Shining light on integrity of a tetracobalt-polyoxometalate water oxidation catalyst by X-ray spectroscopy before and after catalysis†‡

Rafael Schiwon, a Katharina Klingan, b Holger Dau* d and Christian Limberg* a

Modification of the Co-oxo cores of cobalt-polyoxometalate water oxidation catalysts is detectable by X-ray absorption spectroscopy (XAS) as demonstrated by comparison of Na10[Co4(H2O)2 (PW9O34)2] (1) and Na17[[(Co(H2O))Co2PW9O34]2(PW6O26)] (2). XAS reveals the integrity of 1 uncompromised by oxidant-driven water oxidation, which proceeds without formation of catalytic cobalt oxide.

Striving for new solar fuels, the water oxidation reaction is currently considered to be a bottleneck, hampering progress in the development of applicable technologies for the conversion of light into storable fuels.1 Intense research efforts are thus being pursued in order to develop both heterogeneous and molecular catalysts, which enable water oxidation at potentials close to the thermodynamic limit. A breakthrough has recently been achieved in the area of heterogeneous catalysis. Nocera and coworkers reported an in situ formed, self-healing Co-based catalyst (CoCat), which operates at moderate overpotentials as a water oxidation electrocatalyst.2,3 The CoCat is readily formed by electrodeposition from a buffered Co2+ solution as an amorphous film on the electrode surface; its atomic structure is characterized by cobalt oxide units composed of edge-sharing CoO6 octahedra.4 Also homogeneous WOCs are developing rapidly.1,5–9 The majority of the latter are based on (tailor-made) organic ligands which naturally represent the Achilles’ heel of such systems. In this context the use of defective polyoxometalate (POM) derivatives as ligands is an interesting approach for the design of WOCs with enhanced stability, because oxidative ligand degradation is not possible. Therefore, we decided to investigate the hydrolytic stability and possible catalyst degradation during catalysis by XAS.10

The synthesis of 1 has been performed according to a procedure established previously16 and its identity was confirmed by single-crystal X-ray diffraction (XRD, Fig. S1 and Table S2, ESI†) and mass spectroscopy (Table S3 and Fig. S2–S8, ESI†) as well as by XANES and EXAFS. These structural methods were complemented by UV/Vis spectroscopy (Fig. S9–S19, ESI†).

As there were conflicting reports on the solution stability of 1 even before catalysis,10,11,15 we have monitored its UV/Vis spectrum under various conditions. While 1 (1 mM) is indeed stable in pure water, addition of sodium phosphate (NaPi), used in the previous investigations10 to ensure a pH of 8 (30 mM for solutions being 3.2 m), triggers a slow decrease of its main absorbance band at 580 nm, thus indicating decomposition to some extent. Interestingly, the rate depends on the NaPi concentration: for a 30 mM NaPi solution a band decrease of 2% was observed within 1.5 h while it amounted to 3.5% in the case of 400 mM NaPi. However, very recent results20 suggest that such aging does not play a role in catalytic activity. Stability of the oxidant [Ru(bpy)3]3+|ClO4|, used has been investigated before, too.22 Albeit not the focus of our investigation, related results obtained by UV/Vis spectroscopy may be of interest and thus are reported herein. In contrast to the rather slow corrosion of 1 in aqueous solution, decomposition of [Ru(bpy)3]3+ in a 30 mM buffer of NaP, is more significant (Fig. S9, ESI†). Monitoring the UV/Vis absorption maximum of [Ru(bpy)3]3+ at 670 nm with time (Fig. S10, ESI†) suggests redox-degradation with a t1/2 of ca. 75 s. The product(s) showed a new band at 800 nm.

The addition of a 3.2 μM solution of 1 to a solution being 1.5 mM in [Ru(bpy)3]3+|ClO4|, and 30 mM in NaPi, significantly accelerates the
bleaching of the 670 nm band belonging to \([\text{Ru(bpy)}_3]^{3+}\) (Fig. S11 and S12, ESI†), as expected for water oxidation catalyzed by 1, and indeed \(\text{O}_2\) evolution with a yield of 66.7% has been shown.\(^{10}\) Hence, under these conditions reduction of \([\text{Ru(bpy)}_3]^{3+}\) to \([\text{Ru(bpy)}_3]^{2+}\) is much faster than degradation.

