Inorganic Chemistry

Photocatalytic Hydroxylation of Benzene by Dioxygen to Phenol with a Cyano-Bridged Complex Containing Fe^{II} and Ru^{II} Incorporated in Mesoporous Silica–Alumina

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Supporting Information

ABSTRACT: Photocatalytic hydroxylation of benzene to phenol was achieved by using O₂ as an oxidant as well as an oxygen source with a cyano-bridged polynuclear metal complex containing Fe^{II} and Ru^{II} incorporated in mesoporous silica– alumina ($[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41). An apparent turnover number (TON) of phenol production per the monomer unit of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ was 41 for 59 h. The cyano-bridged polynuclear metal complex, $[Fe(H_2O)_3]_2[Ru(CN)_6]$, exhibited catalytic activity for thermal hydroxylation of benzene by H_2O_2 in acetonitrile (MeCN), where the apparent



Combination of photo- and thermal catalysis of [Fe(H₂O)₃]₂[Ru(CN)₆] on sAI-MCM-41

TON of phenol production reached 393 for 60 h. The apparent TON increased to 2500 for 114 h by incorporating $[Fe(H_2O)_3]_2[Ru(CN)_6]$ in sAl-MCM-41. Additionally, $[Fe(H_2O)_3]_2[Ru(CN)_6]$ acts as a water oxidation catalyst by using $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) and $Na_2S_2O_8$ as a photosensitizer and a sacrificial electron acceptor as evidenced by ${}^{18}O$ -isotope labeling experiments. Photoirradiation of an O₂-saturated MeCN solution containing $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 and scandium ion provided H_2O_2 formation, where photoexcited $[Ru(CN)_6]^{4-}$ moiety reduces O_2 as indicated by laser flash photolysis measurements. Thus, hydroxylation of benzene to phenol using molecular oxygen photocatalyzed by $[Fe(H_2O)_3]_2[Ru(CN)_6]$ occurred via a two-step route; (1) molecular oxygen was photocatalytically reduced to peroxide by using water as an electron donor, and then (2) peroxide thus formed is used as an oxidant for hydroxylation of benzene.

INTRODUCTION

Production of phenol from benzene in a one-step reaction has merited significant interest from the viewpoints of an environmentally benign green process and economical efficiency as compared with the current three-step cumene process.¹⁻³ Thus, extensive efforts have so far been devoted to develop the one-step direct hydroxylation of benzene using various oxidants such as $H_2O_2^{4-7} N_2O_r^{8,9} O_2$ with reductants.^{10–15} Catalytic oxidation of benzene using O2 as the oxidant is particularly of high potential interest, because O2 is regarded as an ideal oxidant due to its natural, inexpensive, and environmentally friendly characteristics. However, catalytic aerobic oxidation of benzene via O₂ activation without reductants required harsh reaction conditions such as high temperature and high pressures.^{16–19} Photocatalytic oxidation of benzene with O2 without a reductant has also been reported using organic photocatalysts.²⁰⁻²³ In such a case, water was used as an oxygen source, whereas O_2 acts only as an oxidant.^{20–23} Thus, there has been no report on catalytic hydroxylation of benzene with O2 used as an oxygen source as well as an oxidant under mild conditions at ambient pressure and temperature.

Recently, photocatalytic systems producing H_2O_2 by reduction of O_2 with water as an electron donor have been constructed by utilizing the water oxidation catalysis of cyano-bridged complexes and O_2 reduction catalysis of a Ru complex.^{24–26} Besides, some metal complexes containing Fe ions have been reported to act as a catalyst for hydroxylation of benzene by H_2O_2 .^{27–31} Combination of catalysis for photocatalytic H_2O_2 production and for hydroxylation of benzene by H_2O_2 allows to construct a composite catalyst for benzene hydroxylation by O_2 . A cyano-bridged complex incorporating Ru and Fe ions seems to be a good candidate for such a reaction.

We report herein photocatalytic hydroxylation of benzene to phenol using O_2 as an oxygen source as well as an oxidant with a cyano-bridged polynuclear metal complex containing Fe^{II} and Ru^{II} incorporated in mesoporous silica–alumina ($[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41), in MeCN under photoirradiation at 298 K. As indicated in Figure 1, Fe ions

Received: December 16, 2015



Figure 1. Partial structure of a cyano-bridged complex containing Fe^{II} and Ru^{II} ([Fe(H₂O)₃]₂[Ru(CN)₆]). Three water molecules (in average) bind to Fe^{II} ions to fulfill the octahedral coordination structure.

in $[Fe(H_2O)_3]_2[Ru(CN)_6]$ have extra ligands such as water molecules to fulfill octahedral coordination; however, the coordinating water molecules are easily liberated during the catalytic reaction. The Fe^{II} ions may react with H_2O_2 to produce hydroxyl radicals or iron oxo species, which oxidize benzene to produce phenol. The incorporated metal complex, $[Fe(H_2O)_3]_2$ - $[Ru(CN)_6]$, acts as both an effective photocatalyst for oxidation of water with O_2 to produce H_2O_2 and also an excellent catalyst for hydroxylation of benzene with H_2O_2 to produce phenol.

