characterized by X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy (Figure S5 in the Supporting Information). The binding energies of Mn $2P_{2/3}$ (642.2 eV) and Mn $2P_{1/2}$ (654.2 eV) as well as the shake-up satellite peaks in the XPS of 1 confirm the oxidation state of +2 for manganese in the synthesized samples. The Mn^{II} species in 1 can be also characterized by the strong broad EPR signal with g = 1.997. Because the Mn^{II} coordination sphere consists of three kinds of coordination bonds, a well resolved signal with a hyperfine structure of six principal lines cannot be observed. The shake-up peak is invisible in the XPS of 1', indicating that some Mn^{II} ions have been oxidized.^[12] On the other hand, the EPR spectrum of 1' was silent,^[13] also suggesting the existence of Mn^{III} in 1'. It is worth pointing out that, without protection of a macrocyclic or quasi-macrocyclic ligand, Mn^{III} will be easily oxidized to Mn^{IV} (MnO₂) under alkaline conditions. Even chelated by a Salen ligand in the PCP, H_2O_2 can also break the coordination bond between Mn^{III} and the Salen ligand.^[14] Fourier transformed infrared (IR) spectroscopy of 1' showed the characteristic stretching vibration at 3600 cm⁻¹ (strong and narrow) and in-plane bending vibration at 1500–1300 cm⁻¹ (strong and broad) for the OH⁻ ions^[15] and also the characteristic stretching vibration at 562 cm⁻¹ for the Mn^{III}–OH coordination bond (Figure 2b).^[16] N₂ sorption isotherm of 1' measured at 77 K (Figure 2a) showed a type-I characteristic with saturated uptake of 293 cm³g⁻¹, corresponding to an apparent Langmuir surface area of 1286 m²g⁻¹ and a pore volume of 0.46 cm³g⁻¹. Assuming complete oxidation, the pore volume can be calculated as $0.38 \text{ cm}^3 \text{g}^{-1}$ (void = 48.4%, $\rho_{calcd} = 1.285 \text{ g cm}^{-3}$). Therefore, about 50% Mn^{II} ions were oxidized to be Mn^{III}-OH. Although the crystal easily cracked in the oxidation process, we successfully solved the crystal structure of 1' by Rietveld refinement of its PXRD pattern (Figure 1 d, and Figure S6 and Table S1 in the Supporting Information). The unit-cell volume of guest-free 1' is about 7% smaller than that of 1g, because all coordination bonds in 1' are significantly shortened by about 0.05 Å, being consistent with the smaller ionic radius of Mn^{III}. The refinement also suggests that 1' is composed of about 50:50 Mn^{II}/Mn^{III}-OH. These data further confirm the retention of framework integrity and reduction of pore size mainly due the introduction of coordinated hydroxide groups. Under the oxidation condition for 1, [Mn₂(dobdc)(H₂O)₂] becomes amorphous (Figure S7 in the Supporting Information), which might be ascribed to its poor stability under aqueous/basic solution.^[17] Recently, Dincă et al. demonstrated that oxidation of [Mn2(dobdc)(H2O)2] by iodobenzene dichloride in dichloromethane at -35°C give rise to the oxidized quinoid ligand (2,5-dicarboxyl-p-benzoquinone) rather than Mn^{III} ions. When more aggressive oxidants such as O₃ and Cl₂ were used, [Mn₂(dobdc)(H₂O)₂] decomposed to give Mn_3O_4 .^[8f] In contrast, 1' exhibited high chemical stability in hot acidic/basic solutions similar to 1 (Figure S8 in the Supporting Information), so that it can endure the more severe oxidation

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conditions. In this context, the nitrogen-rich and more stable bistriazolate ligand should play an important role in stabilizing the Mn^{III} ions in **1**'.

Entry

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We compared the catalytic activities of 1 and 1' for oxidation of ethylbenzene (EB). EB oxidation was performed in a mixed solvent of acetonitrile, acetic acid, and water at 80 $^\circ\text{C}$ for 12 h using tert-butyl hydroperoxide (TBHP) as the oxidant. The oxidized product was examined by gas chromatography-mass spectrometry (GC-MS), which showed that 1 can only convert 22% with a selectivity of 76% for acetophenone (entry 1 in Table 1 and Figure S9a in the Supporting Information), which is consistent with the poor catalytic activity of Mn^{II} for oxidation of alkyl aromatics.^[3a] On the other hand, the conversion and selectivity of 1' are 97 and 99%, respectively (entry 2 in Table 1 and Figure S9b), confirming that the Mn^{III} ions in $\mathbf{1}'$ are similar to the well-known Mn[™]–porphyrinate species.^[2a, 3a, 18] It needs to be noted that 1' displayed higher catalytic performance than homogeneous catalysts MnCl₂ and [Mn(TPP)CI] $(H_2TPP = 5, 10, 15, 20$ tetraphenylporphyrin) for the oxidation of the small substrate EB (entries 3 and 4 in Table 1 and Figures S10 and 11 in the Supporting Information).

