

Supplementary Information

Preparation of Inorganic-organic Hybrid Mesoporous Material Incorporating Organoruthenium Complexes ($-[C_6H_4RuCp]PF_6-$) and Its Application for Heterogeneous Catalyst

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Materials. Octadecyltrimethylammonium chloride, 1-hexyne, and triethylsilane were purchased from Tokyo Kasei Kogyo Co., Ltd. 1,4-bis(triethoxysilyl) benzene was obtained from Aldrich. Thallium cyclopentadienide, bis-benzeneruthenium(II) chloride, and ammonium hexafluorophosphate were obtained from Wako Pure Chemical Ind., Ltd. Dry acetonitrile, dry chloroform, and HCl (37%) were also obtained from Nacalai Tesque Inc. All chemicals were used without further purification.

Characterization methods. Powder X-ray diffraction (XRD) patterns were recorded using Cu K α radiation ($\lambda=1.5406\text{ \AA}$) on a Shimadzu XRD-6100 diffractometer operating at 40 kV and 30 mA. Diffuse reflectance UV-vis spectra were measured at 298 K with a Shimadzu UV-2200A double-beam digital spectrophotometer. XAFS (XANES and EXAFS) spectra were obtained at the BL-01B1 facility of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI). The Ru K-edge X-ray absorption spectra were recorded in fluorescence mode with a Si(111) two-crystal monochromator at room temperature. The extended X-ray absorption fine structure (EXAFS) data were examined using the analysis program (Rigaku REX2000). The pre-edge peaks in the X-ray absorption near-edge structure (XANES) regions were normalized for atomic absorption, based on the average absorption coefficient of the spectral region. Fourier transformations were performed on k^3 -weighted EXAFS oscillations in the range 3–16 \AA^{-1} to obtain the radial structure function. Nitrogen adsorption-desorption isotherms were recorded by using a BEL-SORP max (BEL Japan, Inc.) at 77 K after degassing of samples under vacuum at 473 K for 2 h.

Hydrosilylation of 1-hexyne. The hydrosilylation of 1-hexyne with triethylsilane was performed by using specially manufactured vacuum line system equipped with 1-hexyne and triethylsilane reservoir. The fixed amount of catalyst (30 mg) was charged into the reaction vessel (volume: 80 ml) and pre-evacuated at 473 K for 1 h. The hydrosilylation of 1-hexyne (540 μmol) with triethylsilane (540 μmol) was carried out at each temperature (298, 473, 523, 573, and 623 K) for 15 h. The analysis of the products was performed on a gas chromatograph (Shimadzu GC-14B with a flame ionization detector) equipped InertCap[®]1 capillary column. The turnover number (TON) was determined as the total amounts (in mol) of products (α -vinylsilane and β -vinylsilanes) divided by the amount (in mol) of $-\text{[C}_6\text{H}_4\text{RuCp]PF}_6-$ moieties within HMM-phRuCpPF₆ used for the reaction (30 mg).

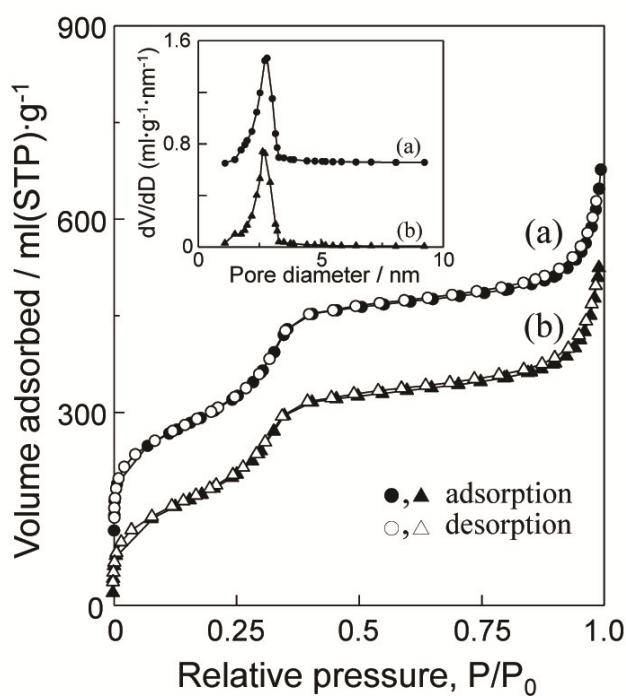


Figure S1. Nitrogen adsorption/desorption isotherms and (inset) pore size distribution curve of (a) HMM-ph and (b) HMM-phRuCpPF₆.

Table S1. Textual properties of HMM-ph and HMM-phRuCpPF₆.

Samples	Surface area / $\text{m}^2 \text{g}^{-1}$	Pore volume ^a / $\text{cm}^3 \text{g}^{-1}$
HMM-ph	809	0.78
HMM-phRuCpPF ₆	789	0.72

^a Determined from the Barret-Joyner-Halenda (BJH) method.