



Title	Aqueous Electrochemical Partial Oxidation of Gaseous Ethylbenzene by a Ru-Modified Covalent Triazine Framework
Author(s)	Kato, Shintaro; Iwase, Kazuyuki; Harada, Takashi et al.
Citation	ACS Applied Materials and Interfaces. 2020, 12(26), p. 29376-29382
Version Type	AM
URL	https://hdl.handle.net/11094/103985
rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS Applied Materials & Interfaces, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/acsami.0c07228 .
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Aqueous Electrochemical Partial Oxidation of Gaseous Ethylbenzene by a Ru-Modified Covalent Triazine Framework

Shintaro Kato,[§] Kazuyuki Iwase,^{†,‡} Takashi Harada,[‡] Shuji Nakanishi,^{,‡,§} and Kazuhide Kamiya,^{*,‡,§}*

[§] Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.

[‡] Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikane-yama, Toyonaka, Osaka 560-8531, Japan.

[†] Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan.

KEYWORDS

Covalent triazine frameworks, Gas diffusion electrode, hydrocarbon oxidation, Aqueous electrolyte, Ruthenium

ABSTRACT

Aqueous electrochemical oxidation of hydrocarbons into valuable compounds, such as alcohols and carbonyl compounds, has attracted much attention because these systems can operate under mild conditions without toxic oxidants or flammable solvents. The key requirements to achieve such oxidation reactions are (1) highly reactive species on an electrocatalyst for the activation of C-H bonds and (2) efficient transportation pathway for water-insoluble hydrocarbons to an electrodes surface. We have determined that a gas diffusion electrode (GDE) supporting Ru atom-modified covalent triazine frameworks (Ru-CTF) has activity for the electrooxidation of gaseous ethylbenzene to acetophenone using an aqueous electrolyte. A high-valency Ru=O species was formed in Ru-CTF as an effective active site for O-atom insertion into stable C-H bonds. Furthermore, Ru-CTF showed excellent stability during four consecutive cycles with replacement of the electrolyte every 12 h although the reactive Ru=O species is generated. As for the transportation pathway for substrates, the amount of acetophenone generated from gaseous ethylbenzene was much larger than that from ethylbenzene dissolved in an electrolyte. This result indicates that the three-dimensional microstructures in the GDE maximize the transportation of gaseous hydrocarbons and the oxidation reaction occurs at the triple phase boundary, which enables the use of aqueous electrolytes.

1. INTRODUCTION

Selective and efficient technologies to convert abundant organic substrates into valuable products by the oxidative functionalization of CH bonds in hydrocarbons are highly demanded for a sustainable society.¹⁻² Various methodologies for oxidative upgrading of hydrocarbons have been widely investigated to date, such as thermal, biological, and photochemical conversion.¹⁻⁴ Among these, the electrochemical oxidation of substrates in aqueous solutions is a promising approach because the reaction can proceed under mild conditions without toxic oxidants or flammable solvents.⁵⁻⁶ However, there are two major problems for the further dissemination of electrochemical hydrocarbon oxidation in aqueous solution.

Green and cost-effective aqueous electrochemistry is ideal as a sustainable technology; however, the first problem is that many raw organic substances are poorly soluble in aqueous media.⁷ Therefore, the electrochemical oxidation of hydrocarbons such as alkanes, alkenes and arenes is generally conducted in organic electrolytes,⁸⁻¹⁰ where oxygen functionalized organics (e.g., alcohol, aldehyde and carboxylic acid) are employed as substrates for electrochemical reactions in aqueous solutions. Here we focus on gas diffusion electrodes (GDEs) that have been originally developed for hydrogen/oxygen fuel cells in an attempt to overcome the low solubility of hydrocarbons.¹¹⁻¹² Gaseous substrates can be directly supplied to the triple phase boundary at the GDE, where the catalyst material, electrolyte, and gas pores intersect. Thus, GDEs have recently been applied not only to fuel cells but to the electrochemical conversion of gaseous substrates for the production of valuable products, such as the CO₂ reduction reaction.¹³⁻¹⁴ We consider that GDEs could be applicable even to electrochemical oxidation reactions of vaporized hydrocarbons using aqueous electrolytes.

The other major challenging issue is that electrocatalysts with highly reactive species as active centers are required for the activation of stable C–H bonds in hydrocarbons. High-

valency ruthenium-oxo species ($\text{Ru}^{\text{IV}}=\text{O}$ or $\text{Ru}^{\text{V}}=\text{O}$) formed by the water oxidation reaction are candidates to satisfy this requirement.^{9-10, 15-16} $\text{Ru}=\text{O}$ species formed on Ru-organometallics are reported to catalyze O-insertion into stable C-H bonds of hydrocarbons.⁹⁻¹⁰ However, such Ru-based molecular electrocatalysts generally exhibit poor robustness and also catalyze the oxygen evolution reaction (OER) from the water oxidation reaction, which competes with hydrocarbon oxidation in aqueous solutions.¹⁷⁻¹⁸ Our group has recently demonstrated that metal-doped covalent triazine frameworks (CTF), which consist of microporous conjugated polymers with 1,3,5-triazine linker units,¹⁹⁻²⁸ can serve as metal supports for heterogeneous electrocatalysts.²⁹⁻³⁷ Various electrocatalytic functions, such as oxygen reduction³²⁻³³ and carbon dioxide reduction³⁴, can be achieved simply by changing the metal species in the CTF, and these metal-doped CTFs are stable over a wide pH and under electrochemical conditions, compared with the corresponding organic complexes.³¹⁻³² In particular, we have reported that Ru-doped CTFs (Ru-CTF) effectively oxidize benzyl alcohol in aqueous electrolytes without the OER.³¹ Although only alcohols have been reported as substrates with Ru-CTF, $\text{Ru}=\text{O}$ on Ru-CTF is also expected to have the ability to oxidize more stable CH bonds than those in alcohol, such as the methyl- and ethyl-groups of hydrocarbons, in a similar manner to that for Ru-based organometallics. Here, we attempt to realize electrochemical hydrocarbon oxidation reactions in aqueous solutions using a GDE that supports Ru-CTFs (Ru-CTF/GDE). The partial oxidation of ethylbenzene (EB) to acetophenone was adopted as a model reaction. Acetophenone is the raw chemical for perfumes, pharmaceuticals, resins, and alcohol and currently produced by the oxidation of EB using cobalt acetate as a homogeneous catalyst in acetic acid under high-pressure oxygen conditions.³⁸⁻³⁹ Therefore, aqueous electrochemical oxidation of EB to acetophenone is attractive because they can operate under milder conditions than the existing industrial method.

