Electronic Supplementary Information

General

RuCl₃·xH₂O (N.E. Chemcat, Co.) and MgO (Ube Industries, Ltd.) were used as received. CeO₂ (JRC-CEO-2), TiO₂ (JRC-TIO-2), Al₂O₃ (JRC-ALO-8) were obtained from the Catalysis Society of Japan. Carbon was purchased from Wako Pure Chemical Industries, Ltd. All other chemicals were purchased from Wako Pure Chemical Industries, Ltd., the Tokyo Kasei Co., and Sigma-Aldrich Inc. and were used following purification. ¹H NMR and ¹³C NMR spectra were obtained using a JEOL GSX-270 or JNM-ESC400 spectrometer and chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Ru K-edge X-ray absorption data were collected in quick mode and recorded in transmission mode using a BL01B1 station attached to a Si(311) monochromator at the SPring-8 (JASRI) facility in Harima, Japan (Proposal Nos. 2015A1575, 2016A1103, and 2017A1239). Data analysis was carried out using the REX2000 program (ver. 2.5.7, Rigaku). Powder X-ray diffraction (XRD) patterns were recorded using a Philips X'Pert-MPD with Cu-Kα radiation. X-ray fluorescence (XRF) measurements were carried out using a Supermini benchtop wavelength-dispersive X-ray fluorescence spectrometer (Rigaku). Transmission electron microscopy (TEM) images were obtained using a Hitachi HF-2000 type microscope, operating at 200 kV, at the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University.

Preparation of the Ru/magadiite catalyst

Magadiite (H₂Na₂Si₁₄O₃₀) was synthesized via a hydrothermal reaction between SiO₂ (Wakogel Q-69), NaOH, and deionized water according to a previously reported procedure. Magadiite (0.6 g) was added to an aqueous solution (50 mL) containing RuCl₃·xH₂O (0.0612 g, Ru: 250 μmol), and the resulting mixture was stirred at room temperature for 12 h. The obtained solid was filtered, washed, and dried, affording Ru/magadiite as a dark grey powder. The Ru content was determined to be 3.42 wt.% by X-ray fluorescence measurements.

Preparation of other supported Ru catalysts

The other supported Ru catalysts were prepared through deposition methods. The support (CeO₂, Al₂O₃, TiO₂, MgO, or C, 0.6 g) was added to an aqueous solution containing RuCl₃·xH₂O (0.0612 g,
Ru: 250 μmol). An aqueous NaOH solution (1N, 500–1000 μL) was then added to the above mixture and the resulting slurry was stirred at room temperature for 12 h. The obtained solid was filtered, washed, and dried, affording the corresponding supported Ru catalysts.

**Preparation of other magadiite-supported metal catalysts (M/magadiite)**

The other magadiite-supported metal catalysts were prepared via deposition methods. Proton-exchanged magadiite (0.6 g) was added to an aqueous solution containing Na$_2$PdCl$_4$, RhCl$_3$$\cdot$H$_2$O, (NH$_3$)$_4$PtCl$_4$, or Ni(NO$_3$)$_2$$\cdot$6H$_2$O (M: 250 μmol) prior to the addition of an aqueous NaOH solution (1N, 1000 μL) to the above mixture. The resulting slurry was then stirred at room temperature for 12 h, and the obtained solid was filtered, washed, and dried, affording the desired M/magadiite catalysts.

**Oxidative coupling of phenol derivatives with O$_2$**

The oxidative coupling of phenol derivative 1a (0.5 mmol) was conducted under O$_2$ (1 atm) in a Schlenk flask using Ru/magadiite (Ru: 16 μmol) in t-BuOH (3 mL). After the reaction, hexadecane (internal standard) and CHCl$_3$ (solvent to solve the products) were added, and the Ru/magadiite was separated by filtration. The filtrate was evaporated to remove t-BuOH and CHCl$_3$. The resulting solid was solved in CDCl$_3$ and analysed by $^1$HNMR.

