

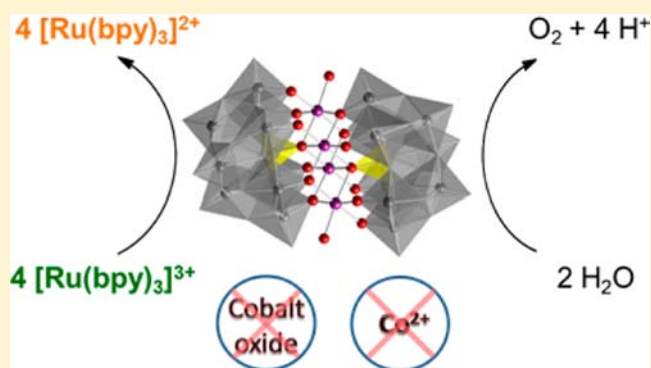
Differentiating Homogeneous and Heterogeneous Water Oxidation Catalysis: Confirmation that $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ Is a Molecular Water Oxidation Catalyst

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S Supporting Information

ABSTRACT: Distinguishing between homogeneous and heterogeneous catalysis is not straightforward. In the case of the water oxidation catalyst (WOC) $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (Co_4POM), initial reports of an efficient, molecular catalyst have been challenged by studies suggesting that formation of cobalt oxide (CoO_x) or other byproducts are responsible for the catalytic activity. Thus, we describe a series of experiments for thorough examination of active species under catalytic conditions and apply them to Co_4POM . These provide strong evidence that under the conditions initially reported for water oxidation using Co_4POM (Yin et al. *Science*, 2010, 328, 342), this POM anion functions as a molecular catalyst, not a precursor for CoO_x . Specifically, we quantify the amount of $\text{Co}^{2+}(\text{aq})$ released from Co_4POM by two methods (cathodic adsorptive stripping voltammetry and inductively coupled plasma mass spectrometry) and show that this amount of cobalt, whatever speciation state it may exist in, cannot account for the observed water oxidation. We document that catalytic O_2 evolution by Co_4POM , $\text{Co}^{2+}(\text{aq})$, and CoO_x have different dependences on buffers, pH, and WOC concentration. Extraction of Co_4POM , but not $\text{Co}^{2+}(\text{aq})$ or CoO_x into toluene from water, and other experiments further confirm that Co_4POM is the dominant WOC. Recent studies showing that Co_4POM decomposes to a CoO_x WOC under electrochemical bias (Stracke and Finke, *J. Am. Chem. Soc.*, 2011, 133, 14872), or displays an increased ability to reduce $[\text{Ru}(\text{bpy})_3]^{3+}$ upon aging (Scandola, et al., *Chem. Commun.*, 2012, 48, 8808) help complete the picture of Co_4POM behavior under various conditions but do not affect our central conclusions.



INTRODUCTION

The production of solar fuel is a consensus goal of the research community based on the projected need for enormous quantities of high density energy in the coming decades.^{1–3} Central to the production of solar fuels, either by water splitting ($\text{H}_2\text{O} + h\nu (\text{sun}) \rightarrow \text{H}_2 + 1/2 \text{O}_2$) or carbon dioxide reduction ($2 \text{CO}_2 + 4 \text{H}_2\text{O} + h\nu (\text{sun}) \rightarrow 2 \text{CH}_3\text{OH} + 3 \text{O}_2$) is the oxidation of water. This four-electron process ($2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$) continues to be viewed as a central challenge in realizing solar fuel generating prototypes (electron-donor nanostructures, photoelectrochemical cells, etc.).^{4–6} As a consequence, there continues to be exceptional research activity aimed at developing viable (fast, selective, stable) both homogeneous^{7–25} and heterogeneous^{26–41} water oxidation catalysts (WOCs).^{31,40,42–49}

Pioneering work has provided criteria for distinguishing homogeneous catalysts from heterogeneous ones, largely for reactions under reducing conditions.^{50–52} In continuation with this, we sought to develop a series of new experiments which can be used to not only differentiate a homogeneous catalyst

from a heterogeneous one under oxidizing conditions, but also distinguish particular molecular species generated in solution during turnover. Furthermore, these techniques can rule out activity from decomposition products which are known catalysts and show which species is responsible for the observed catalytic activity. These studies can be divided into two categories: (1) those quantifying the amount of catalyst decomposition during catalytic turnover or the amount of some decomposition product that could be involved in catalysis, and (2) those assessing the kinetic behavior of each catalytically competent species as a function of the reaction variables. For reactions in aqueous media, these variables include pH, buffer, and buffer concentration. The combined knowledge of the quantities and kinetic behaviors of potential catalytic species provides a complete picture of which species is responsible for observed catalytic activity, in this case, but not limited to water oxidation.

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Table 1. Experimental Conditions from Various Studies Examining Catalytic Activity and Stability of Co₄POM

SF	SSB	HG Science	HG JACS	HG This Work
Electrochemical 1.1 V vs Ag/AgCl	Nanosecond Flash Photolysis	Dark (with stoichiometric oxidant)	Photochemical 420–470 nm Xe lamp 16.8 mW	Photochemical 455 nm LED 17 mW
pH = 8.0 100 mM NaP _i 500 μM Co ₄ POM	pH = 8.0 80 mM NaP _i 50 μM Co ₄ POM 0.05 mM [Ru(bpy) ₃] ²⁺ 5.0 mM Na ₂ S ₂ O ₈	pH = 8.0 30 mM NaP _i 3.2 μM Co ₄ POM 1.5 mM [Ru(bpy) ₃] ³⁺	pH = 8.0 80 mM NaB 5 μM Co ₄ POM 1.0 mM [Ru(bpy) ₃] ²⁺ 5.0 mM Na ₂ S ₂ O ₈	pH = 8.0 80 mM NaB 2 μM Co ₄ POM 1.0 mM [Ru(bpy) ₃] ²⁺ 5.0 mM Na ₂ S ₂ O ₈
O ₂ measured TON not reported	O ₂ not measured	TON = 78.1	TON = 224	TON = 302 ± 1