2. EXPERIMENTAL SECTION

The preparation of CTF has been detailed in our previous reports.²⁹⁻³⁴ Briefly, a mixture of ZnCl_2 (1.0 g, Wako), 2,6-dicyanopyridine (100 mg, Sigma-Aldrich), and Ketjenblack EC600JD (KB, 100 mg, Lion Corp.) was filled into a vacuum glass tube and then heated at 400 °C for 40 hours. KB is important to add electrical conductivity. As reported in our previous paper, the electrical conductivity of CTF without KB was a few orders lower than that with KB.³³ Besides, the particle size of CTF without KB became too large (1–5 μm). As a result, the CTF without KB showed almost no electrocatalytic activity. Notably, we confirmed that the hybridization with KB did not influence on the electronic properties of nitrogen and metal atoms in M-CTFs.³³ The resulting CTF powder was washed with distilled water, tetrahydrofuran (Wako) and 1 M hydrochloric acid (Wako). Ru atoms were then impregnated into the CTF using 0.91 mM RuCl_3 ethanol solution for 6 h at 100 °C. The resultant Ru-CTF catalyst was washed with distilled water and dried.

All electrochemical experiments were conducted with an electrochemical station at 298 K (HZ-7000, Hokuto Denko). Triple-chamber electrochemical cells, where two electrolyte chambers are divided by a Nafion 117 membrane, were used (Figure S1). A Ag/AgCl (KCl sat.) and titanium wire were used as the reference and counter electrodes, respectively. All potentials were converted to a reversible hydrogen electrode (RHE). Hydrocarbon oxidation activities were investigated in a 0.1 M phosphate buffer solution (pH 7). ^{18}O -labeled water (H_2^{18}O ; Taiyo Nissan Corp.) was used for the quantitative analysis of OER. A catalyst ink was prepared by dispersing 4.0 mg Ru-CTF in 38 μL Nafion solution (5 wt%; SigmaAldrich) and 400 μL ethanol by using a homogenizer, which was then added dropwise onto the GDE (GDL38BC, Sigracet, catalyst area: ca. 1 cm^2) on a hot plate at 70 °C. The weight of the loaded catalyst was controlled to be ca. 4.0 mg cm^{-2} . Reaction products in the electrolytes were quantitatively analyzed using high-performance liquid chromatography (LC-UV; ELITE

LaChrom, L-2455, L-2130, Hitachi, Japan) in conjunction with an inert sustain C18 column (GL Science Inc.). The mobile phase was composed of 60% methanol (HPLC grade, Wako) and 40% deionized water, with a flow rate of 1 mL min⁻¹. The standard HPLC charts and UV-Vis recorded by HPLC for acetophenone and possible side products are shown in Figure S2.

High-resolution transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis were performed using a spherical aberration-corrected TEM system (ARM-200F, JEOL). Ru-K edge X-ray absorption fine structure (XAFS) spectra were obtained using the BL01B1 beamline at SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI). Double-crystal Si (311) monochromator were employed to obtain XAS data. The measurements for as prepared Ru-CTF and the reference complex were performed in the transmission mode and for Ru-CTF on GDEs before and after electrolysis were performed in the fluorescence yield mode using 19 elements of Ge solid-state detectors. Extended X-ray absorption fine structure (EXAFS) spectra were analyzed using the ATHENA software package.⁴⁰ Fourier-transformation (FT) of EXAFS spectrum were conducted over the *k*-space range of 3-16 Å⁻¹ for Ru-CTF powder and the reference samples. Peak fittings for EXAFS for Ru-CTF and the reference complex were conducted by ARTEMIS software package between the *R* range of 1–3 Å. FT EXAFS for Ru-CTF on GDEs were conducted over the *k*-space range of 3-10 Å⁻¹ due to the lower Ru content on electrodes in the similar way. Surface inspection was carried out with a field emission scanning electron microscope (FE-SEM; Hitachi, S-5000). X-ray photoelectron spectra (XPS; Axis Ultra, Kratos Analytical Co.) were taken with monochromated Al Kα X-rays at *hν* = 1486.6 eV. The generated oxygen concentration was quantitatively measured with a gas chromatography mass spectrometer (GCMS-QP 2010 Plus, Shimadzu) with micropacked ST MP-01 column (Shincarbon-ST 80/100 mesh). The N₂ isotherm was obtained using a Micromeritics 3 Flex at 77 K.

3. RESULTS AND DISCUSSION

Physical and electrochemical characterization of Ru-CTF powder. The CTF was synthesized via the polymerization of 2,6-dicyanopyridine in the presence of conductive carbon particles (CPs) to incorporate electron conductivity, and the resulting CTF was then impregnated with RuCl₃ ethanol solution. Figure S3 shows the nitrogen adsorption-desorption isotherms and the pore size distribution. Our Ru-CTF possesses micro- and mesopores, and the estimated BET surface area was 888 m²/g. The more detailed characterization of the framework structure and microporosity of the CTF and CP hybrid material has been reported in our previous on platinum-doped CTF.^{30, 33} Here, the detailed structure related to Ru metal sites in Ru-CTF is characterized. N 1s X-ray photoelectron spectroscopy (XPS) spectra of CTF and Ru-CTF are shown in Figure S4. The N 1s peak of Ru-CTF could be deconvoluted into C2NH (398-400 eV) and C3N (400-401 eV).³¹ The peak C2NH peak shifted to higher energy by Ru loading, which suggests that the electron density of the N atoms was decreased by the formation of Ru-N coordination bonds. The TEM image of Ru-CTF (Figure S5) showed that the particle size was about 30 nm. High-resolution TEM and corresponding high-angle annular dark-field scanning TEM (HAADF-STEM) indicated that the bright spots assignable to Ru atoms (<0.5 nm) were uniformly dispersed and almost no Ru or RuO_x aggregation was evident (Figure 1a).^{33, 41} FT-EXAFS spectra in the previous work revealed that the Ru atoms in Ru-CTF are individually isolated.³¹ Curve fitting of the FT-EXAFS spectra was conducted to further identify the coordination structure of Ru atoms in the Ru-CTF powders. The estimated coordination numbers (CN) and distances (R) between Ru atoms and their nearest neighbors in Ru-CTF and bis(2,2-bipyridine)dichlororuthenium(II) are listed in Table S1, and fitting curves for the FT-EXAFS spectra of these two molecules are shown in Figures 1b and S6, respectively. The first coordination sphere of as-prepared Ru-CTF consisted of three nitrogen and three chlorine atoms, as shown in Figure 1c. The EXAFS spectrum of Ru-CTF shows that the

coordination structure of Ru-CTF was different from that of RuCl_3 and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (for detail, see Figure S7), and we confirmed that only carbon particles without CTF could not immobilize Ru atoms. These results also suggested that Ru atoms were anchored by CTF via the N coordination. Notably, these chlorine atoms were replaced with hydroxyl ions during electrolysis (Figure S8), which is consistent with our previous work.³¹

Cyclic voltammograms (CV) of Ru-CTF on glassy carbon electrode in phosphate buffer solutions were measured, as shown in Figure 1d. Two pairs of redox peaks were clearly observed, and the pair of peaks with a mid-point potential around 0.5 V and 1.2 V were assignable to $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}=\text{O}$ or $\text{Ru}^{\text{III}}/\text{Ru}^{\text{V}}=\text{O}$, respectively.^{16, 42-43} The high-valency $\text{Ru}=\text{O}$ species formed at 1.2-1.3 V is known to serve as an active center for C-H oxidation reactions.

