Water Oxidation Catalyzed by Cobalt(II) Adsorbed on Silica Nanoparticles

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Experimental Procedures

The catalysts were prepared by pH-jump flow mixing solutions of colloidal silica (SnowTex ST-40, Nissan Chemicals Inc.) and $CoSO_4$. The silica stock contained nanoparticles narrowly distributed around 10 nm, which corresponds to a specific surface of 270 m^2/g. The particles are stabilized by the negative charges of ~260 $Si-O^-$ surface groups per particle with Na^+ as the counterion. A Y-mixer and 20 mL/s flow rate were employed to provide uniform conditions for Co hydrolysis and adsorption on silica.

The Co(II) adsorption was investigated by pressure-assisted ultrafiltration through a 10 kDa cut-off polyethersulfone Omega membrane (PALL Corp.) that is impermeable to silica nanoparticles (Table S1). The concentration of dissolved Co species in equilibrium with adsorbed Co was determined by analysis of filtrate with atomic absorption spectroscopy. To avoid interference with the adsorption equilibrium the filtrate to retentate volume ratio was kept below 0.2.

Oxygen yields in thermal water oxidation by $Ru(bpy)_3^{3+}$ were measured using a home-made, robotic syringe flow mixing system enclosed in a nitrogen-filled box to ensure anaerobic conditions. Two argon purged solutions were flow mixed into a head-space-free flow cell equipped with a Clark-type, polarographic, calibrated oxygen probe and a magnetic stirrer. One solution contained $Ru(bpy)_3^{3+}$ stabilized against self-decomposition by adding 5 mM H_2SO_4 and the other solution contained the $SiO_2/Co(OH)_2$ catalyst, borate, and NaOH. Oxygen yields in the $Ru(bpy)_3^{2+}$/persulfate photochemical system were measured in a similar way, except Ar-purged $Ru(bpy)_3^{2+}$ in water and $Na_2S_2O_8$ in borate were flow mixed into an a head-space-free optical quartz cell using a positive inert gas pressure. The cell was equipped with a magnetic stirrer and a Clark-type oxygen probe shielded from the direct laser light exposure.

Electron microscopy was performed with JEOL2100F high resolution microscope, operating at 200 kV. After dilution with water to a proper concentration of 10-15 mM in [SiO2], a small sample drop was placed atop an ultrathin carbon film on holey carbon support film covering a 400 mesh copper grid (Ted Pella Inc. product #01824), gently blotted, and dried under cover in air.
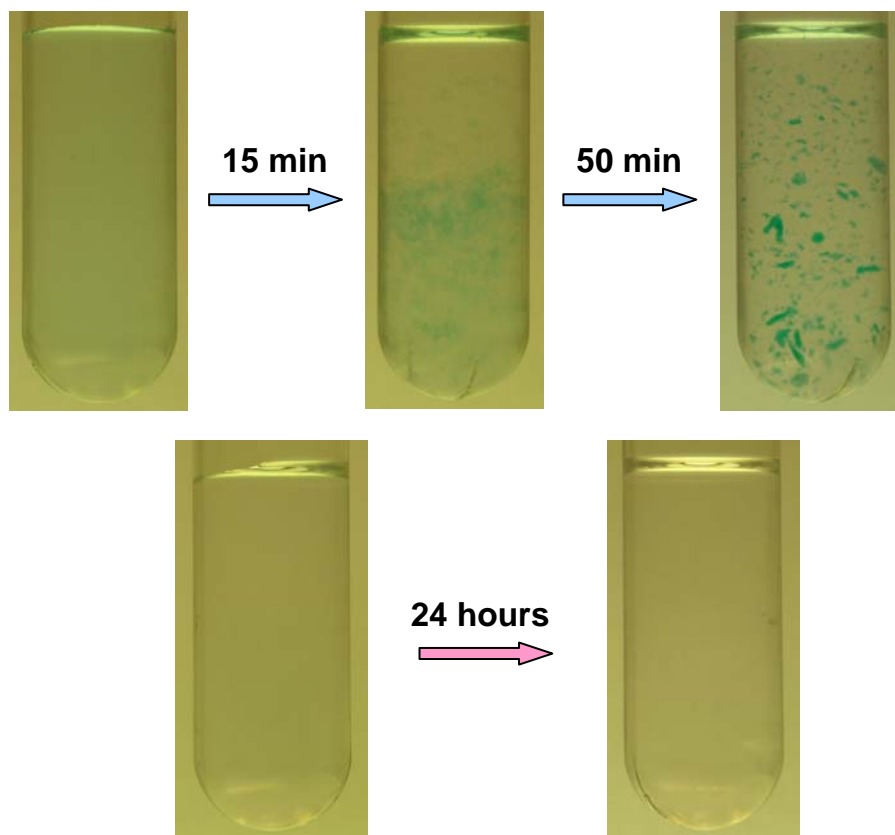
Figure S1. Temporal changes upon flow mixing solutions of CoSO$_4$ and borate buffer with and without silica. Upper row: without silica at pH 9.1. Formation of precipitating Co(OH)$_2$ is apparent (the sample was shaken at 50 min to stir up the precipitated blue Co(OH)$_2$). Lower row: with 89 mM SiO$_2$ at pH 9.3. No increased scatter or precipitation is observed in 24 hours and during subsequent storage for over two months. Both solutions contain 0.72 mM Co(II) and 10 mM borate. The solubility limits for Co(II) at pH 9.1 and 9.3 are 0.06 and 0.03 mM, respectively.