One of the most promising classes of WOCs are polyoxometalates (POMs) because of their oxidative, thermal, and tendency toward kinetic hydrolytic (over pH ranges dictated by the POM metal) stability. Some of these systems are among the fastest WOCs available to date.^{53–55} Recently, several groups have reported POM WOCs based on abundant 3d elements (Co and Ni)^{56–59} in addition to earlier Ru-containing POM WOCs.^{60–64} After publication of the first precious-metal-free POM WOC, [Co₄(H₂O)₂(PW₉O₃₄)₂]^{10–} (Co₄POM) in 2010 (henceforth “HG”),^{65,66} its stability, as well as the nature of the active species, became the subject of multiple investigations under a range of experimental conditions (Table 1). The initial claim of a fast, stable, molecular WOC was first brought into question by Stracke and Finke (Stracke and Finke, *J. Am. Chem. Soc.*, **2011**, *133*, 14872, henceforth “SF”) who in electrochemical experiments demonstrated that the activity of Co₄POM could be explained by the formation of CoO_x films on the electrode surface. Another group (Scandola, Sartorel, Bonchio et al., *Chem. Commun.*, **2012**, *48*, 8808, henceforth “SSB”) studied Co₄POM by nanosecond flash photolysis experiments suggesting that the catalyst was a soluble molecular species, but that it was not Co₄POM. These three studies report on the WOC activity of Co₄POM in different systems using different techniques and draw conflicting conclusions. A follow-up paper by SF at conditions of higher potential, and lower Co₄POM concentration, could not distinguish Co₄POM from CoO_x as the WOC. Their work shows that the specific conditions of WOC matter under their electrochemical oxidation system as well as when using a chemical oxidant.⁶⁷ While Co₄POM has been well documented to be hydrolytically unstable above pH 7.5–8.0 in sodium phosphate buffer,^{68–70} its kinetic stability under water oxidation conditions remains a subject of debate. A recent review noted a general need to address in detail the fate of Co₄POM under a variety of conditions.⁷¹ Thus Co₄POM is a prime example of a system where there is need to differentiate an initial molecular catalyst from its various possible decomposition products which are also known catalysts.

RESULTS

Quantification of Active Species Leached from the Initial Molecular Catalyst. Cobalt oxides (henceforth “CoO_x”) and aqueous cobalt ions are the simplest and most likely decomposition products of Co₄POM and are known WOCs.^{29,30,72} Thus it was important to test the hypothesis that some cobalt containing species (henceforth “Co_{app}”, as defined by Finke⁷³) or cobalt oxides, in amounts that have been shown

to be present, might be able to account for the O₂ yields we observe. The results herein show that they cannot.

The first step in examining whether decomposition products of Co₄POM are able to account for the observed catalysis is quantifying the amount of decomposition and the decomposition products formed. To this end two techniques have been developed.

We conducted an analysis showing quantitatively that the maximum amount of Co_{app} present in solutions of Co₄POM and the equivalent quantity of CoO_x formed from this Co_{app} do not account for the observed catalytic water oxidation rates. Previous work⁷⁴ estimated decomposition based on the decrease in absorbance at 580 nm from a solution of Co₄POM. Due to the low molar absorptivity of Co₄POM, high concentrations (≥500 μM) are required to obtain a sufficient absorbance. However, these experimental conditions do not convincingly reflect conditions where Co₄POM was reported to be catalytically active (~5 μM; a complete listing of the vary different studies are given in Table 1). To more accurately quantify the amount of Co_{app} present in solution when Co₄POM is aged in catalytic conditions (low concentrations), cathodic adsorptive stripping voltammetry (CA_{SV}), a technique first applied to these systems by SF,⁷⁴ was used (see SI). This technique has been reported to determine the amount of Co_{app} in a high Co₄POM concentration sodium phosphate buffered (NaP_i) system,⁷⁴ as well as at 2.5 μM in the same buffer,⁶⁷ released as a function of aging time. After aging 2 μM of Co₄POM in 80 mM pH 8 borate buffer for 3 h, the concentration of Co_{app} was found to be 0.07 ± 0.01 μM. Complete results are listed in Table S1.

A second new and general method to address catalysis by soluble molecular species (POMs or otherwise) versus insoluble metal oxides or soluble hydrated metal cations as catalysts for reactions in aqueous solution has been devised and is reported here for the first time. This method is a two-step process where a soluble, anionic catalyst is separated from solution containing all species present during turnover, then the remaining cobalt containing species (Co_{app}) in solution are quantified. Here, a toluene solution of tetra-*n*-heptylammonium nitrate (THpANO₃) is used to extract Co₄POM from the aqueous layer. THpA⁺ is well-known to quantitatively extract most POMs from the aqueous phase to a second toluene phase.⁷⁵ This extraction technique was applied to the aqueous solution of Co₄POM after light-driven catalytic water oxidation and this removal of Co₄POM effectively stops catalysis decreasing catalytic water oxidation by ~98%, (experimental section in SI, Figure S1, and Figure 1, green triangles). Control