Characterization of Ru-CTF/GDE and gaseous EB oxidation. Ru-CTF was deposited on a carbon paper with a microporous layer (MPL) composed of carbon nanoparticles and a hydrophobic layer to obtain Ru-CTF/GDE (Figure 2a). The Ru-CTF/GDE was characterized using XPS (Table S2, Figure S9). Elemental analyses using semi-quantitative XPS revealed that the concentration of Ru atoms in Ru-CTF/GDE was 0.43 at%. The narrow XPS spectrum (Figure S9) showed the $\text{Ru-3p}_{3/2}$ peak at 464 eV, which indicates that Ru^{III} was dominant in Ru-CTF/GDE,⁴⁴ as supported by the XANES reported in our previous results for the powder form of Ru-CTF.³¹ Scanning electron microscopy (SEM) observations revealed that the thickness of the catalyst layer on the MPL of the GDE was ca. 40 μm (Figure 2b).

The hydrocarbon oxidation activity of Ru-CTF/GDE was evaluated using EB as a model substrate. Figures 2c and S1 show a schematic illustration and photograph of the GDE setup, respectively. EB saturated (1.2×10^3 Pa at 298 K)⁴⁵ with argon gas was prepared by bubbling of the liquid EB, which was then supplied to the gas chamber as a substrate. We adopted the slow flow rate (1 mL min^{-1}) to certainly obtain the saturated gas. The blue and black curves in Figure

3a show the current densities on Ru-CTF/GDE at 1.5 V vs. RHE over time, with and without gaseous EB, respectively. The anodic current on Ru-CTF/GDE with gaseous EB was larger than that in the absence of EB. The generation of acetophenone was observed in the electrolyte with the supply of gaseous EB (Figures 3b and S10). The total amounts of acetophenone generated are listed in Table 1. After electrolysis for 6 h, the amount of acetophenone generated reached 4.7 μmol , whereas acetophenone generation without EB was negligible ($<0.01 \mu\text{mol}$, see entry 2 in Table 1). These results clearly indicate that the acetophenone generated is the product of EB oxidation reactions. Additionally, after the electrolysis with gaseous EB, we confirmed that the EB concentration in the electrolyte was below the detection limit ($<0.02 \text{ mM}$). The potential dependence of acetophenone generation on Ru-CTF/GDE (Figure 4) indicated that the onset potential of acetophenone generation was ca. 1.2-1.3 V vs. RHE. In addition, we have confirmed that RuO_2 supported by carbon nanoparticles (RuO_2/C) exhibited almost no activity for acetophenone generation (for detail, see Figure S11 and its caption). This report is the first demonstration of EB oxidation in aqueous electrolytes. Table S3 summarises the comparison between this work and other studies on the electrochemical oxidation of EB in organic electrolytes. Notably, the supply rate of gaseous EB was much higher than its consumption (reaction) rate (for the detail calculation, see the Supporting Information), although further studies on the effects of flow rate dependence are required to improve the catalytic activity.

For comparison, electrochemical measurements of Ru-CTF/GDE with 0.2 mM EB in the electrolyte instead of gaseous EB were also conducted using the same GDE electrochemical cell (Figure S1). We slowly added EB to the GDE cell and waited for the adsorption. After the EB concentration in electrolyte becomes stable (c.a. 0.2 mM), the electrolysis started. In this case, the gas chamber was filled with pure argon gas. The current density on Ru-CTF/GDE at 1.5 V vs. RHE with dissolved EB was similar or a little lower than that without EB (red curve

in Figure 3a). The amount of acetophenone generated from gaseous EB was much larger than that from the electrolyte (see Figure 3b and entries 1 and 3 in Table 1). Figure S12 shows the EB concentration during the electrolysis. Although the EB concentration of 0.2 mM is about one-seventh lower than the saturated concentration (solubility of EB in water: 1.4 mM)⁷, the acetophenone generation rate from the dissolved EB was over one-twentieth lower than that from the gaseous EB. This result demonstrates that a GDE is effective for the aqueous electrochemical oxidation of hydrophobic organic compounds. The reason for the comparable current density from dissolved EB to that in the absence of EB is also explained by the low solubility of EB (Figure 3a). Additionally, the small current originated from the oxidation of dissolved EB might be buried by the side reaction (see below section).

Detailed discussion on gaseous EB oxidation by Ru-CTF/GDE. The EB oxidation activities of Ru-CTF and CTF were compared to identify the active center. The GDE electrode with the bare CTF exhibited only a small anodic current (Figure S13a) and did not generate any product (Figure S13b and entry 4 in Table 1). These results indicate that the Ru sites in Ru-CTF serve as active centers for EB oxidation to acetophenone. Figure S8 shows that the EXAFS peak corresponding to Ru-Cl had disappeared after the electrolysis, suggesting that the Cl ions on Ru atoms were substituted with water molecules during the electrolysis. This result is consistent with our previous paper.³¹ There are several reports that single Ru atoms coordinated with water molecules are oxidized to Ru(IV)=O or Ru(V)=O over 1.3 V.⁴⁶⁻⁴⁷ Therefore, Ru=O was likely generated through oxidation of the coordinated water molecules even for Ru-CTF in a common manner to the case of Ru-based complexes. Furthermore, the onset potential of acetophenone generation (ca. 1.2-1.3 V) is similar to the potential at which Ru=O is formed (Figure 1d),^{16, 42-43} which suggests that acetophenone generation from EB oxidation was mediated by Ru=O in Ru-CTF. We confirmed that the turnover number with respect to Ru atoms exceeded 20, which indicates that Ru-CTF/GDE functioned as a catalyst

for acetophenone generation (for the detail of the TON calculation, see the Supporting Information). We propose the reaction mechanism shown in Scheme S1. A high-valency Ru-oxo ($\text{Ru}=\text{O}$) species, which is generated by two-electron water oxidation, is the active center for the oxidation of organic substrates. High-valent metal-oxo species are known to efficiently catalyze a net O-atom insertion into C-H bonds in hydrocarbons.^{10, 48-51} Thus, the $\text{Ru}=\text{O}$ species with high oxidation power facilitates O-atom insertion into C-H of EB to form 1-phenylethanol. The adsorbed alcohol is then further oxidized to acetophenone via the 2-electron transfer step.¹⁰ We would like to obtain the direct evidence of this reaction mechanism using *in situ* Raman or IR as a future study.