**One-pot transformation of phenol derivatives to the corresponding biphenols**

The oxidative coupling of phenol derivative 1a (0.5 mmol) was conducted under O$_2$ (1 atm) in a Schlenk flask using Ru/magadiite (Ru: 16 μmol) in t-BuOH (3 mL). After completion of the coupling reaction, the reaction mixture was cooled to room temperature, and the atmosphere was changed from O$_2$ to H$_2$ (1 atm). The subsequent hydrogenation reaction was then conducted. Upon completion of the reaction, the Ru/magadiite catalyst was separated by filtration and washed with EtOH. The filtrate was evaporated to remove t-BuOH, affording the corresponding biphenols.

**Product identification**

The reaction products were identified by $^1$H NMR spectroscopy and, in each case, the chemical shifts of the products corresponded with those reported in the literature, as summarized below.

- 3,3′,5,5′-Tetramethylbiphenol (TMBP, 2a) (CAS-RN 2417-04-1)$^{52}$
- 3,3′,5,5′-Tetraisopropylbiphenol (2b) (CAS-RN 2416-95-7)$^{52}$
- 3,3′,5,5′-Tetra-t-butylbiphenol (2c) (CAS-RN 128-38-1)$^{52}$
3,3′-Di-t-butyl-5,5′-dimethylbiphenol (2d) (CAS-RN 3432-00-6)\textsuperscript{53}

3,3′,5,5′-Tetramethoxybiphenol (2e) (CAS-RN 612-69-1)\textsuperscript{54}

**XAFS measurements**

The Ru K-edge XAFS spectra of a series of Ru/magadiite catalysts were recorded in transmission mode at room temperature. Fourier transformations of the $k^3$-weighted EXAFS spectra were performed in the 4 Å < $k$ < 12 Å range to obtain radial structural functions.

![Figure S1. XRD patterns of Ru/magadiite (blue), the proton-exchanged magadiite (H-magadiite) (red), and the parent magadiite (Na-magadiite) (green).](image-url)
Figure S2. TEM images and size distributions of a) the fresh Ru/magadiite and b) the Ru/magadiite after the one-pot reaction (used Ru/magadiite).
Figure S3. EXAFS spectra of (a) the fresh Ru/magadiite, (b) the Ru/magadiite after treatment of (a) with H₂, (c) the Ru/magadiite after treatment of (b) with air, (d) used Ru/magadiite, (e) the used Ru/magadiite after treatment of (d) with H₂, (f) the used Ru/magadiite after treatment of (e) with O₂, (g) Ru powder, (h) Ru(OH)₃, (i) RuO₂.

Figure S4. XANES spectra of (a) used Ru/magadiite, (b) the used Ru/magadiite after treatment of (a) with H₂, (c) the used Ru/magadiite after treatment of (b) with O₂, (d) Ru powder, (e) Ru(OH)₃.
The edge position of XANES spectrum of the used Ru/magadiite (Figure S4(a)) was similar to that of Ru(OH)₃ (Figure S4(e)), indicating that the Ru NP in the used Ru/magadiite exists as Ru³⁺ species. After treatment of the used Ru/magadiite with H₂, the edge position of the used Ru/magadiite shifted towards lower energy, which was assigned to Ru(0) species (Figure S4(b)). This change shows the reduction of Ru³⁺ species to the Ru(0) species under H₂ atmosphere. Furthermore, when the H₂-treated used Ru/magadiite was exposed to O₂, the XANES spectrum returned to that of the used Ru-magadiite (Figure S4(c)). This result suggests that the Ru³⁺ species is regenerated by re-oxidation of the Ru(0) species with O₂. These phenomena were also supported by EXAFS spectra and almost the same in the case of in situ XAFS measurement of the freshly prepared Ru/magadiite. Accordingly, the redox property of the Ru/magadiite maintained after the one-pot reaction.

Table S1. Aerobic oxidative coupling of DMP using various supported metal catalysts

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a Determined by ¹H NMR standard technique. b The ratio of total yield of DPQ and TMBP to conversion of DMP.

References