EXPERIMENTAL SECTION

Materials. All chemicals used for synthesis were obtained from chemical companies and used without further purification. Purified water was provided by a water purification system, Millipore Direct-Q3 UV, where the electronic conductance was 18.2 M Ω cm. Tetraethyl orthosilicate, copper(II) sulfate pentahydrate, cobalt(II) nitrate hexahydrate, manganese(II) perchlorate hexahydrate, cetyltrimethylammonium bromide, sodium aluminate, aqueous ammonia, benzene, sodium iodide, and an aqueous solution of hydrogen peroxide (30 wt %) were purchased from Wako Pure Chemical Industries. Iron(II) perchlorate hydrate and potassium hexacyanoruthenate(II) hydrate were delivered by Sigma-Aldrich. Acetonitrile was obtained from Nacalai tesque. Potassium hexacyanorhodate(III) and scandium(III) nitrate was supplied by Mitsuwa Chemicals Co, Ltd.

Syntheses of $[Mn(H_2O)_3]_2[Ru(CN)_6]$, $[Fe(H_2O)_3]_2[Ru(CN)_6]$, $[Co(H_2O)_3]_2[Ru(CN)_6]$, $[Cu(H_2O)_n]_2[Ru(CN)_6]$.³² An aqueous solution (10 mL) of manganese(II) perchlorate hexahydrate, iron(II) perchlorate hydrate, cobalt(II) nitrate hexahydrate, or copper(II) sulfate pentahydrate (0.14 mmol) was slowly added to an aqueous solution (10 mL) of potassium hexacyanoruthenate(II) hydrate (0.073 mmol) for 2 h with stirring magnetically. The formed precipitate was collected by filtration, washed with water, and dried in vacuo.

Synthesis of $[Fe(H_2O)_2]_{1.5}[Rh(CN)_6].^{32}$ An aqueous solution (10 mL) of iron(II) perchlorate hydrate (0.20 mmol) was slowly added to an aqueous solution (10 mL) of potassium hexacyanorhodate(III) (0.13 mmol) for 2 h with stirring magnetically. The obtained precipitate was collected by filtration, washed with water, and dried in vacuo.

Synthesis of Spherical Mesoporous Silica–Alumina (sAl-MCM-41).³³ sAl-MCM-41 was synthesized by a reported method with modifications.³³ Cetyltrimethylammonium bromide (14.6 g) was dissolved to a mixed solution (814 mL) composed of water, aqueous NH₃, and ethanol [270:444:100 (v/v/v)]. Tetraethylorthosilicate (27.4 g, 131 mmol) was added dropwise to the aqueous solution for 2 h and magnetically stirred for further 19 h at room temperature, and the formed precipitate was collected by filtration. The obtained precipitate was washed with an ethanol solution (100 g) containing ammonium nitrate (500 mg, 6.25 mmol) at 60 °C and then washed with water and ethanol, successively. The precipitate was collected by filtration and dried at 200 °C. The obtained spherical MCM-41 was suspended to an aqueous solution (400 mL) of sodium aluminate

(1.33 g, 21.7 mmol) and stirred for 22 h at room temperature. The obtained solid was collected by filtration and dried at 200 °C for 1 h. The dried sample was calcined at 550 °C for 6 h under atmospheric conditions to obtain sAl-MCM-41. The obtained powder was characterized by N_2 adsorption–desorption at 77 K and powder X-ray diffraction.

Preparation of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 and $[Cu-(H_2O)_n]_2[Ru(CN)_6]$ @sAl-MCM-41. $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 and $[Cu(H_2O)_n]_2[Ru(CN)_6]$ @sAl-MCM-41 were prepared by a similar procedure. sAl-MCM-41 (0.20 g) was added to an aqueous solution (10 mL) of iron(II) perchlorate hydrate (0.20 g, 0.56 mmol) or copper(II) sulfate pentahydrate (0.14 g, 0.56 mmol) and magnetically stirred for 2 h at room temperature. The obtained solid collected by centrifugation was washed with water two times and dried in vacuo. The obtained Fe²⁺@sAl-MCM-41 or Cu²⁺@sAl-MCM-41 (50 mg) was added to an aqueous solution of potassium hexacyanoruthenate(II) hydrate (57 mg, 0.14 mmol) for 2 h on a magnetic stirrer. The obtained solid was collected by filtration and washed with water and dried in vacuo to obtain $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 or $[Cu(H_2O)_n]_2[Ru(CN)_6]$ @sAl-MCM-41 were determined by X-ray fluorescence (XRF) measurements to be 8.7 × 10⁻⁴ and 5.7 × 10⁻⁵ mol g⁻¹, respectively.³⁴