The side reactions of acetophenone generation were investigated next. First, other products of EB oxidation were considered. HPLC-UV measurement showed no signal at 244 nm, which corresponds to aromatic compounds, except for the peak assignable to acetophenone, as shown in Figure S2 and S10. Besides, after the electrolysis using gaseous EB, we attempted to extract adsorbed products from the GDE and Nafion membrane using methanol, and we have confirmed that there was no adsorbed side product on them. Considering that the decomposition of aromatic rings does not readily proceed on $\text{Ru}=\text{O}$ at 1.5 V,³¹ these results indicate that no other major products were generated from EB oxidation. The O_2 evolution from water oxidation was also investigated during EB oxidation using isotope-labeled water. The O_2 generation was below the detection limit of GC-MS. In addition, we have shown in our previous work that the OER activity of Ru-CTF was similar to that of a bare glassy carbon electrode.³¹ Thus, we conclude that the OER for Ru-CTF during EB oxidation was almost negligible. This is likely because, although the OER is facilitated on two contiguous Ru sites bridged by O ($\text{Ru}-\text{O}-\text{Ru}$) sites for ruthenium-based catalysts,¹⁷⁻¹⁸ the Ru atoms in Ru-CTF were mostly isolated. However, Ru-CTF/GDE without EB exhibited a larger anodic current than that for bare CTF/GDE (Figure S13a). The faradaic efficiencies (FEs) for acetophenone

at 1.3, 1.5, and 1.7 V were calculated to be 26, 24, and 22 %, respectively (Table S4). Therefore, Ru sites in Ru-CTF possibly catalyze undetectable reactions, such as the oxygenation of carbon particles in the MPL.⁵²⁻⁵³ We are planning to fabricate the GDE with high corrosion-resistant materials, such as metal, metal oxides, or boron-doped diamond.³

Stability test. The stability of Ru-CTF on GDE was investigated by repeated tests in which an EB oxidation reaction was performed over four consecutive cycles with replacement of the electrolyte every 12 h. Figure 5 shows that Ru-CTF on GDE had negligible deactivation for both I-t profiles and acetophenone generation with repeated use. These results indicate that Ru-CTF on GDE has good stability at 1.5 V vs. RHE. In addition, the Ru 3p XPS spectra of Ru-CTF/GDE did not change after the catalyst test (Figure S14). Therefore, undetectable side reactions such as MPL oxidation did not significantly affect EB oxidation within this time scale. The stability is likely attributable to the fully covalent and densely cross-linked structure of the CTFs. In contrast, the acetophenone generation rate gradually decreased with time in the absence of replacing electrolytes (Figure S15). Although the effect of the replacement of the electrolyte is still unclear, we assume that the gradual flooding of the gas diffusion layer due to water pressure was recovered or suppressed by the electrolyte replacement to some extent.¹³

4. Conclusions

Gaseous EB was successfully oxidized to acetophenone in aqueous electrolyte using a GDE that supported Ru-CTF. Singly isolated Ru-atoms coordinated with nitrogen atoms in Ru-CTF were converted to high-valency Ru=O by water oxidation, and O-atom insertion into the C-H bond of EB was facilitated. Considering that Ru-CTF is highly stable during the long-term electrolysis in aqueous solution, Ru-CTF is a novel platform as a heterogeneous electrocatalyst

for partial hydrocarbon oxidation reactions. This is the first demonstration of electrochemical hydrocarbon oxidation in aqueous electrolytes using GDEs. The three-dimensional microstructures in the GDE maximized the transportation of gaseous hydrocarbons, and the oxidation reaction occurred at the triple phase boundary. The present results clearly demonstrate that GDEs are a promising approach for the electrochemical oxidative upgrading of hydrophobic organics. However, toward the real application, we need to largely increase the total reaction rate. The improvement of both catalysts (i.e., FE, stability, and turnover frequency) and systems (i.e., electrochemical cells and flow conditions) is required to achieve a high reaction rate. These projects are in progress in our laboratory.

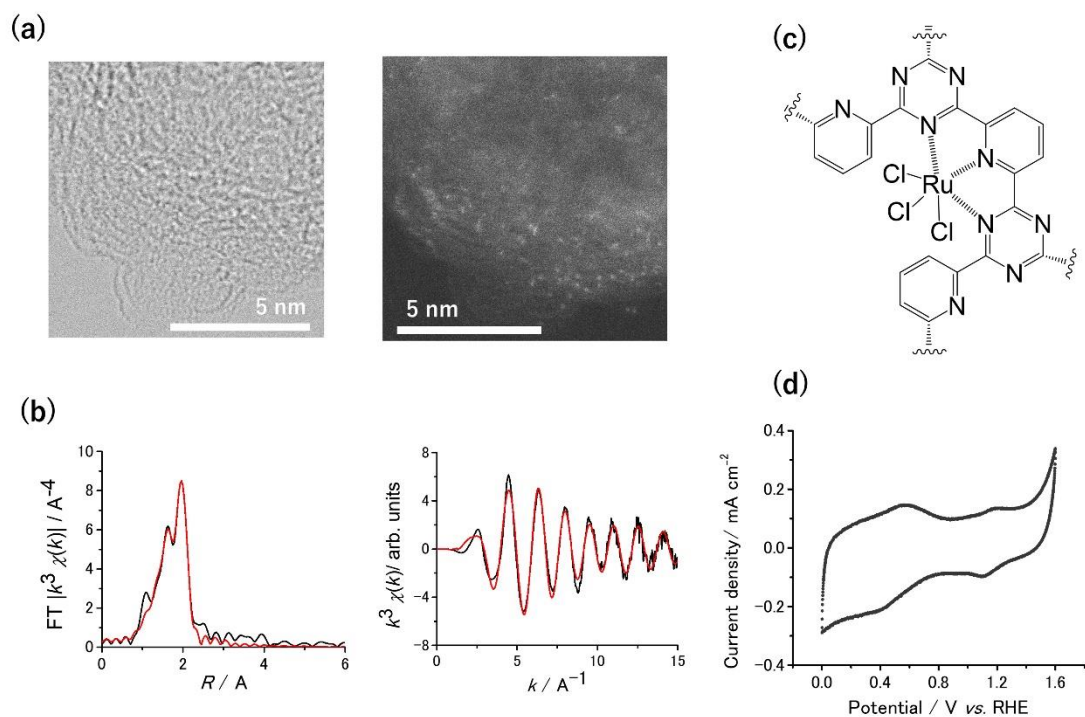


Figure 1 (a) (left) High resolution TEM and (right) the corresponding HAADF-STEM images for Ru-CTF. (b) (left) FT-EXAFS spectra and (right) for k -plot spectra for Ru-CTF powder. Black and red lines represent the measured and fitted results, respectively. (c) Schematic illustration of Ru-CTF. (d) j vs. U curves for Ru-CTF on a glassy carbon electrode in 0.1 M phosphate buffer solution (pH 7). Scan rate, $10\ mV\ s^{-1}$.