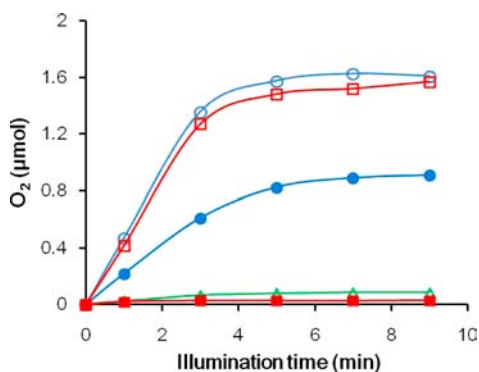


Figure 1. Kinetics of light-driven catalytic O_2 evolution from water catalyzed by Co_4POM in 0.12 M borate buffer at pH 8. Conditions: 455 nm LED light (17 mW, beam diameter ~ 0.5 cm), 5.0 mM $\text{Na}_2\text{S}_2\text{O}_8$, 1.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. Blue open circles, 2 μM Co_4POM initial run; blue solid circles, 2 μM Co_4POM second run; red solid squares, extraction of the 2 μM Co_4POM solution in borate buffer with a toluene solution of THpANO_3 , followed by addition of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and $\text{Na}_2\text{S}_2\text{O}_8$; green triangles, the aqueous catalyst solution after the first run followed by extraction using a toluene solution of THpANO_3 ; red open squares, control reaction where 2 μM Co_4POM solution in borate buffer extracted by a toluene solution of THpANO_3 , followed by addition of 2 μM Co_4POM , $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, and $\text{Na}_2\text{S}_2\text{O}_8$.

experiments show that neither the extraction method nor the presence of residual toluene or THpA^+ significantly affect catalysis by $\text{Co}^{2+}(\text{aq})$, or CoO_x (Figure S1). Catalysis of Co_4POM is also not significantly affected by residual toluene or THpA^+ (Figure 1, red open squares). Extraction of Co_4POM before catalytic reaction reduces the O_2 yield to effectively zero.

After extraction of Co_4POM from solutions aged in buffer, inductively coupled plasma mass spectrometry (ICP-MS) was performed to quantify the amount of Co_{app} .⁷⁶ Aging 2 μM of Co_4POM in 80 mM pH 8 sodium borate buffer (NaB_4) for 3 h, followed by the extraction technique, yielded a concentration of Co_{app} at $0.07 \pm 0.01 \mu\text{M}$ remaining in the reaction solution, exactly as was found by CADSV above. Complete results and the procedure are reported in the SI (Table S2).

In order to gauge the catalytic role of the quantified cobalt containing species, water oxidation was conducted either by a dark reaction where the reaction kinetics are monitored by a decrease in absorbance of the sacrificial oxidant tris-(bipyridine)ruthenium(III) perchlorate ($[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_3$), or by a photochemical method whereby O_2 is monitored by gas chromatography (GC) using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as a photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ as a sacrificial electron acceptor with visible light. Both methods were previously reported^{65,77} and are fully elaborated in the SI. To show that $\sim 0.07 \mu\text{M}$ Co_{app} could not account for the observed catalytic activity, several control experiments were conducted. Addition of 0.10 μM $\text{Co}(\text{NO}_3)_2$ (approximating Co_{app} as in SF, more than double the amount) to a buffered solution of 2 μM Co_4POM (more than double the amount of Co_{app}) produces less than 5% increase in the overall rate of $[\text{Ru}(\text{bpy})_3]^{3+}$ reduction (dark reaction): compare the blue dashed curve in Figure 2 and the red solid curve which has no added $\text{Co}(\text{NO}_3)_2$. Similar results were obtained under photochemical conditions, where water oxidation by 0.15 μM $\text{Co}(\text{NO}_3)_2$, twice the amount found to be present by both techniques, gives a negligible O_2 yield and addition of 0.15 μM $\text{Co}(\text{NO}_3)_2$ to 2 μM Co_4POM shows no effect on the kinetics or yield of oxygen evolution (Figure 3).

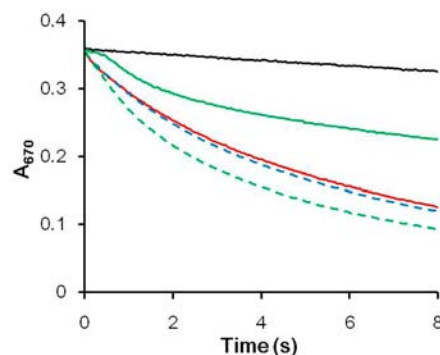


Figure 2. Kinetics of $[\text{Ru}(\text{bpy})_3]^{3+}$ reduction in 80 mM sodium borate buffer at pH 8.0 and 25 $^\circ\text{C}$, measured as the decrease in absorbance at 670 nm: No catalyst (black), 2.0 μM Co_4POM (red), 0.5 μM $\text{Co}(\text{NO}_3)_2$ (green), 2.0 μM Co_4POM in the presence of 0.10 μM $\text{Co}(\text{NO}_3)_2$ (blue dashed), 2.0 μM Co_4POM in the presence of 0.50 μM $\text{Co}(\text{NO}_3)_2$ (green dashed).

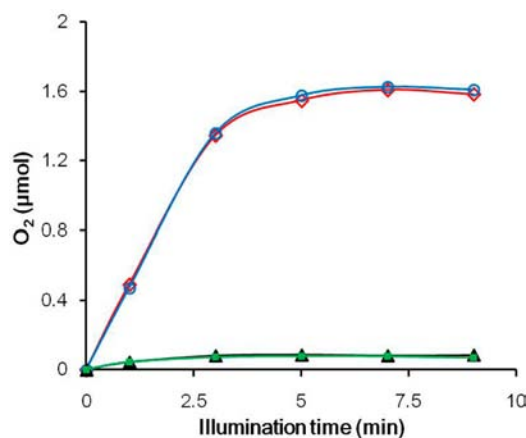


Figure 3. Kinetics of light-driven catalytic O_2 evolution from water catalyzed by Co_4POM and $\text{Co}(\text{NO}_3)_2$. Conditions: 455 nm LED light (17 mW, beam diameter ~ 0.5 cm), 5.0 mM $\text{Na}_2\text{S}_2\text{O}_8$, 1.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 2.0 μM Co_4POM (blue), 2.0 μM Co_4POM + 0.15 μM $\text{Co}(\text{NO}_3)_2$ (red), 0.15 μM $\text{Co}(\text{NO}_3)_2$ (black) all in 120 mM borate buffer, and 0.15 μM $\text{Co}(\text{NO}_3)_2$ (green) in 80 mM borate buffer. Initial pH = 8.0, total volume 2.0 mL.