 N_2 Adsorption–Desorption Isotherms. Nitrogen adsorption– desorption isotherms at 77 K were recorded by an instrument for volumetric adsorption measurements, Belsorp-mini II (BEL Japan, Inc.), within a relative pressure range from 0.01 to 101.3 kPa. The mass of a sample was ca. 100 mg for an adsorption analysis after pretreatment at 393 K for ca. 1 h under vacuum conditions and kept in N_2 atmosphere until N_2 -adsorption measurements. The sample was exposed to a mixed gas of He and N_2 with a programmed ratio, and adsorbed amount of N_2 was calculated from the change of pressure in a cell after reaching the equilibrium.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were recorded on a Rigaku MiniFlex 600. Incident X-ray radiation was produced by a Cu X-ray tube operating at 40 kV and 15 mA with Cu K α radiation (λ = 1.54 Å). The scan rate was 1° min⁻¹ from $2\theta = 2-40^{\circ}$.

Physical Measurements. UV-vis absorption spectra of solutions were recorded on a Hewlett-Packard 8453 diode array spectrometer. UV-vis diffused reflectance spectra were measured by a Jasco V-670 spectrometer equipped with an SIN-768 attachment. IR spectra were recorded on a Jasco FT/IR-6200 spectrometer for the samples pelletized with KBr. The electron paramagnetic resonance (EPR) spectra were taken on a JEOL X-band spectrometer (JES-REIXE) with a quartz EPR tube (4.5 mm) at 150 K. The g values were calibrated using a Mn²⁺ marker. Sub-nanosecond laser-induced transient absorption spectra were collected by a customized measuring system equipped with a picosecond-pulse laser for the photoexcitation and a photomultiplier detector developed by UNISOKU Co., Ltd.³⁵ Nanosecond laser flash photolysis experiments were performed using an Nd:YAG laser (Continuum, SLI-20, 4–6 ns fwhm) at $\lambda = 266$ nm with the power of 0.5 mJ per pulse.³⁶ The transient absorption measurements were performed using a continuous wave xenon lamp (150 W) and a photomultiplier (Hamamatsu 2949) as a probe light and a detector, respectively. The output from a photomultiplier was recorded on a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). XRF measurements were performed to determine the loading amount of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ on sAl-MCM-41 by a Rigaku ZSX-100e, which is a wavelength-dispersive spectrometer equipped with a 4 kW Rh X-ray tube.

Hydroxylation of Benzene by H_2O_2. Typical reaction conditions are as follows: $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 (1.0 mg, 17 μ M of $[Fe(H_2O)_3]_2[Ru(CN)_6]$) was suspended in MeCN (2.5 mL). Benzene (0.40 mL, 1.4 M) and aqueous hydrogen peroxide (30 wt %; 0.40 mL, 1.2 M) was added to the suspension successively under vigorous stirring at 298 K. A small portion of the reaction solution was taken out and injected to a Shimadzu QP-5000 GC/MS to analyze products.

Photocatalytic Production of H₂O₂. Typical reaction conditions are as follows: $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 (1.0 mg, 17 μ M

of $[Fe(H_2O)_3]_2[Ru(CN)_6]$) was suspended to an O₂-saturated mixed solution (3.3 mL) composed of MeCN and water [2.9:0.40 (v/v)] containing Sc(NO₃)₃ (0.10 M). The suspension was gently stirred by a magnetic stirrer under photoirradiation with a xenon lamp (Ushio Optical, Model X SX-UID 500X AMQ) at room temperature. The amount of produced H₂O₂ at each reaction time was determined by the titration of iodide ion. The photocatalytic production of H₂O₂ was also performed in ¹⁶O₂-saturated H₂¹⁸O containing [Fe(H₂O)₃]₂[Ru(CN)₆]. After removal of ¹⁶O₂ and ¹⁸O₂ in the gas phase by passing He gas, the reaction solution was moved to a sealed vial containing MnO₂, which catalyzes H₂O₂ decomposition, via cannula under He atmosphere. The evolved oxygen gas in the headspace was analyzed by a gas chromatograph [He carrier, TC-FFAP column (GL Science, 1010–15242) at 313 K] equipped with a mass spectrometer (Shimadzu, QP-5000 GC/MS).