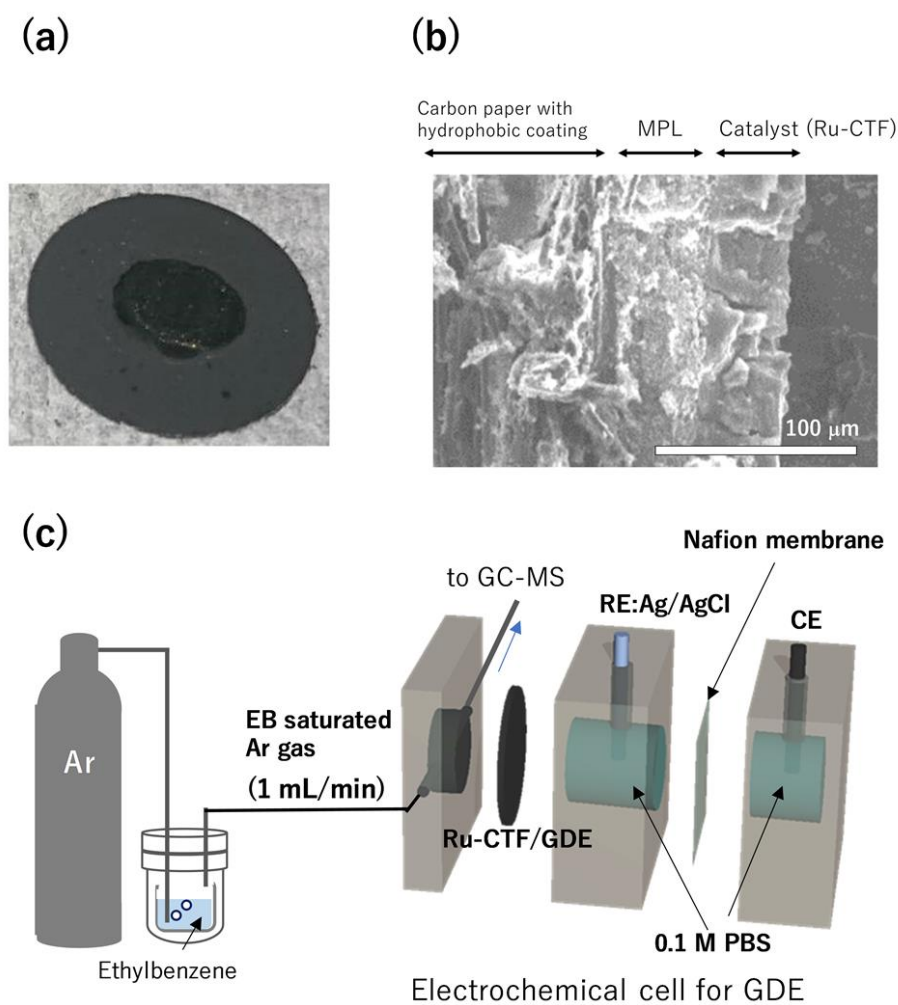


Figure 2 (a) Photograph of Ru-CTF/GDE. (b) Cross-sectional SEM image of the Ru-CTF/GDE. (c) Schematic illustration of the setup for electrochemical gaseous EB oxidation.

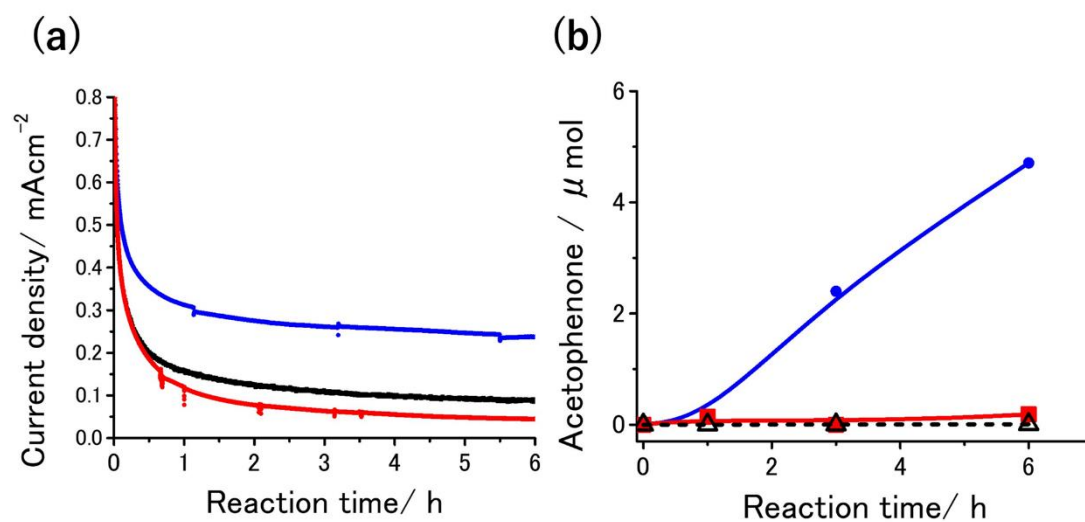


Figure 3. (a) Current densities (j) and (b) the amount of acetophenone generated as a function of time at 1.5 V vs. RHE for Ru-CTF/GDE (blue) with gaseous EB, with 0.2 mM aqueous EB (red) and without EB (black). Electrodes: GDE (1 cm^{-2}), 25 °C.

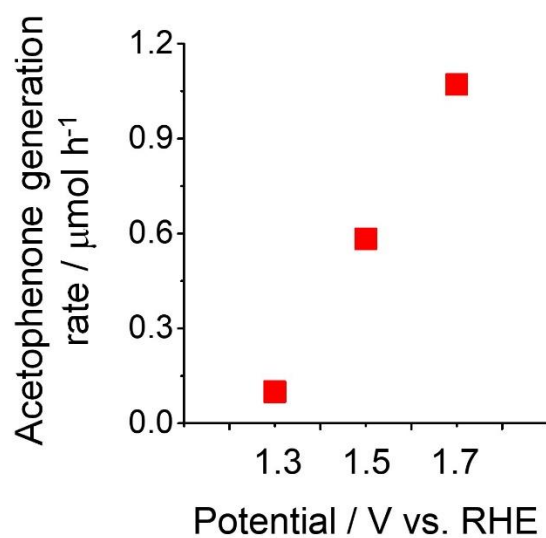


Figure 4. Dependence of the generation rate of acetophenone on the potential over Ru-CTF/GDE with gaseous EB.

