Supporting Information

Acceptorless dehydrogenative coupling of primary alcohols to esters by heterogeneous Pt catalysts

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Experimental

General. Commercially available organic compounds (from Tokyo Chemical Industry or Kanto Chemical) were used without further purification. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA'-1 (Frontier Laboratories Ltd.) using nitrogen and He as the carrier gas.

Catalyst preparation. SnO2 was prepared by calcination of H2SnO3 (Kojundo Chemical Laboratory Co., Ltd.) at 500 °C for 3 h. Nb2O5 was prepared by calcination of niobic acid (CBMMI) at 500 °C for 3 h. SiO2 (Q-10, 300 m2 g−1) was supplied from Fuji Silysia Chemical Ltd. HBEA zeolite (JRC-Z-HB25, SiO2/Al2O3= 25±5), MgO (JRC-MGO-3), TiO2 (JRC-TIO-4), CeO2 (JRC-CEO-3) was supplied from Catalysis Society of Japan. γ-Al2O3 was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) for 3 h at 900 °C. ZrO2 was prepared by calcination (500 °C for 3 h) of ZrO2·nH2O prepared by hydrolysis of zirconium oxynitrate 2-hydrate in water by aqueous NH4OH solution, followed by filtration of precipitate, washing with water three times, and drying at 100 °C for 12 h.

Precursor of Pt/SnO2 was prepared by an impregnation method; a mixture of SnO2 and an aqueous HNO3 solution of Pt(NH3)2(NO3)2 was evaporated at 50 °C, followed by drying at 90 °C for 12 h. Before each catalytic experiment, the Pt/SnO2 catalyst (with Pt loading of 5 wt%) was prepared by in situ pre-reduction of the precursor in a pyrex tube under a flow of H2 (20 cm3 min−1) at 150 °C for 0.5 h. Other supported Pt catalysts (Pt = 5 wt%) were prepared by the same method. SnO2–supported metal catalysts, M/SnO2 (M = Ni, Cu, Co, Ag, Pd, Ru, Rh, Re, Ir) with metal loading of 5 wt% were prepared by the impregnation method in the similar manner as Pt/SnO2 using aqueous solution of metal nitrates (for Ni, Cu, Co, Ag), RuCl3, IrCl3·nH2O or NH4ReO4 or aqueous HNO3 solution of Pd(NO3)2. A commercial Pt-loaded carbon catalyst (Pt/C, Pt = 5 wt%) was purchased from N.E. Chemcat, Corporation.

Catalytic reactions. Pt/SnO2 was used as a standard catalyst. After the pre-reduction at 150 °C, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air as follows. The mixture of alcohol (1 mmol) and n-dodecane (0.2 mmol) was injected to the
pre-reduced catalyst inside the reactor (cylindrical glass tube, 18 cm$^3$) through a septum inlet, followed by filling 1 atm N$_2$.

Then, the resulting mixture was stirred and heated at 180 °C. Conversion and yields of products were determined by GC using n-dodecane as an internal standard adopting the GC-sensitivity estimated using the isolated product. The products were identified by GC-MS equipped with the same column as GC. The analysis of the gas phase product (H$_2$) was carried out by the mass spectrometer (BELMASS). Another set of catalytic experiments was carried out to determine isolated yields of ester as follows. After the reaction, the catalyst was removed by filtration and the reaction mixture was concentrated under vacuum evaporator to remove the volatile compounds. Then, the esters in Table 3 were isolated by column chromatography using silica gel 60 (spherical, 63-210 μm, Kanto Chemical Co. Ltd.) with hexane/ethylacetate (2/98 or 5/95) as the eluting solvent, followed by analyses by $^1$H NMR, $^{13}$C NMR and GCMS.