Photocatalytic Water Oxidation. Typical reaction conditions are as follows: a hetero-polynuclear cyanide complex (0.54 mM) was suspended to an Ar-saturated phosphate buffer (50 mM, pH 8.0, 2.0 mL) containing Na₂S₂O₈ (10 mM) and [Ru(bpy)₃]Cl₂ (1.0 mM). The solution was then irradiated with the xenon lamp through a color filter glass (Asahi Techno Glass) transmitting λ > 390 nm at room temperature. The concentration of oxygen gas in a headspace was quantified by a Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 1909SPMS0, 30 m × 0.53 mm) at 313 K] equipped with a thermal conductivity detector (TCD) at a certain reaction time.

Thermal Water Oxidation. $[Ru^{II}(bpy)_3](PF_6)_3$ (0.50 mM) and $[Fe(H_2O)_3]_2[Ru(CN)_6]$ (1.0 mg) were dissolved to a phosphate buffer (2.0 mL, 50 mM, pH 8.0) in a sealed vial under Ar atmosphere. After a certain reaction time, the concentration of oxygen gas in the headspace of the reaction vial was quantified by a gas chromatograph with a TCD.

¹⁸O-Isotope Labeling Experiments. $[Fe(H_2O)_3]_2[Ru(CN)_6]$ (5.0 mg, 6.8 mM) was suspended to an He-saturated $H_2^{18}O$ (2.0 mL) containing $Na_2S_2O_8$ (10 mM) and $[Ru(bpy)_3]Cl_2$ (1.0 mM). The suspension was then irradiated with a xenon lamp ($\lambda > 390$ nm) at room temperature. The concentration of oxygen gas in a headspace was quantified by a gas chromatograph equipped with a mass spectrometer (Shimadzu, QP-5000 GC/MS).

Hydroxylation of Benzene with O₂. Typical reaction conditions are as follows: $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 (1.0 mg, 17 μ M of $[Fe(H_2O)_3]_2[Ru(CN)_6]$) was suspended to an O₂-saturated mixed solution (3.3 mL) composed of MeCN and benzene [2.9:0.40 (v/v)]. The suspension was magnetically stirred under photoirradiation at room temperature. Product analyses were performed by a Shimadzu QP-5000 GC/MS.

RESULTS AND DISCUSSION

Catalytic Hydroxylation of Benzene by H₂O₂ Using [Fe(H₂O)₃]₂[Ru(CN)₆]@sAl-MCM-41. Nanosized spherical mesoporous silica-alumina (sAl-MCM-41), which is highly dispersible to a solvent and can efficiently prevent the growth of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ particles in mesopores, was synthesized by using a mixture of tetraethyl orthosilicate and sodium aluminate as precursors under basic (aqueous NH_3) conditions.³³ The addition of Al³⁺ to silica results in formation of cation-exchange sites, which are important to enhance interaction between metal ions and the surfaces. The Brunauer-Emmett-Teller (BET) surface area of sAl-MCM-41 was determined to be 758 m² g⁻¹ based on the N2 adsorption-desorption isotherms [Figure S1a in Supporting Information]. The powder X-ray diffraction pattern of sAl-MCM-41 indicates that the pore diameter is 3.7 nm, which is the same value determined by the Barrett-Joyner-Halenda (BJH) pore size distribution (Figures S1b and S2 in Supporting Information). $[Fe(H_2O)_3]_2[Ru(CN)_6]$ was incorporated in sAl-MCM-41 by the reaction of Fe^{2+} adsorbed on sAl-MCM-41 and $K_4[Ru^{II}(CN)_6]$ ([Fe(H₂O)₃]₂[Ru(CN)₆]@sAl-MCM-41) in water. When sAl-MCM-41 without loading Fe^{2+} was used instead of the Fe²⁺ adsorbed sAIMCM-41, no incorporation of [Ru^{II}(CN)₆]⁴⁻ was observed (Figure S3 in Supporting Information). The formation and incorporation of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ was confirmed by a diffuse reflectance UV-vis absorption spectrum, powder X-ray diffraction, and transmission electron microscopy images with elemental mappings of Ru and Fe as shown in Figures S4 and S5 in Supporting Information, where the absorption band and diffraction patterns due to $[Fe(H_2O)_3]_2$ - $[Ru(CN)_6]$ were observed. The amount of incorporated $[Fe(H_2O)_3]_2[Ru(CN)_6]$ was determined to be 5.7 \times 10⁻⁵ mol g^{-1} , which corresponds to 2.1% of the cation exchange sites of sAl-MCM-41, by XRF measurements. The BET surface area and pore volume of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 were determined to be 526 m² g⁻¹ and 0.439 cm³ g⁻¹, respectively, which are lower than those of bare sAl-MCM-41 (758 m² g⁻¹ and 0.491 cm³ g⁻¹; Figure S6 in Supporting Information). The lower BET surface area mainly resulted from the decrease of the inner surface area to 478 from 708 $m^2 g^{-1}$. No significant change in the BJH pore size distribution for both samples suggested that $[Fe(H_2O)_3]_2[Ru(CN)_6]$ mainly located inside mesopores and partly filled them.