Table 1. Electrochemical oxidation of EB to acetophenone^[a]

Entry	Substrate	Catalyst	Total acetophenone generation [μmol]
1	EB saturated Ar gas ^[b]	Ru-CTF	4.7
2	None ^[c]	Ru-CTF	<0.1
3	0.2 mM EB in electrolyte ^[c]	Ru-CTF	0.18
4	EB saturated Ar gas ^[b]	CTF	<0.01

[a] Electrolyte : 0.1 M phosphate buffers solutions (pH 7), Reaction times: 6 h, Electrodes: GDE (1 cm^2), Potential: 1.5 V vs. RHE, 25 °C, [b] Partial pressure of EB : 1.2×10^3 Pa, [c] Only Ar gas was supplied to the gas chamber.

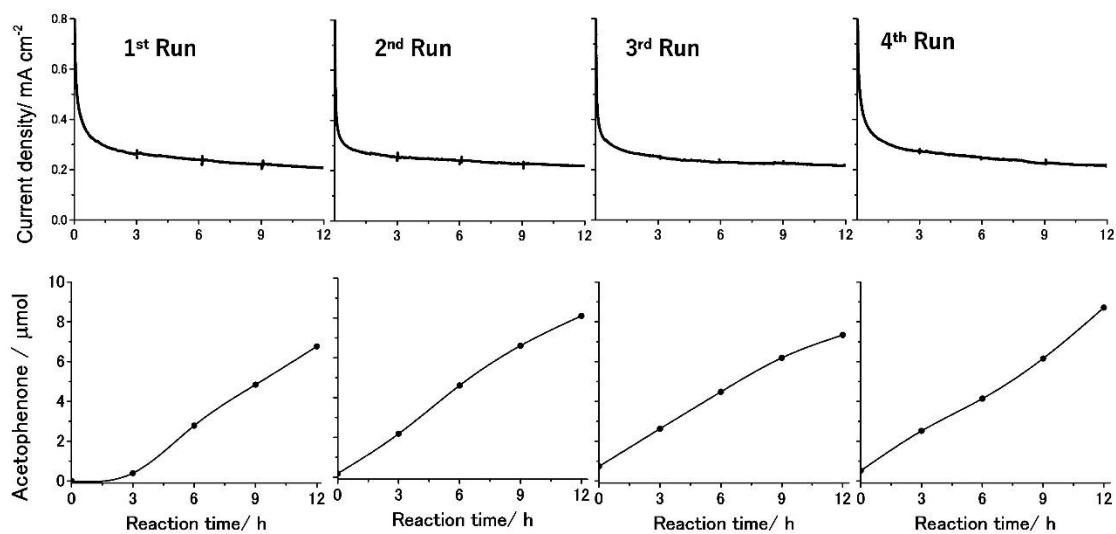


Figure 5 *j-t* curves (top) and acetophenone generation (bottom) during the reuse test of EB oxidation to acetophenone over Ru-CTF/GDE. The electrolyte (0.1 M phosphate buffer solution) was replaced every 12 h. Electrodes: GDE (1 cm²), Potential: 1.5 V vs. RHE, 25 °C.

ASSOCIATED CONTENT

Supporting Information.

GDE cell, TEM, XPS and BET results, and EXAFS analyses of bis(2,2-bipyridine)dichlororuthenium and HPLC chart.

AUTHOR INFORMATION

Corresponding Author

*E-mail for K.K.: kamiya@chem.es.osaka-u.ac.jp, S.N. : nakanishi@chem.es.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was also supported by a JSPS KAKENHI Program (grant no. 17H04798 and 20H02568). This work was also supported by CREST (grant no. JPMJCR18R3) of the Japan Science and Technology Agency (JST). Synchrotron radiation experiments were performed using the BL01B1 Beam Line of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal Nos. 2018A1349, 2019A1394, and 2019B1159). We thank Dr. T. Ina for providing technical support with the XAFS measurements at SPring-8.

REFERENCES

1. Murahashi, S. I.; Zhang, D. Ruthenium Catalyzed Biomimetic Oxidation in Organic Synthesis Inspired by Cytochrome P-450. *Chem. Soc. Rev.* **2008**, *37*, 1490-1501.
2. Que, L.; Tolman, W. B. Biologically Inspired Oxidation Catalysis. *Nature* **2008**, *455*, 333-340.
3. Amano, F.; Shintani, A.; Tsurui, K.; Mukohara, H.; Ohno, T.; Takenaka, S. Photoelectrochemical Homocoupling of Methane under Blue Light Irradiation. *ACS Energy Lett.* **2019**, *4*, 502-507.
4. Hughes, M. D.; Xu, Y. J.; Jenkins, P.; McMorn, P.; Landon, P.; Enache, D. I.; Carley, A. F.; Attard, G. A.; Hutchings, G. J.; King, F.; Stitt, E. H.; Johnston, P.; Griffin, K.; Kiely, C. J. Tunable Gold Catalysts for Selective Hydrocarbon Oxidation Under Mild Conditions. *Nature* **2005**, *437*, 1132-1135.
5. Arshadi, M.; Ghiaci, M.; Rahmanian, A.; Ghaziaskar, H.; Gil, A. Oxidation of Ethylbenzene to Acetophenone by a Mn Catalyst Supported on a Modified Nanosized SiO₂/Al₂O₃ Mixed-Oxide in Supercritical Carbon Dioxide. *Appl. Catal., B* **2012**, *119*, 81-90.
6. Fuchigami, T.; Tajima, T. Development of New Methodologies toward Green Sustainable Organic Electrode Processes. *Electrochemistry* **2006**, *74*, 585-589.
7. Bohon, R. L.; Claussen, W. F. The Solubility of Aromatic Hydrocarbons in Water. *J. Am. Chem. Soc.* **1951**, *73*, 1571-1578.
8. Khenkin, A. M.; Somekh, M.; Carmieli, R.; Neumann, R. Electrochemical Hydroxylation of Arenes Catalyzed by a Keggin Polyoxometalate with a Cobalt(IV) Heteroatom. *Angew. Chem. Int. Ed.* **2018**, *57*, 5403-5407.
9. Kojima, T.; Nakayama, K.; Ikemura, K.; Ogura, T.; Fukuzumi, S. Formation of a Ruthenium(IV)-Oxo Complex by Electron-Transfer Oxidation of a Coordinatively Saturated Ruthenium(II) Complex and Detection of Oxygen-Rebound Intermediates in C-H Bond Oxygenation. *J. Am. Chem. Soc.* **2011**, *133*, 11692-11700.
10. Vannucci, A. K.; Chen, Z. F.; Concepcion, J. J.; Meyer, T. J. Nonaqueous Electrocatalytic Oxidation of the Alkylaromatic Ethylbenzene by a Surface Bound Ru^V(O) Catalyst. *ACS Catal.* **2012**, *2*, 716-719.
11. Jang, J.; Shen, K. Z.; Morales-Guio, C. G. Electrochemical Direct Partial Oxidation of Methane to Methanol. *Joule* **2019**, *3*, 2589-2593.
12. McIntosh, S.; Gorte, R. J. Direct Hydrocarbon Solid Oxide Fuel Cells. *Chem. Rev.* **2004**, *104*, 4845-4865.
13. Dinh, C. T.; Burdyny, T.; Kibria, M. G.; Seifitokaldani, A.; Gabardo, C. M.; De Arquer, F. P. G.; Kiani, A.; Edwards, J. P.; De Luna, P.; Bushuyev, O. S.; Zou, C. Q.; Quintero-Bermudez, R.; Pang, Y. J.; Sinton, D.; Sargent, E. H. CO₂ Electroreduction to Ethylene via Hydroxide-Mediated Copper Catalysis at an Abrupt Interface. *Science* **2018**, *360*, 783-787.
14. Higgins, D.; Hahn, C.; Xiang, C. X.; Jaramillo, T. F.; Weber, A. Z. Gas-Diffusion Electrodes for Carbon Dioxide Reduction: A New Paradigm. *ACS Energy Lett.* **2019**, *4*, 317-324.
15. Goldstein, A. S.; Beer, R. H.; Drago, R. S. Catalytic-Oxidation of Hydrocarbons with O₂ or H₂O₂ Using a Sterically Hindered Ruthenium Complex. *J. Am. Chem. Soc.* **1994**, *116*, 2424-2429.
16. Hornstein, B. J.; Dattelbaum, D. M.; Schoonover, J. R.; Meyer, T. J. Reactivity of an Adsorbed Ru(VI)-Oxo Complex: Oxidation of Benzyl Alcohol. *Inorg. Chem.* **2007**, *46*, 8139-8145.