**In situ IR.** In situ IR spectra were recorded using a JASCO FT/IR-4200 equipped with an MCT detector. The closed IR cell surrounded by the Dewar vessel was connected to an evacuation system. During the IR measurement, the IR cell was cooled by freezing mixture of dry ice/ethanol in the Dewar vessel, and the thermocouple near the sample showed -50 ± 3 °C. The sample was pressed into a 30 mg of self-supporting wafer ($\phi$ = 2 cm) and mounted into the IR cell with CaF$_2$ windows. Spectra were measured accumulating 15 scans at a resolution of 4 cm$^{-1}$. After in situ pre-evacuation of the sample at 500 °C for 0.5 h, a reference spectrum of the sample disc (SnO$_2$, γ-Al$_2$O$_3$ or SiO$_2$) was measured at -50 °C. Then, the sample was exposed to 2 Pa of benzaldehyde at -50 °C for 120 s, followed by evacuation for 1000 s. Then a differential IR spectrum, with respect to the reference spectrum, was recorded at -50 °C.

**NMR and GCMS analysis**

H and $^{13}$C NMR spectra were recorded using at ambient temperature on JEOL-ECX 600 operating at 600.17 and 150.91 MHz, respectively with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and $d$-solvent peaks (77.00 ppm, chloroform), respectively. Abbreviations used in the NMR experiments: s, singlet d, doublet; t, triplet; m, multiplet. GC-MS spectra were recorded by SHIMADZU QP2010.

**Octanoic acid octyl ester (C$_{16}$H$_{32}$O$_2$) .\(^1\)**

![Octanoic acid octyl ester](image)

$^1$H NMR (600.17 MHz, CDCl$_3$), TMS: δ 4.04 (t, J = 6.84 Hz, 2H ), 2.28 (t, J = 7.56 Hz, 2H), 1.62-1.58 (m, 4H), 1.33-1.24 (m, 18H), 0.86 (t, J = 6.90 Hz, 6H); $^{13}$C NMR (150.91 MHz, CDCl$_3$) δ 174.37, 64.53, 34.41, 31.90, 31.76, 31.64, 29.19, 29.16, 29.08, 28.90, 28.60, 25.91, 25.00, 22.61, 22.57, 14.01; GC-MS m/e 256.24.

**Decanoic acid decyl ester (C$_{20}$H$_{40}$O$_2$) .\(^2\)**

![Decanoic acid decyl ester](image)
1H NMR (600.17 MHz, CDCl$_3$), TMS: δ 4.05 (t, $J = 6.84$ Hz, 2H), 2.28 (t, $J = 7.56$ Hz, 2H), 1.63-1.60 (m, 4H), 1.32-1.19 (m, 26H), 0.88 (t, $J = 6.90$, 6H); 13C NMR (150.91 MHz, CDCl$_3$) δ 173.91, 64.36, 34.41, 31.97, 29.75, 29.58, 29.48 (C×2), 29.35, 29.32 (C×2), 29.31, 29.20 (C×2), 28.70, 25.98, 25.06, 25.86, 22.70 (C×2); GC-MS m/e 312.41.

Heptanoic acid heptyl ester (C$_{14}$H$_{28}$O$_2$):$^3$

\[\text{\textsuperscript{1}}\text{H NMR (600.17 MHz, CDCl}_3\text{), TMS: δ 4.05 (t, } J = 6.90 \text{ Hz, 2H), 2.27 (t, } J = 7.56 \text{ Hz, 2H), 1.64-1.57 (m, 4H), 1.34-1.24 (m, 14H), 0.98-0.85 (m, 6H); 13C NMR (150.91 MHz, CDCl}_3\text{) δ 173.88, 64.30, 34.34, 31.69, 31.43, 28.88, 28.79, 28.63, 25.86, 24.94, 22.53, 22.45, 13.99, 13.94; GC-MS m/e 228.20.}\]