First, catalytic hydroxylation of benzene (0.40 mL, 1.4 M) by 30 wt % aqueous H_2O_2 (0.40 mL, 1.2 M) to produce phenol was examined by using $[M(H_2O)_3]_2[Ru(CN)_6]$ without sAl-MCM-41 (0.10 mg, 82 μ M; M = Mn, Fe, Co, or Cu) as a heterogeneous catalyst in MeCN (2.5 mL; Figure 2). Among



Figure 2. Time profiles of production of phenol in catalytic hydroxylation of benzene (0.40 mL, 1.4 M) with 30 wt % aqueous H_2O_2 (0.40 mL, 1.2 M) in MeCN (2.5 mL) containing [M- $(H_2O)_3]_2$ [Ru(CN)₆] (M = Mn, Fe, Co, or Cu; 0.10 mg, 82 μ M) at 323 K.

the catalysts, $[Fe(H_2O)_3]_2[Ru(CN)_6]$ showed the highest reactivity in terms of a yield and a rate of phenol production. The apparent turnover number (TON) of phenol production per the monomer unit of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ was 393 at 60 h. The overoxidation products such as *p*-benzoquinone were not produced, and the product selectivity to phenol was >99% (Figure 3). When the concentration of benzene was decreased to 4.3 mM, the yield of phenol increased to 15% with >99% selectivity. No further oxidation of phenol to p-benzoquinone occurred at 323 K when the conversion of benzene was lower than 15%. The high selectivity to phenol may result from the interaction of formed phenol with Lewis acid sites, which suppresses further oxidation.^{6a,37–39} The initial rate of formation of phenol (<2 h) was proportional to concentrations of benzene and $[Fe(H_2O)_3]_2[Ru(CN)_6]$, whereas the rate remains constant irrespective of different concentrations of H_2O_2 (see Figure S7 in Supporting Information). The first-order



Figure 3. Time profiles of production of phenol (red \bullet) and *p*-benzoquinone (black \blacksquare) in catalytic hydroxylation of benzene (0.40 mL, 1.5 M) with aqueous H₂O₂ (0.40 mL, 1.3 M) in MeCN (2.5 mL) containing [Fe(H₂O)₃]₂[Ru(CN)₆] (0.10 mg, 82 μ M) at 323 K.

dependence of the rate on the catalyst concentration suggests that the monomer unit of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ acts as the catalyst when no dissociation or association of $[Fe(H_2O)_3]_2$ - $[Ru(CN)_6]$ may be involved in the catalytic hydroxylation of benzene with H_2O_2 . No dependence of the rate on concentration of H_2O_2 suggests that the catalyst forms a complex with H_2O_2 such as metal-peroxo or metal-oxo species during the catalytic reaction.

When $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 was employed as a catalyst, the apparent TON of phenol production per the monomer unit of incorporated $[Fe(H_2O)_3]_2[Ru(CN)_6]$ reached 2500 at 114 h (Figure 4). The incorporation of $[Fe(H_2O)_3]_2[Ru-$



Figure 4. Time profiles of production of phenol in catalytic hydroxylation of benzene (0.40 mL, 1.5 M) with 30 wt % aqueous H_2O_2 (0.40 mL, 1.3 M) in MeCN (2.5 mL) containing $[Fe(H_2O)_3]_2$ - $[Ru(CN)_6]$ @sAl-MCM-41 (1.0 mg, 17 μ M of $[Fe(H_2O)_3]_2$ [Ru(CN)₆], red ●), Fe²⁺@sAl-MCM-41 (1.0 mg, 34 μ M of Fe²⁺, ▲), and Ru²⁺@sAl-MCM-41 (2.3 mg, 17 μ M of Ru²⁺, ■) at 323 K.

 $(CN)_6$ in sAl-MCM-41 resulted in significant improvement of the catalytic durability by increasing the number of true active sites.