17. Comninellis, C. Electrocatalysis in the Electrochemical Conversion/Combustion of Organic Pollutants for Waste Water Treatment. *Electrochim. Acta* **1994**, *39*, 1857-1862.
18. Fang, Y. H.; Liu, Z. P. Mechanism and Tafel Lines of Electro-Oxidation of Water to Oxygen on RuO₂(110). *J. Am. Chem. Soc.* **2010**, *132*, 18214-18222.
19. Bavykina, A. V.; Goesten, M. G.; Kapteijn, F.; Makkee, M.; Gascon, J. Efficient Production of Hydrogen from Formic Acid Using a Covalent Triazine Framework Supported Molecular Catalyst. *ChemSusChem* **2015**, *8*, 809-812.
20. Bavykina, A. V.; Olivos-Suarez, A. I.; Osadchii, D.; Valecha, R.; Franz, R.; Makkee, M.; Kapteijn, F.; Gascon, J. Facile Method for the Preparation of Covalent Triazine Framework Coated Monoliths as Catalyst Support: Applications in C1 Catalysis. *ACS Appl. Mater. Interfaces* **2017**, *9*, 26060-26065.
21. Bavykina, A. V.; Rozhko, E.; Goesten, M. G.; Wezendonk, T.; Seoane, B.; Kapteijn, F.; Makkee, M.; Gascon, J. Shaping Covalent Triazine Frameworks for the Hydrogenation of Carbon Dioxide to Formic Acid. *ChemCatChem* **2016**, *8*, 2217-2221.
22. Huang, W.; Byun, J.; Rörich, I.; Ramanan, C.; Blom, P. W. M.; Lu, H.; Wang, D.; Caire da Silva, L.; Li, R.; Wang, L.; Landfester, K.; Zhang, K. A. I. Asymmetric Covalent Triazine Framework for Enhanced Visible-Light Photoredox Catalysis via Energy Transfer Cascade. *Angew. Chem. Int. Ed.* **2018**, *57*, 8316-8320.
23. Huang, W.; Ma, B. C.; Lu, H.; Li, R.; Wang, L.; Landfester, K.; Zhang, K. A. I. Visible-Light-Promoted Selective Oxidation of Alcohols Using a Covalent Triazine Framework. *ACS Catal.* **2017**, *7*, 5438-5442.
24. Huang, W.; Wang, Z. J.; Ma, B. C.; Ghasimi, S.; Gehrig, D.; Laquai, F.; Landfester, K.; Zhang, K. A. I. Hollow Nanoporous Covalent Triazine Frameworks via Acid Vapor-Assisted Solid Phase Synthesis for Enhanced Visible Light Photoactivity. *J. Mater. Chem. A* **2016**, *4*, 7555-7559.
25. Gunasekar, G. H.; Park, K.; Ganesan, V.; Lee, K.; Kim, N. K.; Jung, K. D.; Yoon, S. A Covalent Triazine Framework, Functionalized with Ir/N-Heterocyclic Carbene Sites, for the Efficient Hydrogenation of CO₂ to Formate. *Chem. Mater.* **2017**, *29*, 6740-6748.
26. Liu, T. T.; Xu, R.; Yi, J. D.; Liang, J.; Wang, X. S.; Shi, P. C.; Huang, Y. B.; Cao, R. Imidazolium-Based Cationic Covalent Triazine Frameworks for Highly Efficient Cycloaddition of Carbon Dioxide. *ChemCatChem* **2018**, *10*, 2036-2040.
27. Rajendiran, S.; Natarajan, P.; Yoon, S. A Covalent Triazine Framework-Based Heterogenized Al-Co Bimetallic Catalyst for the Ring-Expansion Carbonylation of Epoxide to β -Lactone. *RSC Advances* **2017**, *7*, 4635-4638.
28. Xu, R.; Wang, X. S.; Zhao, H.; Lin, H.; Huang, Y. B.; Cao, R. Ruthenium-Modified Porous Covalent Triazine Framework for Highly Efficient Photocatalytic Carbon Dioxide Reduction in a Solid-Gas System. *Catalysis Science & Technology* **2018**, *8*, 2224-2230.
29. Kamiya, K.; Tatebe, T.; Yamamura, S.; Iwase, K.; Harada, T.; Nakanishi, S. Selective Reduction of Nitrate by a Local Cell Catalyst Composed of Metal-Doped Covalent Triazine Frameworks. *ACS Catal.* **2018**, *8*, 2693-2698.
30. Kamai, R.; Kamiya, K.; Hashimoto, K.; Nakanishi, S. Oxygen-Tolerant Electrodes with Platinum-Loaded Covalent Triazine Frameworks for the Hydrogen Oxidation Reaction. *Angew. Chem. Int. Ed.* **2016**, *55*, 13184-13188.
31. Yamaguchi, S.; Kamiya, K.; Hashimoto, K.; Nakanishi, S. Ru Atom-Modified Covalent Triazine Framework as a Robust Electrocatalyst for Selective Alcohol Oxidation in Aqueous Electrolytes. *Chem. Commun.* **2017**, *53*, 10437-10440.