Hexanoic acid hexyl ester (C$_{12}$H$_{24}$O$_2$):$^4$

\[\text{\textsuperscript{1}}\text{H NMR (600.17 MHz, CDCl}_3\text{), TMS: δ 4.05 (t, } J = 6.90 \text{ Hz, 2H), 2.28 (t, } J = 6.90 \text{ Hz, 2H), 1.66-1.56 (m, 4H), 1.38-1.19 (m, 10H), 0.88-0.83 (m, 6H); 13C NMR (150.91 MHz, CDCl}_3\text{) δ 173.95, 64.33, 34.32, 31.39, 31.28, 28.57, 25.55, 24.67, 22.49, 22.28, 13.93, 13.86; GC-MS m/e 200.10.}\]

Cyclohexane methanoic acid cyclohexane methyl ester (C$_{13}$H$_{22}$O$_2$):$^4$

\[\text{\textsuperscript{1}}\text{H NMR (600.17 MHz, CDCl}_3\text{); TMS: δ 3.86-3.84(m, 2H), 2.30-2.26 (m, 1H), 1.90-1.88 (m, 2H), 1.72-1.62 (m, 8H), 1.45-1.39 (m, 2H), 1.29-1.11 (m, 6H), 0.98-0.92 (m, 1H); 13C NMR (150.91 MHz, CDCl}_3\text{) δ 176.18, 69.23, 43.31, 37.15, 29.65 (C×2), 29.06 (C×2), 26.36, 25.76, 25.68 (C×2), 25.46; GC-MS m/e 224.20.}\]

4-Fluro benzoic acid 4-fluro benzyl ester (C$_{14}$H$_{10}$F$_2$O$_2$):$^5$

\[\text{\textsuperscript{1}}\text{H NMR (600.17 MHz, CDCl}_3\text{); TMS: δ 8.11-8.06 (m, 2H), 7.42 (d, } J = 5.52 \text{ Hz, 2H), 7.12-7.05 (m, 4H), 5.31 (s, 2H); 13C NMR (150.91 MHz, CDCl}_3\text{) δ 165.84 (d, } J = 254.50 \text{ Hz), 165.39, 162.70 (d, } J = 247.58 \text{ Hz), 161.88, 132.23 (d, } J = 9.20 \text{ Hz), 131.70 (d, } J = 3.1 \text{ Hz), 130.27 (d, } J = 8.07, 126.24 (d, } J = 3 \text{ Hz), 115.56 (d, } J = 21.88 \text{ Hz), 66.12; GC-MS m/e 248.19.}\]

Benzoic acid benzyl ester (C$_{14}$H$_{12}$O$_2$):$^5$

\[\text{\textsuperscript{1}}\text{H NMR (600.17 MHz, CDCl}_3\text{); TMS: δ 8.11-8.06 (m, 2H), 7.42 (d, } J = 5.52 \text{ Hz, 2H), 7.12-7.05 (m, 4H), 5.31 (s, 2H); 13C NMR (150.91 MHz, CDCl}_3\text{) δ 165.84 (d, } J = 254.50 \text{ Hz), 165.39, 162.70 (d, } J = 247.58 \text{ Hz), 161.88, 132.23 (d, } J = 9.20 \text{ Hz), 131.70 (d, } J = 3.1 \text{ Hz), 130.27 (d, } J = 8.07, 126.24 (d, } J = 3 \text{ Hz), 115.56 (d, } J = 21.88 \text{ Hz), 66.12; GC-MS m/e 248.19.}\]
\(^1\)H NMR (600.17 MHz, CDCl\(_3\)); TMS: \(\delta\) 8.10-8.09 (m, 2H), 7.56 (t, \(J = 6.90\) Hz, 1H), 7.47-7.44 (m, 4H), 7.40 (t, \(J = 7.50\) Hz, 2H), 7.37-7.34 (m, 1H), 5.36 (s, 2H); \(^{13}\)C NMR (150.91 MHz, CDCl\(_3\)) \(\delta\) 166.38, 136.01, 132.98, 130.09, 129.66 (C×2), 128.55(C×2), 128.33(C×2), 128.20, 128.12(C×2), 66.64; GC-MS m/e 212.16.

**References**