Furthermore, increasing the concentration of the added $\text{Co}(\text{NO}_3)_2$ to 0.5 μM (green dashed curve) increases the overall rate of the reaction by $\sim 15\%$. Thus, the concentration of $\text{Co}(\text{NO}_3)_2$ can be made so great that it effects the catalysis, but even at this elevated level, seven times higher than what is found to exist, the majority of catalysis still derives from Co_4POM .

Behavioral Distinction between a Molecular Catalyst and Decomposition Product Catalysts. Examining behavioral differences between each catalytically competent species under specific conditions provides further evidence to differentiate Co_4POM from Co_{app} , CoO_x , or other possible decomposition products. By analyzing differences in the kinetics of the dark reaction or the yields of the photochemical reaction, when changing only a single variable of the conditions, we can determine the identity of the catalytically active species. Several additional control experiments to compare the catalytic behavior of freshly prepared and aged solutions of Co_4POM and $\text{Co}(\text{NO}_3)_2$ were performed. First, it has been established that these two species have quite different time profiles for O_2

Table 2. Light-Driven Water Oxidation Activity of Co₄POM, Co²⁺(aq) and Amorphous CoO_x as a Function of pH, Buffer, and Buffer Concentration^a

entry	complex	complex concentration (μM)	pH	buffer (mM)	TON	O ₂ yield (%)
1	Co ₄ POM	2	9	80 NaB _i	410 ± 4	32.8 ± 0.3
2	Co ₄ POM	2	8	80 NaB _i	302 ± 1	24.2 ± 0.1
3	Co ₄ POM (aged 3 h) ^b	2	8	80 NaB _i	290 ± 4	23.2 ± 0.2
4	Co ₄ POM	2	8	120 NaB _i	399 ± 4	31.9 ± 0.4
5 ^c	Co ₄ POM	2	7.6	120 NaB _i	226 ± 4	18 ± 0.3
6	Co ₄ POM	2	8	80 NaP _i	125 ± 1	9.9 ± 0.1
7	Co ₄ POM (aged 3 h) ^b	2	8	80 NaP _i	130 ± 2	10.4 ± 0.2
8 ^d	Co ₄ POM	50	8	80 NaP _i	0.35 ± 0.11	0.71 ± 0.22
9 ^d	Co ₄ POM (aged 3 h) ^b	50	8	80 NaP _i	0.38 ± 0.02	0.75 ± 0.04
10	Co ₄ POM	2	8	100 NaP _i	44 ± 3	3.6 ± 0.2
11	Co ₄ POM	2	7.2	100 NaP _i	4.3 ± 0.1	0.34 ± 0.01
12	Co ₄ POM	2	6.2	100 NaP _i	2.8 ± 0.2	0.23 ± 0.02
13	Co(NO ₃) ₂	2	9	80 NaB _i	596 ± 8	47.7 ± 0.6
14	Co(NO ₃) ₂	2	8	80 NaB _i	509 ± 5	40.8 ± 0.5
15	Co(NO ₃) ₂	2	8	120 NaB _i	423 ± 11	33.9 ± 0.9
16 ^c	Co(NO ₃) ₂	2	7.6	120 NaB _i	100 ± 1	8.1 ± 0.1
17	Co(NO ₃) ₂	8	8	120 NaB _i	600 ± 11	48 ± 1
18 ^c	Co(NO ₃) ₂	8	7.6	120 NaB _i	160 ± 11	12.8 ± 1.1
19	Co(NO ₃) ₂	2	8	80 NaP _i	7.7 ± 0.2	0.61 ± 0.01
20	Co(NO ₃) ₂	2	8	100 NaP _i	6.4 ± 0.4	0.51 ± 0.04
21	Co(NO ₃) ₂	2	7.2	100 NaP _i	3.4 ± 0.1	0.27 ± 0.01
22	Co(NO ₃) ₂	2	6.2	100 NaP _i	0.5 ± 0.04	0.04 ± 0.01
23	CoO _x ^e	8 ^f	9	80 NaB _i	40 ± 3	3.2 ± 0.1
24	CoO _x ^e	8 ^f	8	80 NaB _i	144 ± 2	11.5 ± 0.1
25	CoO _x ^e	8 ^f	8	100 NaP _i	2.6 ± 0.6	0.19 ± 0.02
26	CoO _x ^e	8 ^f	7.2	100 NaP _i	0.78 ± 0.08	0.07 ± 0.01
27	CoO _x ^e	8 ^f	6.2	100 NaP _i	0.25 ± 0.01	0.02 ± 0.001

^aConditions unless otherwise noted: 1 mM Ru(bpy)₃²⁺, 5 mM Na₂S₂O₈, 455 nm LED light (17 mW, beam diameter ~0.5 cm), 2 mL total solution volume, all stock solutions prepared in DI water. ^bAged in the corresponding buffer solution. ^cCatalyst reusability test: 2.38 mg Na₂S₂O₈ was added for the second run. ^dSSB conditions (50 μM [Ru(bpy)₃]Cl₂ and 50 μM Co₄POM). ^eCoO_x was prepared by electrochemical deposition as described in the SI. ^fNot soluble, the suspension obtained after 10 min of sonication, 8 μM equivalents of Co²⁺ was used for catalytic reaction. The errors are calculated as the standard deviation from multiple experiments.

formation and [Ru(bpy)₃]³⁺ reduction. Similar findings were reported for the kinetics of Co²⁺(aq) as a WOC.⁷⁸ Second, it was confirmed that water oxidation by Co(NO₃)₂ exhibits an induction period, as observed by a characteristic sigmoidal-shape (green curve, Figure 2), indicating that the initial Co(NO₃)₂ is a precursor of a catalytically active species. In contrast Co₄POM shows no induction period (red solid and blue dashed curve Figures 2, S2, and S3).