Table S1: Co Recovery Measured by Atomic Absorption Spectroscopy after Filtering through a 0.22 μm Filter at pH 9.1 – 9.7 (10 mM borate).[1]

| Added [Co], mM	Added 90 mM SiO$_2$	Co recovery in filtrate,[2] %
0.07	No	0.3
0.07	Yes	95
0.7	No	0.7
0.7	Yes	94
1.4	No	0.2
1.4	Yes	98
2.4	No	0.2
2.4	Yes	98

[1]All samples were prepared by flow mixing solutions of CoSO$_4$ in water and buffer with or without silica and allowed to equilibrate for 20 hours before filtering. [2] Estimated uncertainties are ±10% of the printed values.

Table S2: Ultrafiltration through a 10 kDa Cut-off Membrane and Atomic Absorption Spectroscopy Analyses of ST-40 Colloidal Silica.

Sample	Silicon, %	Sodium, %
Before filtering[1]	100	100
Retentate[2]	100 ± 5	102 ± 5
Filtrate[2]	0.3 ± 0.1	14 ± 5

[1] A 25 mL sample was prepared by a 5-fold dilution with water of ST-40 stock that contained [Si] = 8.86 M, [Na] = 0.21 M at pH 10.5.

[2] Volumes: 23 and 2 mL for retentate and filtrate, respectively. Although Na^+ can readily permeate the membrane, most of sodium is retained for reasons of electroneutrality.
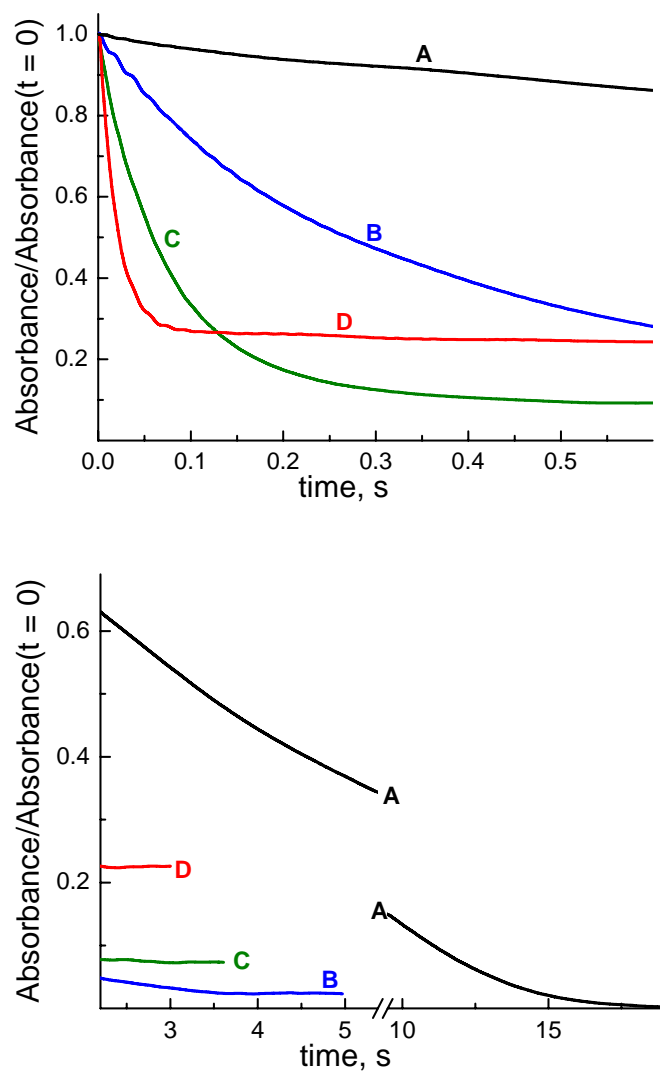
Figure S2. Stopped flow kinetic traces of $Ru(bpy)_3^{3+}$ decay in 10 mM borate at pH 9.4 recorded at 675 nm without added catalyst (curve A) and in the presence of the $Co(OH)_2/SiO_2$ catalyst: Co(II) = 0.72, 3.6, and 7.2 μM (curves B, C, and D, respectively). Top panel: at short time. Bottom panel: at longer time up to complete conversion of $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$; note the time axis break and residual absorption in B, C, and D. Initial concentrations of $Ru(bpy)_3^{3+}$ upon mixing were in the 0.17 − 0.22 mM range, and the [Co(II)]/[SiO_2] ratio was kept constant at 8×10^{-3}. Control experiments have shown that $Ru(bpy)_3^{3+}$ decay is not accelerated by the Co-free silica particles.

