Dispersed Ru nanoclusters transformed from grafted trinuclear Ru complex on SiO₂ for selective alcohol oxidation

Satoshi Muratsugu*a,b,c, Min Hwee Limad, Takahiro Itohc, Wipavee Thumrongpatanaraksa,c, Mio Kondoa,c, Shigeyuki Masaoka*c, T. S. Andy Horde and Mizuki Tada*a,b,c,g

a Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki, Aichi 444-8585, Japan.
b Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8602, Japan.
E-mail: smuratsugu@chem.nagoya-u.ac.jp
c Department of Structural Molecular Science, The Graduate University for Advanced Studies (SOKENDAI), 38 Nishigo-Naka, Myodaiji, Okazaki, Aichi 444-8585, Japan.
d Department of Chemistry, National University of Singapore, 3 Science Drive 3, S117543, Singapore.
e Center for Catalysis, Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Ratchatewi, Bangkok, 10400 Thailand.
f Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 3 Research Link, S117602, Singapore.
g Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8602, Japan.
E-mail: mtada@chem.nagoya-u.ac.jp; Tel: +81-52-788-6200.
Fig. S1. (A, B) FT-IR spectra for Py-et-Si(OEt)$_3$ and B in (A) the vibration region and (B) in the ring-vibration and the rotation region. (C) FT-IR spectra for A, A-Py$_3$, B, C, and A+SiO$_2$ (impregnated).
Fig. S2. $^{13}$C liquid-state NMR of Py-et-Si(OEt)$_3$ (in DMSO-$d_6$) and $^{13}$C SS MAS NMR of B.
Fig. S3. (A) $k^3$-Weighted Ru K-edge EXAFS oscillations and (B) their Fourier transforms for Ru powder, RuO$_2$, A, C, D, E, and F (Ru: 3 wt%). Black solid lines in (B): observed data and red dashed lines: fitted data.
**Fig. S4.** Normalized Ru K-edge XANES spectra of Ru powder, RuO$_2$, A, C, D, E, and F.
Fig. S5. XRD spectra of Ru powder, RuO₂, D, E, and F (Ru: 3 wt%).
Fig. S6. TEM images of (A) D and (B) E.
Fig. S7. TEM images of D (Ru: 1 wt%, 3 wt%, and 6 wt%).
Fig. S8. $k^3$-Weighted Ru K-edge EXAFS Fourier transforms for D (fresh, Ru: 3 wt%) and D (after the benzyl alcohol oxidation, Ru: 3 wt%) measured at 20 K.
Fig. S9. Conversion – time plot for the selective oxidation of benzyl alcohol on D (●), and test of heterogeneous nature after the removal of solid part (□). Reaction conditions: Ru$_3$ = 1.0 $\times$ 10$^{-5}$ mol, Ru$_3$/benzyl alcohol/dodecane (internal standard) = 1/100/50 (molar ratio), 0.33 mol L$^{-1}$ of benzyl alcohol in toluene, 353 K, 101.3 kPa of O$_2$, 6 h.