Third, the pH dependence of Co₄POM and other species were compared. In general, different pH dependencies of O₂ yields are consistent with the presence of different catalytically active species during turnover. Therefore, the response of a catalytic system to pH change can and should be used to probe the nature of the catalyst in aqueous media. Here, the pH dependence of O₂ yields for Co₄POM, Co²⁺(aq), and CoO_x catalysts were compared. As seen in Table 2, the activity of Co₄POM strongly depends on pH: lines 10 and 11 show that when the pH is increased from 7.2 to 8.0, with all other conditions held constant, the yield increases by over an order of magnitude. In contrast, the O₂ yield from both Co(NO₃)₂ and CoO_x is weakly dependent on pH: under the same conditions the yields increase only about 2- and 3-fold, respectively. The different dependences on pH provide further evidence that the catalytic activity observed from Co₄POM is not due to either Co²⁺(aq) or CoO_x.

Fourth, the behavioral dependence in different buffers was studied. The overall rate of Co₄POM loss is faster in phosphate buffer than in borate as seen in high concentrations quantified by UV-vis (Figure 4). The decrease in absorbance is also slower in the presence of CAPS buffer, where Co₄POM shows only slight decomposition even at pH 10.⁶⁹ The amount of Co_{app} quantified by ICP-MS and CAdSV at lower catalytic

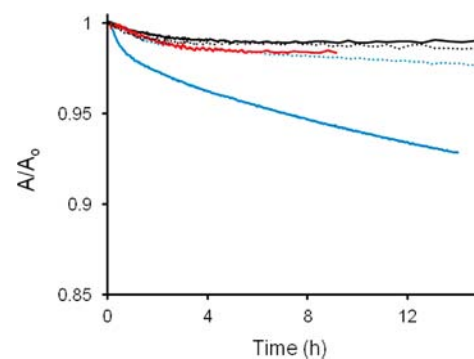


Figure 4. Normalized peak absorbance at 580 nm of Co₄POM as a function of time. Conditions: 0.5 mM Co₄POM in 0.03 and 0.1 M NaP_i (blue dotted and solid lines, respectively), in 0.1 M sodium borate buffer 0.45 and 0.8 mM Co₄POM at pH 8 and 9 (black solid and dotted lines, respectively); 1.15 mM Co₄POM in 0.05 M CAPS buffer at pH 10 (red); 25 °C.

conditions corroborates this relationship (over 6-fold greater $[\text{Co}_{\text{app}}]$ for both techniques in NaP_i over NaB_i , Tables S1 and S2). The effect of aging Co_4POM solutions in buffer on the catalytic activity under HG conditions was also examined. Data show that the kinetic curves for reduction of 0.83 mM $[\text{Ru}(\text{bpy})_3]^{3+}$ by 2 μM Co_4POM are nearly identical for both freshly prepared and 1.5 h-aged solutions in 0.1 M phosphate or borate buffer at pH 8.0 suggesting that any Co_{app} has little effect on catalytic activity (Figure S4). The photochemical reactions give similar results where the catalytic solutions in both NaB_i and NaP_i show only a minimal decrease in turnover number (TON) after several hours aging (entries 2 and 3, 6, and 7, respectively).

In addition to the dependence on the nature of the buffer, the concentration of the buffer was also investigated as a fifth behavioral test. If the concentration of NaP_i is that in HG, the decrease in absorbance for Co_4POM is $\sim 2.5\%$ compared to $\sim 7.5\%$ when the concentration of NaP_i is increased to that used in SF (after 16 h of aging). A similar trend is observed in catalytic water oxidation activities; when the concentration of NaP_i is increased from 80 mM to 100 mM, the TON decreases from 125 ± 1 to 44 ± 3 (entries 6 and 10, Table 2). Importantly, Co_4POM and $\text{Co}^{2+}(\text{aq})$ show the opposite buffer concentration dependence when NaB_i is used. When the concentration of NaB_i is increased from 80 mM to 120 mM with all other conditions held constant, the TON increases from 302 ± 1 to 399 ± 4 for Co_4POM (entries 2 and 4, Table 2), and decreases from 509 ± 5 to 423 ± 11 for $\text{Co}^{2+}(\text{aq})$ (entries 14 and 15, Table 2). Thus, the nature of buffer, its concentration, and pH of the solution are all critical parameters in the decomposition of Co_4POM and, in general, POM–metal oxide equilibria.

As a sixth behavioral metric, when the photochemical reactions were completed, a second identical molar amount of $\text{Na}_2\text{S}_2\text{O}_8$ was added. This provides a test of the reusability of the entire catalytic system (buffer, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, etc.) and not solely the catalyst. The addition of a second aliquot of $\text{Na}_2\text{S}_2\text{O}_8$ to the Co_4POM solution results in a $43.6 \pm 2\%$ drop in O_2 yield relative to the first run (entries 4–5 in Table 2 and Figure S5). The lower O_2 yield in the second runs results primarily from partial decomposition of the $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ photosensitizer (Figure S6), and a slight decrease of pH from the water oxidation reaction itself. In contrast, $\text{Co}(\text{NO}_3)_2$ shows a dramatically decreased O_2 yield in the second run ($76.1 \pm 0.9\%$ drop relative to the first run, entries 15–16 in Table 2 and Figure S5). Although 8 μM $\text{Co}(\text{NO}_3)_2$ (same Co equivalents as that of 2 μM Co_4POM) gives a higher O_2 yield in the first run, the second run produces far less O_2 than for the Co_4POM -catalyzed reactions ($75 \pm 3\%$ drop relative to the first run, entries 17–18 in Table 2 and Figure S5).