For investigation of the atomic structure of the WOCs, Co K-edge XAS spectra of the following samples were collected: (a) microcrystalline powder of 1, (b) \(3.2 \mu\text{M}\) of 1, (c) \(3.2 \mu\text{M}\) of 1 with 1.5 mM \([\text{Ru(bpy)}_3]^{3+}\), (d) 1 mM of 1, (e) 1 mM of 1 with 8 mM \([\text{Ru(bpy)}_3]^{3+}\) (b–e, 1 in aqueous solutions being 30 mM in NaPi, pH 8). All samples were frozen in liquid nitrogen and spectra were collected at 20 K.

The oxidant-containing samples were not immediately frozen but were frozen in liquid nitrogen and spectra were collected at 20 K. We estimate the edge position of CoCat is close to +3, as reported before;\(^{4}\) the oxidation state of the \(\text{Co}^{2+}\) hexaaquo complex was estimated to be \(2.0 \pm 0.1\) as expected. Thus we conclude that the oxidation state of 1 is conserved upon dissolution of the microcrystalline powder and upon water oxidation using \([\text{Ru(bpy)}_3]^{3+}\). We note that the latter finding does not exclude that higher cobalt oxidation states are formed during water oxidation because the herein investigated samples were frozen at a point where water oxidation had come to an end because of exhaustion of the \([\text{Ru(bpy)}_3]^{3+}\) oxidant.

Whereas the XANES region is sensitive mostly to oxidation states and the coordination geometry in the first coordination sphere, the EXAFS region of the spectrum can provide specific structural information on the first, second, third and higher coordination spheres. The indicated reduced distances are by about 0.4 Å shorter than the real distances obtained by EXAFS simulations and presented in Table 1 as well as Table S4 (ESI†). The five prevalent FT-peaks (a–e) of the POM samples are assigned to atom pairs as shown in Fig. 3.

Visual comparison of the EXAFS spectra (Fig. 2) as well as the structural parameters determined by EXAFS simulation (Table 1)
reveal that neither dissolving 1 in aqueous buffer nor oxidant exposure and water oxidation catalysis causes structural modification. The comparison with CoCat reveals that the Co–Co peak distance of 2.81 Å typical of edge-sharing octahedra in CoCat (FT peak labeled as β) is fully absent for 1, before and after catalysis of water oxidation.

Comparison of 1 and 2 illustrates the high sensitivity of the EXAFS spectra to structural changes within Co oxide cores: the two POMs only differ in the number of Co atoms interconnected by oxo-bridges and sandwiched between oxo tungstates (four Co in 1 versus three Co in 2, see Fig. S20, ESI†). Consequently the number of Co–Co vectors per X-ray absorbing Co ion is 2.5 in 1 and 1.5 in 2. The EXAFS simulations reproduce the predicted difference in the coordination number perfectly well \(N_{\text{Co-Co}}\) of 1.5 in 2 vs. 2.5 in 1, Table 1. We conclude that for CoPOM 1 even the loss of a single Co ion would be detectable by qualitative comparison of EXAFS spectra (i.e., visual comparison of Fourier-transformed spectra) and quantitative analysis (that is, determination of structural parameters by curve-fitting).

In conclusion, the EXAFS analysis corroborates the absence of hydrolytic or oxidative transformation of 1. Recently it was shown that electrocatalytic water oxidation in the presence of 1 involves its partial decomposition and release of Co\(^{2+}\) followed by deposition of a thin CoCat oxide film on the working electrode; not 1 but the amorphous Co oxide was suggested to be the WOC.\(^{11}\) Avoiding relatively harsh electrocatalytic conditions and using a chemical oxidant at neutral pH, there are no indications of formation of a catalytically active Co oxide. We cannot exclude that, e.g., 5% of the Co ions are transformed into CoCat-type oxides. If these 5% of the Co ions were responsible for water oxidation catalysis, their TOF would exceed 2 s\(^{-1}\), though, whereas the TOF for the CoCat is clearly below 0.1 s\(^{-1}\). Thus it is highly unlikely that a minority fraction of Co ions present in oxide form could be responsible for WOC. A further recent proposal has been hydrolytic fragmentation of 1 into soluble species,\(^{15}\) which then perform the catalysis. If so, these fragments reassemble to give back 1 after catalysis, according to our results or would exhibit an extreme activity.

The herein presented evidence suggests that Co-POMs, which are composed exclusively of chemical elements of relatively high abundance, can be stable under catalytic conditions and thus are indeed promising WOCs.

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Notes and references