32. Iwase, K.; Yoshioka, T.; Nakanishi, S.; Hashimoto, K.; Kamiya, K. Copper-Modified Covalent Triazine Frameworks as Non-Noble-Metal Electrocatalysts for Oxygen Reduction. *Angew. Chem. Int. Ed.* **2015**, *54*, 11068-11072.
33. Kamiya, K.; Kamai, R.; Hashimoto, K.; Nakanishi, S. Platinum-Modified Covalent Triazine Frameworks Hybridized with Carbon Nanoparticles as Methanol-Tolerant Oxygen Reduction Electrocatalysts. *Nat. Commun.* **2014**, *5*, 5040.
34. Su, P. P.; Iwase, K.; Harada, T.; Kamiya, K.; Nakanishi, S. Covalent Triazine Framework Modified with Coordinatively-Unsaturated Co or Ni Atoms for CO₂ Electrochemical Reduction. *Chem. Sci.* **2018**, *9*, 3941-3947.
35. Hou, Y.; Huang, Y. B.; Liang, Y. L.; Chai, G. L.; Yi, J. D.; Zhang, T.; Zang, K. T.; Luo, J.; Xu, R.; Lin, H.; Zhang, S. Y.; Wang, H. M.; Cao, R. Unraveling the Reactivity and Selectivity of Atomically Isolated Metal-Nitrogen Sites Anchored on Porphyrinic Triazine Frameworks for Electroreduction of CO₂. *CCS Chemistry* **2019**, *1*, 384-395.
36. Yi, J. D.; Xu, R.; Chai, G. L.; Zhang, T.; Zang, K.; Nan, B.; Lin, H.; Liang, Y. L.; Lv, J.; Luo, J.; Si, R.; Huang, Y. B.; Cao, R. Cobalt Single-Atoms Anchored on Porphyrinic Triazine-Based Frameworks as Bifunctional Electrocatalysts for Oxygen Reduction and Hydrogen Evolution Reactions. *J. Mater. Chem. A* **2019**, *7*, 1252-1259.
37. Yi, J. D.; Xu, R.; Wu, Q.; Zhang, T.; Zang, K. T.; Luo, J.; Liang, Y. L.; Huang, Y. B.; Cao, R. Atomically Dispersed Iron-Nitrogen Active Sites within Porphyrinic Triazine-Based Frameworks for Oxygen Reduction Reaction in both Alkaline and Acidic Media. *ACS Energy Lett.* **2018**, *3*, 883-889.
38. Kirar, J. S.; Khare, S. Cu(II) Schiff Base Complex Intercalated into Layered Double Hydroxide for Selective Oxidation of Ethylbenzene Under Solvent-Free Conditions. *RSC Advances* **2018**, *8*, 18814-18827.
39. Qi, J. Y.; Ma, H. X.; Li, X. J.; Zhou, Z. Y.; Choi, M. C. K.; Chan, A. S. C.; Yang, Q. Y. Synthesis and Characterization of Cobalt(III) Complexes Containing 2-Pyridinecarboxamide Ligands and their Application in Catalytic Oxidation of Ethylbenzene with Dioxxygen. *Chem. Commun.* **2003**, 1294-1295.
40. Ravel, B.; Newville, M. Athena, Artemis, Hephaestus: Data Analysis for X-ray Absorption Spectroscopy Using IFEFFIT. *Journal of Synchrotron Radiation* **2005**, *12*, 537-541.
41. Yang, S.; Kim, J.; Tak, Y. J.; Soon, A.; Lee, H. Single-Atom Catalyst of Platinum Supported on Titanium Nitride for Selective Electrochemical Reactions. *Angew. Chem. Int. Ed.* **2016**, *55*, 2058-2062.
42. Lebeau, E. L.; Adeyemi, S. A.; Meyer, T. J.; Water Oxidation by [(tpy)(H₂O)₂Ru^{III}ORu^{III}(H₂O)₂(tpy)]⁴⁺. *Inorg. Chem.* **1998**, *37*, 6476-6484.
43. Meyer, T. J.; Huynh, M. H. V. The Remarkable Reactivity of High Oxidation State Ruthenium and Osmium Polypyridyl Complexes. *Inorg. Chem.* **2003**, *42*, 8140-8160.
44. Morgan, D. J. Resolving Ruthenium: XPS Studies of Common Ruthenium Materials. *Surf. Interface Anal.* **2015**, *47*, 1072-1079.
45. Rintelen, J. C.; Saylor, J. H.; Gross, P. M. The Densities and Vapor Pressures of Some Alkylbenzenes, Aliphatic Ketones and N-Amyl Chloride. *J. Am. Chem. Soc.* **1937**, *59*, 1129-1130.
46. Dobson, J. C.; Meyer, T. J. Redox Properties and Ligand Loss Chemistry in Aqua/Hydroxo/Oxo Complexes Derived from Cis- and Trans-[(bpy)₂Ru^{II}(OH)₂]²⁺. *Inorg. Chem.* **1988**, *27*, 3283-3291.
47. Hirai, Y.; Kojima, T.; Mizutani, Y.; Shiota, Y.; Yoshizawa, K.; Fukuzumi, S. Ruthenium-Catalyzed Selective and Efficient Oxygenation of Hydrocarbons with Water as an Oxygen Source. *Angew. Chem. Int. Ed.* **2008**, *47*, 5772-5776.

48. Gunay, A.; Theopold, K. H. C-H Bond Activations by Metal Oxo Compounds. *Chem. Rev.* **2010**, *110*, 1060-1081.
49. Kamiya, K.; Kuwabara, A.; Harada, T.; Nakanishi, S. Electrochemical Formation of Fe(IV)=O Derived from H₂O₂ on a Hematite Electrode as an Active Catalytic Site for Selective Hydrocarbon Oxidation Reactions. *ChemPhysChem* **2019**, *20*, 648-650.
50. Murahashi, S.; Naota, T.; Kuwabara, T.; Saito, T.; Kumobayashi, H.; Akutagawa, S. Ruthenium-Catalyzed Oxidation of Amides and Lactams with Peroxides. *J. Am. Chem. Soc.* **1990**, *112*, 7820-7822.
51. Naota, T.; Takaya, H.; Murahashi, S. I. Ruthenium-Catalyzed Reactions for Organic Synthesis. *Chem. Rev.* **1998**, *98*, 2599-2660.
52. Giordano, N.; Antonucci, P. L.; Passalacqua, E.; Pino, L.; Aricò, A. S.; Kinoshita, K. Relationship between Physicochemical Properties and Electrooxidation Behaviour of Carbon Materials. *Electrochim. Acta* **1991**, *36*, 1931-1935.
53. Maass, S.; Finsterwalder, F.; Frank, G.; Hartmann, R.; Merten, C. Carbon Support Oxidation in PEM Fuel Cell Cathodes. *J. Power Sources* **2008**, *176*, 444-451.

Table of contents