A seventh probe addresses particle formation during water oxidation catalyzed by Co_4POM and Co_{app} in separate reactions. Detecting the formation of nanoparticles has been well established as a crucial component in distinguishing homogeneous species from heterogeneous ones.⁷⁹ Dynamic light scattering (DLS) studies of the post-water-oxidation catalytic solutions confirm that no CoO_x particles result from water oxidation catalyzed by Co_4POM above the limit of detection (LoD), while those catalyzed by $\text{Co}^{2+}(\text{aq})$ do produce particles which are presumably CoO_x (Figure S7). This finding is consistent with the observation of others,⁸⁰ indicating that CoO_x is not the actual catalyst under HG turnover conditions.

In summary, these collective experiments establish that when both Co_{app} and Co_4POM are present in solution, the vast majority of catalytic activity, assessed either by $[\text{Ru}(\text{bpy})_3]^{3+}$ reduction or by photochemical O_2 production, is accounted for by Co_4POM . Furthermore, each catalyst exhibits unique kinetic behavior as a function of pH, buffer identity, and buffer concentration. These experiments should be helpful in many other investigations of POM catalysis, particularly in water, to identify the active catalyst. These include but are not limited to other WOC systems.

DISCUSSION

Equilibrium Aspects of POM Systems. While molecular WOCs have been and are now typically coordination complexes or organometallic compounds with one or more transition metals, many POM WOCs have been reported recently.⁵⁹ POMs, metal oxides, and soluble hydrated metal cations constitute equilibrium systems; under some conditions (pH, ionic strength, buffer, and buffer concentration) the metal oxides are more stable, and the POMs convert to metal oxides; under other conditions, the POMs are more stable and metal oxides and hydroxides convert to the POMs.⁸¹ There are examples over the full pH range (0–14) where metal oxides convert to POMs and thus the former are less stable thermodynamically than the latter: at pH 14, the oxide Nb_2O_5 converts fully to the POM, $[\text{Nb}_6\text{O}_{19}]^{8-}$,⁸² and at pH 0, many metal oxides will dissolve and form POMs.^{83,84} Thus a POM system is ideal for the rigorous analysis presented in this paper as it is likely that species other than the initial POM will exist in solution. It has been well established that Co_4POM is hydrolytically unstable above pH 7.5–8.0 in NaP_i buffer.^{68–70} As a consequence we conducted seven control experiments in our original study (HG Science) demonstrating that the catalytic water oxidation derives from Co_4POM and not from $\text{Co}^{2+}(\text{aq})$ or metal oxide CoO_x . The present work further affirms that despite some decomposition, Co_4POM is absolutely the dominant species in solution under HG conditions, including the time scale of the reactions.⁶⁵ Experiments reproduced by others⁸⁵ involve the chelation of $\text{Co}^{2+}(\text{aq})$ leading to quantitative formation of $[\text{Co}(\text{bpy})_3]^{2+}$, where bpy = 2,2'-bipyridine ($\log\beta_3 = 16.02$)⁸⁶ and complete suppression of CoO_x formation provided strong evidence that $\text{Co}^{2+}(\text{aq})$ is not the WOC under the HG conditions.⁶⁵

Analysis of Previous Co_4POM Studies. A series of studies examining the same catalyst, Co_4POM , arrive at apparently different conclusions. The first of these studies by Hill reported homogeneous water oxidation activity of the compound in both dark⁶⁵ and light-driven⁷⁷ systems, and provided seven lines of evidence for a soluble catalyst under their conditions (these and all relevant conditions of the various studies are listed in Table 1). Since then, multiple other groups have analyzed these works,^{48,56,58,87–95} reported additional stability studies,^{69,70} or used Co_4POM for water oxidation.^{85,89} Thus, further analysis of this catalyst and the various systems it has been reported in was required.

A subsequent publication, SF, demonstrated convincingly that Co_4POM , in an electrochemical system, decomposes into a heterogeneous Co-containing film responsible for the water oxidation activity.⁷⁴ However, these were electrocatalytic, rather than homogeneous chemically driven experiments. This difference, coupled with a 156-fold higher Co_4POM concentration and longer aging times, are most likely key factors that lead to formation of CoO_x in catalytically significant quantities.