To demonstrate that the catalytic reaction occurred in the channel of 1', we carried out the Table 1. Oxidation of alkyl benzenes for the formation of phenyl ketones. Conv Substrate Catalyst Product Sel [%] [%] 1 22 76 1' 97 >99 MnCl₂ 68 21 Mn(TPP)Cl 86 66 1 75 97 1′ 23 98 93 1' 64 1 25 94 Mn(TPP)Cl 93 >99 1' **9**4^{[a} 96 37^[b] 79

Reaction conditions: alkyl benzene (0.10 mmol), TBHP (0.15 mmol), catalyst (0.01 mmol), acetonitrile (0.5 mL), acetic acid (0.01 mL), water (2.5 mL), and *m*-dichlorobenzene (internal standard): 0.13 mmol were stirred at 80 °C for 10 h. Conversion [%] and selectivity [%] were determined by GC-MS on an HP-5 MS column. [a] The fifth cycle. [b] Reaction conditions: catalyst (0.05 mmol), EB (20 mmol), water (8 mL), acetic acid (0.05 mL), oxygen pressure (3.0 MPa), T (120 °C) and time (14 h).

oxidation reactions for larger substrates. As showed in entries 5-8 in Table 1 and Figures S12-15 in the Supporting Information, the conversions of propylbenzene and tetralin are obviously lower than for EB, because the molecular sizes of these three substrates are similar to the effective aperture diameter of 1' (6.8 Å) and EB is the smallest one of them (Table S2 in the Supporting Information). For much larger substrates diphenylmethane and 4-ethylbiphyl, the conversions are very low, indicating that they cannot access the internal pores and the catalytic reactions mainly occur on the outer crystal surfaces. On the other hand, the homogeneous catalyst [Mn(TPP)Cl] showed better catalytic activity for oxidation of diphenylmethane than for EB (entries 4 and 9 in Table 1 and Figure S16 in the Supporting Information), because the methylene of diphenylmethane is more activated.

To further demonstrate the heterogeneous nature and stability of 1', it was filtrated out from the reaction mixture and additional reactants were added into the filtrate to carry out the reaction again. As expected, just a trace of product could be generated using the filtrate as catalyst. Inductively coupled plasma-atomic emission spectrometry showed that, just 0.17% Mn ion was leached into the reaction solution after the reaction. Compound 1' can be easily separated from the reaction mixture. After five consecutive catalytic batches, the PXRD pattern and sample weight of recovered 1' were almost unchanged (Figure S7 in the Supporting Information), and the product yield only marginally decreased (entry 10 in Table 1,

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and Figure S17 in the Supporting Information). As shown in Figure S18 in the Supporting Information, we also studied the effect of reaction time in the conversion of EB over 1', which achieved a turnover frequency (TOF) of 118 h^{-1} , being higher than for most heterogeneous catalysts such as metal oxides, polyoxometalates and PCPs.^[18a,19]

It has been shown that aluminophosphate molecular sieves containing Co^{III} or Mn^{III} species can catalyze the oxy-functionalization of alkanes using oxygen or air as a greener oxidant.^[5,20] Considering that PCPs have been rarely studied for catalytic aerobic oxidation,^[1a,b,21] we studied the catalytic activities of **1** and **1**' for aerobic oxidation of EB under a typical reaction condition (in a mixed solvent of acetonitrile and acetic acid at 120 °C for 14 h using oxygen as the oxidant). Compound **1**' exhibited much higher activity and selectivity than **1**, and the blank reaction carried out without oxygen showed no oxidative products (entries 11–12 in Table 1 and Figure S19 in the Supporting Information). It should be noted that, aerobic oxidation of EB using PCP as the catalysts has been rarely realized in the absence of the co-catalyst *N*-hydroxyphthalimide (NHPI).^[21a]

In summary, to avoid the difficulty in direct synthesis and explore new types of catalytic active Mn^{III} PCPs, we designed and constructed a robust PCP consisting of Mn^{II} and a bistriazolate bridging ligand, in which the Mn^{II} ions can be post-oxidized to form catalytic active Mn^{III} sites on the pore surface for enhancing the selective oxidation of alkylbenzenes by using TBHP or molecular oxygen as the oxidant. This strategy should be insightful for future development of new PCP materials with advanced functions.

Experimental Section

Synthesis and characterization

Synthesis of 1g: A mixture of MnCl₂·4H₂O (0.050 g, 0.252 mmol), H₂bbta (0.020 g, 0.126 mmol), and isopropanol (0.8 mL) was sealed in a 2 mL glass tube and heated at 210 °C for 3 days, then cooled to room temperature. The resulting pink, rod-like crystals were collected by filtration, washed with isopropanol and dried in air (yield ca. 43% based on H₂bbta). Microcrystalline powder of **1g** was obtained by heating a mixture of MnCl₂·4H₂O (0.050 g, 0.252 mmol), H₂bbta (0.020 g, 0.126 mmol), *N,N*-dimethylformamide (DMF, 4 mL), methanol (4 mL) and 12 \times HCl (0.2 mL) in a 15 mL Teflon reactor at 70 °C for 72 h (yield 72% based on H₂bbta); anal. calcd (%) for [Mn₂Cl₂(bbta)(H₂O)₂)·0.55 DMF·1.45 H₂O (C_{4.65}H_{9.75}N_{3.55}ClMnO₃): C 22.00, H 3.87, N 19.59; found: C 22.16, H 3.76, N 19.54.

Synthesis of 1: The as-synthesized complex $1\,g$ was placed in the quartz sample tube and dried under high vacuum at $180\,^\circ$ C for 24 h.

Synthesis of 1': A solution of H_2O_2 (0.5 mmol) in water (10 mL) was slowly added in 12 h to a suspension of 1 (0.0169 g, 0.05 mmol) in CH₃CN (5.0 mL), water (5.0 mL), and triethylamine (0.2 mmol) at 0°C under stirring, during which the color of the suspension turned brown gradually. The mixture was further stirred for 2 days at room temperature, and then filtered, washed with CH₃CN and dried in nitrogen flow to give the dark green oxidized sample 1' (0.0152 g, yield 97%).

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Drastic Enhancement of Catalytic Activity via Post-oxidation of a Porous **Mn^{II}** Triazolate Framework



Later could be better: A robust and redox-active, porous coordination framework has been designed and constructed, in which the Mn^{II} ions on the pore surface can be post-oxidized to form unstable Mn^{III} sites with drastically enhanced activity for catalytic oxidation of alkylaromatics (see figure).