Supporting Information For:

Water Oxidation by Cobalt Centers on Various Oxide Surfaces: The Effects of Oxide Surface Acidity and Oxygen Atom Affinity on Catalysis

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Experimental

General. All manipulations were conducted under an inert nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox, unless otherwise stated. Chemicals were purchased from Aldrich and used as received. Dry, oxygen-free solvents were used throughout. The complex $Co[N(SiMe_3)_2]_2^1$, mesoporous SBA-15², and mesoporous AlPO³ were synthesized as reported in the literature. Porous TiO₂, MgO, (Aldrich) and Y-Zeolite (Zeolyst) were purchased and used without further purification. Carbon, hydrogen, and nitrogen elemental analyses were performed at the College of Chemistry's Microanalytical Laboratory at the University of California, Berkeley. DR-FTIR spectra were obtained using a Thermo Nicolet 6700 FTIR spectrometer. The DRUV-Vis spectra were acquired using a Perkin-Elmer Lambda 9 spectrometer equipped with a 60 mm integrating sphere, a slit width of 4 nm, and at a collection speed of 120 nm/min. All samples were run using MgO as a reference background. Powder x-ray diffraction (PXRD) patterns were recorded on a Bruker D-8 GADDS X-ray diffractometer using Co K_{α} radiation ($\lambda = 1.7902$ Å). The pH measurements were conducted using a Thermo Orion 2 Star pH meter. Inductively coupled plasma optical emission spectroscopy (ICP-OES) for cobalt ion detection in post catalytic solutions was performed on a Perkin-Elmer ICP-OES Optima 7000 DV (detection limit for Co ions: 0.25 ppb). Standard solutions were purchased from Perkin-Elmer and used as received. Heat treatments were conducted in a Lindberg 1200 °C three-zone furnace.

Syntheses of surface-supported cobalt catalysts. Catalyst synthesis was performed following a previously published procedure with minor modifications.⁴ In a typical synthesis, $Co[N(SiMe_3)_2]_2$ (16 mg, 42 µmol) in 25 mL of hexanes was added to a hexanes suspension of the material support (1 g in 25 mL; AlPO, SBA-15, TiO₂, MgO, and Y-Zeolite). The green solution of $Co[N(SiMe_3)_2]_2$ instantaneously changed color as it came in contact with the hexanes-suspended material. Reactions with SBA-15 and AlPO resulted in light blue colored mixtures; MgO and TiO₂ gave grey-green mixtures, and the Y-Zeolite gave a pale brown mixture. The reaction mixtures were stirred under nitrogen for 0.5 h. The solid was collected, washed thoroughly with hexanes, and air dried. The dried materials were then calcined under flowing air (110 cc/min) to 300 °C for 6 h to remove residual organics.

X-ray Absorption Spectroscopy (XAS) data collection. The combination of XANES and EXAFS spectra were collected at BL 10.3.2 in the Advanced Light Source (ALS) at LBNL, and at BL 7-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). At the ALS, the synchrotron ring operated at 1.9 GeV at a 500 mA beam current. Energy resolution of the focused incoming X-rays at BL 10.3.2 was achieved using a Si(111) double-crystal monochromator. Fluorescence spectra were collected with a 7-element Ge detector, and transmission spectra were obtained with a I₁ ion chamber filled with N₂ gas. An incident X-ray beam of 0.1 mm (H) x 0.02 mm (V) dimensions was used for the XANES and EXAFS experiments. At SSRL, the electron energy was set at 3.0 GeV with an average current of 450 mA. A Si(220) double-crystal monochromater was

used. Spectra were collected in fluorescence mode in a chamber filled with N_2 gas. Energy calibrations are based on the rising edge energy of Co foil at 7709.0 eV. Each spectrum is the average of 6 to 9 scans. All measurements were done at room temperature.

Water oxidation catalysis experiments and oxygen detection. Light-driven water-oxidation reactions were performed in a buffered aqueous solution at pH 5.5-5.6 (NaHCO₃/Na₂SiF₆) employing Na₂S₂O₈ as a sacrificial electron acceptor. The sensitizer used for the experiments was [Ru(bpy)₃]Cl₂. To remove oxygen, water was sparged with nitrogen for 1 h prior to experiments. A gas-tight glass cell with an internal volume of 37.6 mL was used as the reaction vessel. In a typical experiment, 40 mg of catalyst was suspended in 15 mL of buffered water along with 18 mg of [Ru(bpy)₃]Cl₂, 100 mg of Na₂SO₄, and 36 mg of Na₂S₂O₈. A 488 nm laser with a power output of 260 mW, focused at a beam diameter of 0.5 cm, was used as the light source. The head-space oxygen concentration was monitored in real time by a multi-frequency fluorescence oxygen probe (Ocean Optics FOSPOR-R). Before each experiment, the oxygen probe was calibrated using a five-point calibration method at the following oxygen concentrations (vol. %) in helium: 0, 1.68, 3.62, 6.38, and 20.



Figure S1. The EXAFS spectrum of CoAlPO.



Figure S2. The EXAFS spectrum of CoMgO.



Figure S3. The EXAFS spectrum of CoTiO₂.



Figure S4. The EXAFS spectrum of CoYZ.



Figure S5. The d-d transition region of the DRUV-vis spectrum of CoAlPO.



Figure S6. The d-d transition region of the DRUV-vis spectrum of CoTiO₂.



Figure S7. The d-d transition region of the DRUV-vis spectrum of CoYZ.



Figure S8. The d-d transition region of the DRUV-vis spectrum of CoMgO.



Figure S9. The EXAFS spectra of CoMgO (pre-catalysis) compared to those of CoO and Co₃O₄.



Figure S10. Oxygen evolution over time in the absence of the $[Ru(bpy)_3]Cl_2$ sensitizer (CoTiO₂ catalyst employed; CoSBA, CoYZ, and CoMgO similarly evolved no oxygen without $[Ru(bpy)_3]Cl_2$). No significant increase in the oxygen signal suggests that the ruthenium sensitizer is an essential part of catalysis. Initial blip in the oxygen signal is due to a small leak-in associated with the closing of the reaction vessel. The overall decrease in the oxygen signal is due to evolution of CO₂ from the bicarbonate buffer and subsequent decrease in the partial pressure of O₂.



Figure S11. TOF_{*i*} s of the catalysts were plotted as functions of the Lewis acidity of E^{n+} (aq) in the supporting oxide.⁵ Supporting oxides with more Lewis acidic E exhibited higher rates of catalysis, however, further investigations are required to draw firmer conclusions.

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