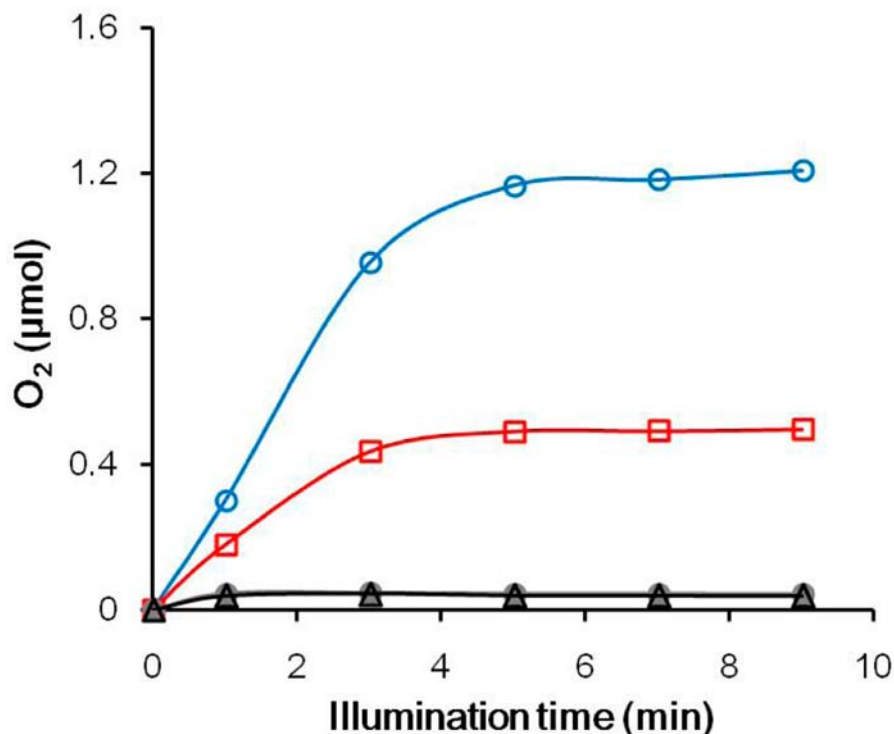


Figure 5. Kinetics of light-driven catalytic O₂ evolution as function of buffer and reactant concentration ratio. Conditions: 455 nm LED light (17 mW, beam diameter ~0.5 cm), and 5.0 mM Na₂S₂O₈. With 1.0 mM [Ru(bpy)₃]Cl₂, 2.0 μM Co₄POM in 80 mM NaB₄ (blue) or 80 mM NaP_i (red), and 50 μM [Ru(bpy)₃]Cl₂, 50 μM Co₄POM, 80 mM NaP_i fresh solution (black) and aged for 3 h (gray) all pH = 8.0. Note: black and gray curves are obtained under the SSB conditions.

Additionally, it was observed that Co₄POM aged in sodium phosphate buffer decomposes to release Co²⁺(aq) in amounts that quantitatively account for all of the observed water oxidation activity in their study within the standard error. As stated in SF, the conditions used in the SF and HG studies differ and conclusions from one work might not apply to the other.⁷⁴

While all the catalytic water oxidation studies by Co₄POM and other multicobalt POM WOCs^{85,96} use NaP_i or NaB₄ buffers, the most detailed thermodynamic hydrolytic (speciation) studies use either no buffer⁷⁰ or HEPES, PIPES, and CAPS buffers.⁶⁹ Potential confusion in catalytic water oxidation by POMs very often arises from neglecting the specific effects of the buffer molecule(s) on both POM speciation in water and POM-catalyzed water oxidation. Both the buffer and the buffer concentration must be kept relatively constant in POM studies if meaningful comparisons are to be made, particularly near the pH where the POM becomes hydrolytically unstable with respect to metal oxide. As discussed above, the equilibria involving a POM, soluble hydrated metal cations, and metal oxides is dependent on concentrations of all soluble species present in the equilibrium, and these are frequently perturbed by the buffer.⁶⁹ The SF study brought this home in the case of Co₄POM, by showing that at a concentration of 500 μM, the absorbance at 580 nm (λ_{\max}) in pH 8.0 NaP_i decreases by $4.3 \pm 0.6\%$ over 3 h. In NaB₄, we observe a decrease of 1.7% over 16 h in agreement with SF (Figure 4), and as described above, we also find that in both buffers the concentration of Co_{app} under photocatalytic conditions is extremely small. Thus, while it has been shown that Co₄POM releases some Co_{app}/CoO_x, these submicromolar quantities of Co species formed by Co₄POM equilibria cannot account for the O₂ yields observed.

A third group, SSB, studied this system by nanosecond flash photolysis and concluded that Co²⁺(aq) was not involved in the catalysis either as a catalyst or as a precursor to CoO_x. These nanosecond flash photolysis experiments dictate that quite different experimental conditions ([Ru(bpy)₃]²⁺:Co₄POM = 1:1^{80,97}) than those of HG ([Ru(bpy)₃]²⁺:Co₄POM = 470:1⁶⁵ or 200:1⁷⁷) are used. Under SSB conditions, it was reported that scavenging of the photogenerated [Ru(bpy)₃]³⁺ (or hole scavenging) by Co₄POM in NaP_i buffer increases with aging time (rapidly in the first 1–8 min and continuing to 90 min) of Co₄POM solutions. From this experiment it was concluded that Co₄POM is not the true WOC and that no CoO_x forms under these water oxidation conditions; therefore, another decomposition product of Co₄POM must be the active catalyst. Certainly it appears that a new species must form, but our stopped flow data show that there is no significant change in the UV–vis spectra of Co₄POM in NaP_i buffer from 2 s to 8 min (Figure S8). Thus, the effect of Co₄POM aging seen by SSB is too fast to be the process observed in this work or the work of SF. Additionally, almost no effect of aging Co₄POM in NaB₄ buffer was observed up to 22 h in SSB.⁸⁰ If the hypothesis in SSB (i.e., some Co₄POM decomposition product and not Co₄POM itself is the actual WOC) is correct, then one should see higher O₂ yields in NaP_i buffer than in NaB₄ buffer, unless the decomposition products exhibit drastically different activity in the two buffers. However, the exact opposite trend is observed experimentally: water oxidation activity in the presence of 2 μM Co₄POM is 3-fold higher in NaB₄ buffer than that in NaP_i buffer (Figure 3 and entries 2–3, 6–7 in Table 2).

This study by SSB did not actually involve measuring water oxidation (O₂ evolution). New experimental evidence in this

work comparing O₂ formation under SSB and HG conditions shows that there is no effect within experimental error of Co₄POM solution aging on catalytic water oxidation activity (entries 6–9 in Table 2, black and gray curves in Figure 5). As noted above, the possible decomposition products proposed by SSB⁹⁸ could not account for observed catalytic activity in the amounts they are produced. Interestingly, we find that the O₂ yield under SSB experimental conditions is negligible with a ~96% decrease in O₂ yield from HG to SSB conditions, and is independent of aging time (entries 2, 8–9 in Table 2 and Figure 5). Thus, the conditions required for nanosecond flash photolysis cannot accurately probe those required for successful catalytic water oxidation. As a possible explanation, we reproducibly see an increase in carbon monoxide from *bpy* ligand oxidation under SSB conditions by gas chromatography, indicating that the bleach recovery observed by SSB is not solely from the hole-scavenging process, i.e., oxidation of Co₄POM (left panel in Figure S6). The UV–vis spectra show that the photosensitizer, [Ru(*bpy*)₃]²⁺, has been almost completely degraded after 11 min of irradiation (right panel in Figure S6).