During the reaction, 100 mM of H_2O_2 was consumed for producing 37 mM phenol, suggesting that the oxidation reaction accompanied by the decomposition of H_2O_2 by disproportionation as evidenced by tiny bubbles formation in the reaction vial. Lower apparent TONs were achieved by employing Fe²⁺ or Ru²⁺ incorporated in sAl-MCM-41 (Fe²⁺@sAl-MCM-41 or Ru^{2+} @sAl-MCM-41) as a catalyst for benzene hydroxylation under the same reaction conditions for the reaction system employing [Fe(H₂O)₃]₂[Ru(CN)₆]@sAl-MCM-41, suggesting that formation of [Fe(H₂O)₃]₂[Ru(CN)₆] is important to exhibit high catalytic activity.

Photocatalytic H_2O_2 Production from H_2O and O_2 Using $[Fe(H_2O)_3]_2[Ru(CN)_6]@sAl-MCM-41$. It was also found that $[Fe(H_2O)_3]_2[Ru(CN)_6]@sAl-MCM-41$ acted as an effective photocatalyst for production of H_2O_2 from H_2O and O_2 by photoirradiation of an O_2 -satuated aqueous dispersion containing $[Fe(H_2O)_3]_2[Ru(CN)_6]@sAl-MCM-41$ and $Sc(NO_3)_3$ as shown in Figure 5. The presence of Sc^{3+} has been reported to



Figure 5. Time course of production of H_2O_2 from H_2O and O_2 in an O_2 -saturated MeCN (2.9 mL) containing $[Fe(H_2O)_3]_2[Ru(CN)_6]@$ sAl-MCM-41 (1.0 mg, 17 μ M of $[Fe(H_2O)_3]_2[Ru(CN)_6])$, water (0.40 mL), and Sc(NO₃)₃ (0.10 M) under photoirradiation with a xenon lamp.

stabilize $O_2^{\bullet-}$, which is converted to H_2O_2 and O_2 by disproportionation.^{25,26} The photocatalytic H_2O_2 formation was also performed by using ${}^{16}O_2$ -saturated mixed solvent of MeCN and $H_2^{-18}O$ [2.9:0.4 (v/v)] under the same reaction conditions other than the solvent. The formed H_2O_2 , which was catalytically decomposed to O_2 by MnO₂ for analyses, contained only ${}^{16}O$, suggesting that ${}^{16}O_2$ is an electron acceptor in this reaction system (Figure S8 in Supporting Information). No H_2O_2 formation was observed when $[Cu(H_2O)_n]_2[Ru(CN)_6]@sAl-MCM-41$ or $K_4[Ru^{II}(CN)_6]$ was used instead of $[Fe(H_2O)_3]_2$ -[Ru(CN)₆]@sAl-MCM-41 in the reaction dispersion (Figure S9 in Supporting Information), indicating that the Fe^{II} moiety is necessary to exhibit the catalysis for H_2O_2 production.

The role of Fe^{II} moiety seemed to be an active site for water oxidation, because some cyano-bridged polynuclear metal complexes have been reported to act as water oxidation catalysts, in which N-bound metal ions are active sites.⁴⁰ Catalysis of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ was examined for the photocatalytic water oxidation by $S_2O_8^{2-}$ in the presence of $[Ru^{II}(bpy)_3]^{2+}$ (bpy = 2, 2'-bipyridine) as a photosensitizer. Steady O₂ evolution was observed for 30 min under visible light irradiation ($\lambda >$ 390 nm) as shown in Figure 6. In a previous report, the intermediate $SO_4^{\bullet-}$ formed by one-electron oxidation of $S_2O_8^{2-}$ is a strong oxidant, so it may oxidize water oxidation catalysts (WOCs) directly.⁴¹ To exclude this possibility, $[Ru^{III}(bpy)_3]^{3+}$ thermally produced by oxidation of $[Ru^{II}(bpy)_3]^{2+}$ with PbO₂ was employed as an oxidant for water oxidation.⁴² O₂ evolved from a phosphate buffer (pH 8.0) contained both $[Ru^{III}(bpy)_3]^{3+}$ and $[Fe(H_2O)_3]_2[Ru(CN)_6]$, whereas no O₂ evolved without $[Fe(H_2O)_3]_2[Ru(CN)_6]$ (Figure S10 in Supporting Information).



Figure 6. Time profiles of O₂ evolution under photoirradiation $(\lambda > 390 \text{ nm})$ of an Ar-saturated phosphate buffer (2.0 mL, 50 mM, pH 8.0) containing Na₂S₂O₈ (10 mM), [Ru^{II}(bpy)₃]²⁺ (1.0 mM) and [Fe(H₂O)₃]₂[Ru(CN)₆] (0.54 mM, •) or [Fe(H₂O)₂]_{1.5}[Rh(CN)₆] (0.54 mM, O).