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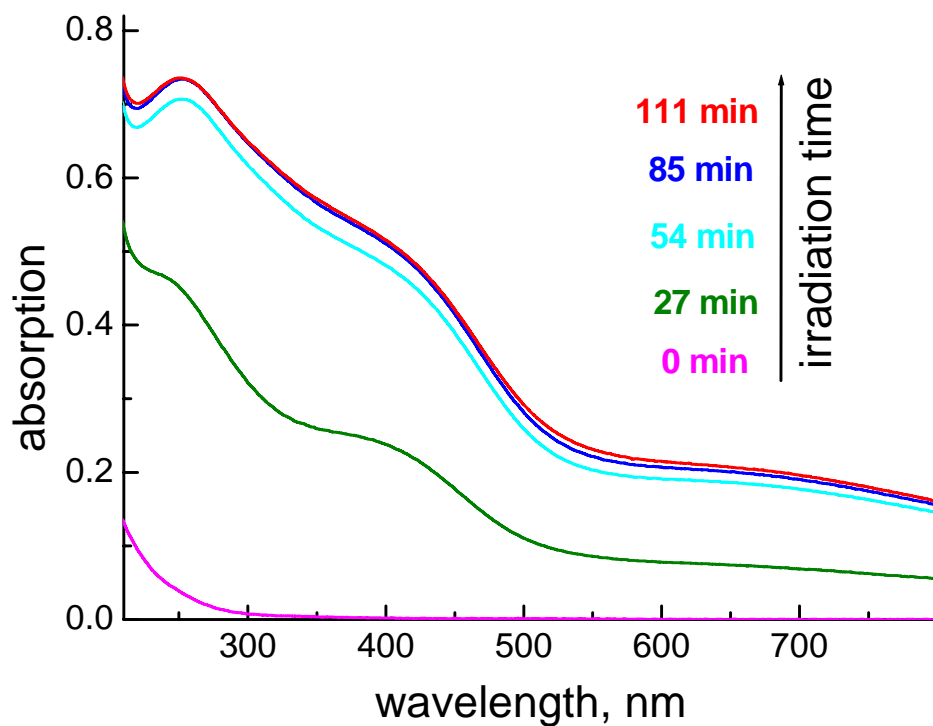
Figure S3. Temporal changes upon γ-radiation of the $Co(OH)_2/SiO_2$ catalyst in a cobalt-60 source at a 143 krad/hour dose rate for the shown periods of time. Conditions: 73 μM Co(II), 9 mM SiO_2 in an N_2O-saturated, 6 mM borate, pH 8.8 solution. Under these conditions, the OH radical constitutes about 90% of the free radicals produced by radiation; the balance is the H atom. As Co(II) is the only species present that is reactive toward OH, the spectral changes are interpreted as the conversion of Co(II) to Co(III): $Co(OH)_2 + OH \rightarrow Co(OH)_3$. From these spectra, $\varepsilon_{675} = 2.7 \times 10^3$ M^{-1} cm^{-1} for Co(III) is obtained.