It was also reported that [Ru(*bpy*)₃]³⁺ does not have sufficient potential to oxidize Co₄POM, or to promote water oxidation catalyzed by Co₄POM; thus Co₄POM itself could not be the active catalyst. Electrochemical studies in SSB show an increase in anodic current at ca. 1.3 V (vs Ag/AgCl) with aging time, data similar to that of SF and their later work.⁶⁷ However, the electrochemical work of SF and HG makes a strong case that the catalytic current observed at ca. 1.1 V results from CoO_x films, not from Co₄POM. Recently, SF also explored the electrochemical activity of 2.5 μM Co₄POM at 1.4 V but concluded that the observed O₂ evolution could not be distinguished as originating from Co₄POM or decomposition products.⁶⁷ Compounding the difficulty in electrochemical studies of Co₄POM, as shown by HG, SF, and others⁹⁹ is that the cobalt-based redox processes in molecular Co₄POM are voltammetrically silent in aqueous media.¹⁰⁰ As such, the driving forces for redox processes involving [Ru(*bpy*)₃]³⁺ and other soluble species in Co₄POM-catalyzed water oxidation studies conditions are not accessible by voltammetry and remain unknown.

CONCLUSIONS

It is frequently challenging to determine whether a given complex or material acts as a heterogeneous or homogeneous catalyst, particularly under oxidizing conditions where POMs or metal oxides are frequently the thermodynamic products. The situation is further complicated when possible catalyst decomposition products are soluble species and known catalysts. Pinpointing all species that may result due to dissociation or other decomposition of a dissolved WOC can be problematical. Based on conflicting reports in the literature, and the nature of POM systems, the WOC Co₄POM was chosen as an ideal system for rigorous study using new techniques to determine the nature of the catalytically active species, and to quantify decomposition products. Supplementing the techniques reported in the initial HG studies, several additional experiments are reported here that distinguish homogeneous WOCs, from their corresponding WOC hydrolysis products (Co²⁺(aq) and CoO_x in this case). Some of these experiments are of general use in distinguishing these three types of WOCs. A new procedure entails extracting the catalyst from the aqueous phase where water oxidation takes

place with a hydrophobic organic solvent containing a hydrophobic quaternary ammonium cation (tetra-*n*-heptylammonium nitrate, “THpA”, in toluene). POMs are extracted quantitatively from the water into toluene, whereas hydrated metal cations and metal oxides are not extracted at all. This procedure clearly distinguishes the initial catalyst from its possible hydrolysis products.

The amount of Co_{app} present in a range of experiments involving Co₄POM was quantified at micromolar concentrations using two complementary techniques, cathodic adsorptive stripping voltammetry (CA_{SV}) and THpA⁺/toluene extraction followed by ICP-MS. Both techniques found the amount of Co_{app} to be 0.07 ± 0.01 μM under catalytic conditions with 2 μM Co₄POM. Control experiments show that this amount of Co_{app}, approximated by Co(NO₃)₂, results in a negligible increase either in catalytic reduction of [Ru(*bpy*)₃]³⁺ (dark reactions) or O₂ production (light-driven reactions). Thus the amount of Co_{app} or CoO_x formed from Co₄POM cannot account for the observed O₂ yields.

While the POM-metal oxide equilibrium can lie on the side of POM or the metal oxide, for all the studies of Co₄POM as a WOC thus far (basic buffered aqueous solutions), this POM is thermodynamically unstable toward hydrolysis. As a consequence, we have systematically examined the kinetic stability (specifically Co²⁺(aq) loss from Co₄POM and CoO_x particle formation) as a function of time and the four main variables that also impact thermodynamic stability (pH, ionic strength, buffer, and buffer concentration). In addition, the WOC activity was assessed by altering the above four variables over a wide range, including the experimental conditions in HG, SF, and SSB. These collective studies establish the crucial role of these four variables in POM stability and reactivity. More importantly, the nature of the oxidation, a soluble oxidant versus applied potential (electrochemical), is paramount in addressing stability. A central corollary here is that catalytic studies of molecular species, especially POM WOCs, under one set of experimental conditions should be compared only with extreme caution, if at all, to those under other conditions.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, dioxygen measurements, stopped-flow kinetics, details of experimental fittings, dynamic light scattering data, gas chromatograms, and calibration curves for cathodic adsorptive stripping voltammetry. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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ABBREVIATIONS

WOC, water oxidation catalyst; Co_4POM , $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$; NaP_i , sodium phosphate buffer; NaB_i , sodium borate buffer; POM, polyoxometalate; CoO_x , cobalt oxide; Co_{app} , Co^{2+} , a Co(II)-POM fragment, or conceivably some other Co(II)-containing species; HG, Hill group work; SSB, Scandola, Sartorel, Bonchio, et al. work; SF, Stracke and Finke work; TON, turnover number; GC, gas chromatography; ICP-MS, inductively coupled plasma mass spectrometry; CAdSV, cathodic adsorptive stripping voltammetry; DLS, dynamic light scattering; LoD, limit of detection; THpANO_3 , tetra-*n*-heptylammonium nitrate; HEPES, 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid; PIPES, piperazine-*N,N'*-bis(2-ethanesulfonic acid) and; CAPS, *N*-cyclohexyl-3-aminopropanesulfonic acid

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