Figure 7. Time profiles of ${}^{16}O_2$ (\blacklozenge), ${}^{18}O^{16}O$ (\blacklozenge), or ${}^{18}O_2$ (\blacktriangle) evolution under photoirradiation ($\lambda > 390$ nm) of a He-saturated H₂¹⁸O (2.0 mL) containing Na₂S₂O₈ (10 mM), [Ru^{II}(bpy)₃]²⁺ (1.0 mM) and [Fe(H₂O)₃]₂[Ru(CN)₆] (6.8 mM).

Thus, the $[Ru^{III}(bpy)_3]^{3+}$ formed during the photocatalytic water oxidation can oxidize the WOC to evolve O_2 .

Similarly, $[Fe(H_2O)_2]_{1.5}[Rh(CN)_6]$, which possesses the Fe^{II} moiety without the $[Ru(CN)_6]$ moiety, exhibits catalytic activity for water oxidation when the reaction system employed $[Fe(H_2O)_2]_{1.5}[Rh(CN)_6]$, instead of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ as the water oxidation catalyst. These results manifested that Fe^{II} moiety acted as a catalytic active site for water oxidation in the cyano-bridged complexes.

 18 O-isotope labeling experiments using H_2^{18} O instead of H_2^{16} O were conducted to obtain the direct evidence for the

water oxidation. The evolved oxygen in the headspace of a vial after photoirradiation of a reaction suspension for a certain time was analyzed by a gas chromatograph equipped with a molecular sieve column and a mass spectrometer (Figure 7). The evolved gas after photoirradiation for 30 min contained ¹⁸O¹⁸O and ¹⁸O¹⁶O with the ratio of 60:40, while the amount of formed ¹⁶O₂ was under the detection limit of the mass spectrometer. The ¹⁶O atom of ¹⁸O¹⁶O originates from water molecules of $[Fe(H_2¹⁶O)_3]_2[Ru(CN)_6]$ contained as the extra ligands.

Nanosecond laser-induced transient absorption spectra of $K_4[Ru^{II}(CN)_6]$ in water were measured to investigate a role of $[Ru^{II}(CN)_6]^{4-}$ moiety in the photocatalytic H_2O_2 formation (Figure S11 in Supporting Information), where the absorption band at 750 nm is assigned to the excited state of $[Ru^{II}(CN)_6]^{4-1}$ moiety. Transient absorption spectra of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ also exhibited the absorption band at 750 nm (Figure S12 in Supporting Information). The lifetime of the excited state of $[Ru^{II}(CN)_{6}]^{4-}$ was determined to be 1.6 μ s in deaerated MeCN. The lifetime of the excited state of $[Ru^{II}(CN)_6]^{4-}$ was shortened by increasing concentration of O_2 (Figure 8a). This suggests that electron transfer from the excited state of $[Ru^{II}(CN)_6]^{4-}$ to O_2 occurs to produce $[Ru^{II}(CN)_6]^{3-}$ and $O_2^{\bullet-}$. In the presence of Sc^{3+} ions, $O_2^{\bullet-}$ is bound to a Sc^{3+} ion to afford the $O_2^{\bullet-}-Sc^{3+}$ complex, which was detected by EPR after photoirradiation of an O₂-saturated MeCN solution of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ at 150 K as shown in Figure 9, where the signal due to $[Ru^{III}(CN)_6]^{3-}$ was also observed (see reference spectra in Figure S13 in Supporting Information).⁴³ The rate constant of electron transfer from the excited state of $[Ru^{II}(CN)_6]^{4-}$ to O₂ was determined from the linear plot of the decay rate constant



Figure 9. EPR spectra observed under dark (black broken line) and photoirradiation (red solid line) with an Hg lamp of an O_2 -saturated MeCN solution (2.0 mL) containing $[Fe(H_2O)_3]_2[Ru(CN)_6]$ (0.20 mg, 0.27 mM) and Sc(NO₃)₃ (0.10 M) at 150 K.



Figure 8. (a) Decay time profiles of absorbance at 750 nm observed in N₂-saturated MeCN containing $K_4[Ru^{II}(CN)_6]$ (1.8 mM) and various concentrations of O₂ (0–0.24 mM). (b) Plot of the decay rate constant vs concentration of O₂.

versus concentration of O₂ (Figure 8b) to be $1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is diffusion-limited.

The mechanism of the photocatalytic production of H_2O_2 from H_2O and O_2 with $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 in MeCN is shown in Scheme 1. Photoexcitation of

Scheme 1. Overall Photocatalytic Cycle for H₂O₂ Production



 $[{\rm Fe}({\rm H_2O})_3]_2[{\rm Ru}({\rm CN})_6]$ resulted in electron transfer from the excited state of $[{\rm Fe}({\rm H_2O})_3]_2[{\rm Ru}({\rm CN})_6]$ to O₂ in the presence of Sc³⁺ to produce $[{\rm Fe}({\rm H_2O})_3]_2[{\rm Ru}^{\rm III}({\rm CN})_6]^+$ and O₂^{•-}-Sc³⁺. The reduction potential of $[{\rm Ru}^{\rm III}({\rm CN})_6]^{3-}$ moiety in the presence of iron ions has been reported as $E_{1/2}$ = 1.24 V versus standard hydrogen electrode (SHE),⁴⁴ which can oxidize the Fe^{II} moiety to high-valent iron species suitable for water oxidation, because the standard electrode potential for water oxidation to evolve oxygen at the pH of the reaction solution (2.8) is 1.06 V versus SHE. The O₂^{•-}-Sc³⁺ complex disproportionates in the presence of H⁺ to produce H₂O₂.^{25,26}

Photocatalytic Benzene Hydroxylation by O₂ Using $[Fe(H_2O)_3]_2[Ru(CN)_6]@sAl-MCM-41$. The catalytic hydroxylation of benzene with H_2O_2 to phenol (eq 1) was combined with the photocatalysis of $[Fe(H_2O)_3]_2[Ru(CN)_6]@sAl-MCM-41$ for production of H_2O_2 from H_2O and O_2 (eq 2). The overall catalytic reaction is given by eq 3, which shows the photocatalytic

$$C_6H_6 + H_2O_2 \xrightarrow{[Fe(H_2O)_3]_2[Ru(CN)_6]@sAl-MCM-41]} C_6H_5OH + H_2O$$
(1)

$$H_2O + 1/2O_2 \xrightarrow[[Fe(H_2O]_3]_2[Ru(CN)_6]@sAl-MCM-41]{} H_2O_2$$
(2)

$$C_{6}H_{6} + 1/2O_{2} \xrightarrow[Fe(H_{2}O)_{3}]_{2}[Ru(CN)_{6}]@sAl-MCM-41]} C_{6}H_{5}OH$$
(3)

hydroxylation of benzene to phenol using O₂ as an oxygen source as well as an oxidant. The time profile of production of phenol by photoirradiation of an O₂-saturated MeCN solution of benzene (0.40 mL, 1.5 M) containing $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 (1.0 mg, 17 μ M of $[Fe(H_2O)_3]_2[Ru(CN)_6]$) at 298 K is shown in Figure 10. The TON reached 41 after photoirradiation for 59 h. Benzene hydroxylation to phenol was catalyzed by $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41 with H_2O_2 even at a low concentration (3.0 mM) (Figure S14 in Supporting Information).

CONCLUSIONS

Hydroxylation of benzene to phenol has been achieved by using O_2 as an oxygen source as well as an oxidant by combination of the catalytic hydroxylation of benzene to phenol with H_2O_2 and the photocatalytic production of H_2O_2 from H_2O and O_2 with use of $[Fe(H_2O)_3]_2[Ru(CN)_6]$ @sAl-MCM-41, which acts as a catalyst for both benzene hydroxylation and water oxidation as well as a photocatalyst for O_2 reduction to H_2O_2 . The combination of the catalytic hydroxylation of benzene to



Figure 10. Time course of formation of phenol under photoirradiation of an O₂-saturated MeCN solution (2.9 mL) containing $[Fe(H_2O)_3]_2$ - $[Ru(CN)_6]@sAl-MCM-41 (1.0 mg, 17 \mu M of [Fe(H_2O)_3]_2[Ru(CN)_6])$ and benzene (1.5 M, 0.40 mL) with a xenon lamp.

phenol with H_2O_2 and the photocatalytic production of H_2O_2 from H_2O and O_2 in this study provides a new strategy to achieve one-pot hydroxylation of benzene with O_2 as an ideal oxygen source as well as an oxidant.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02909.

N₂-adsorption and desorption isotherms and BJH pore size distribution of sAl-MCM-41 and $[Fe(H_2O)_3]_2[Ru-(CN)_6]$ @sAl-MCM-41, powder X-ray diffraction patterns, UV-vis spectra, TEM images with elemental mappings, time profiles of phenol production, distribution of O₂ in ¹⁸O-labeling experiment, time profiles of H₂O₂ production, time profiles of O₂ evolution, transient absorption spectra, and EPR spectra (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This work was supported by ALCA and SENTAN projects from JST (to S.F.) and JSPS KAKENHI (No. 16H02268 to S.F., Nos. 24350069 and 15K14223 to Y.Y.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We sincerely acknowledge Dr. T. Nakagawa and Mr. K. Okamoto, UNISOKU Co. Ltd, for the measurements of the laser-induced transient absorption spectra. We are thankful to Mr. Masatsugu Ishimoto, Osaka City University, for EDS-STEM measurements.

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