Supporting information

Hydrogenation of *n*-octanoic acid to 1-octanol over a heterogeneous Mo-Pt/SiO_2 catalyst under solvent-free conditions

Masazumi Tamura,[a],* Kohei Yugeta,[b] Yoshinao Nakagawa,[b] Keiichi Tomishige[b],*

[a]Research Center for Artificial Photosynthesis, Osaka Metropolitan University, 3-3-138 Sugimoto, Sumiyoshi, Osaka, 558-8585, Japan.

[b]Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan.

*Corresponding authors: E-mail: mtamura@osaka-cu.ac.jp, tomi@erec.che.tohoku.ac.jp

Experimental

Catalyst preparation

Pt/SiO_2 (Pt = 2 wt%) and Mo/SiO_2 (Mo = 20 wt%) catalysts were prepared by impregnating silica with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Soekawa Chemicals) and $(NH_4)_7Mo_7O_{24}\cdot 4H_2O$ (FUJIFILM Wako Pure Chemical Corporation). The silica (G-6, BET surface area 535 m^2/g) was supplied by Fuji Silysia Chemical Ltd. After the impregnation procedure and drying at 383 K for 12 h, they were calcined in air at 673 K for 3 h. $Mo\text{-}Pt/SiO_2$ catalysts were prepared by impregnating Pt/SiO_2 after the drying procedure with an aqueous solution of $(NH_4)_7Mo_7O_{24}\cdot 4H_2O$. The loading amount of Pt was 0.2-4 wt%, and that of Mo was 5-30 wt%. All catalysts were in powder form. Other $Mo\text{-}M/SiO_2$ (M=Rh, Ir, Ru and Pd) catalysts were also prepared by the same method by using the corresponding precursors: $RhCl_3\cdot 3H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Ir(NO_3)_4$ (Furuya Metal Co., Lrd.), $Ru(NO)(NO_3)_{3-x}(OH)_x$ (Sigma-Aldrich) and $Pd(NO_3)_2$ (Sigma-Aldrich).

Activity tests

Activity tests were performed in a 190-mL stainless steel autoclave with an inserted glass vessel. The calcined catalysts were reduced in H_2 flow (100% H_2 30 mL/min) at temperature (873-1273 K) for 1 h by using a quartz glass tube before the reaction. The reduced catalysts were introduced to an autoclave under N_2 atmosphere by using a glove box in order to avoid exposing the catalyst to air. A spinner and *n*-octanoic acid (Wako Pure Chemical Industries, Ltd., >95.0%) were added in the autoclave. After sealing the reactor, the air content was purged by flushing three times with 1 MPa H_2. The autoclave was then heated to appropriate temperatures (333-413 K), and the temperature was monitored using a thermocouple inserted in the autoclave. After the temperature reached the desired one, the

H_2 pressure was increased to appropriate pressures (typically 8 MPa). During the experiment, the stirring rate was fixed at 250 rpm (magnetic stirring). After an appropriate reaction time, the reactor was cooled down and the gases were collected in a gas bag. The autoclave contents were transferred to a vial with THF and 2-methoxyethanol as a washing solvent and internal standard, respectively, and the catalyst was separated by centrifugation.

The products were analyzed by using a gas chromatograph equipped with FID (Shimadzu GC-2014). A HP-FFAP capillary column (diameter 0.25 mm, 30 m) was used for the separation of products in the liquid phase such as *n*-octanoic acid, 1-octanol, *n*-octane and *n*-heptane. A Porapak N (diameter 3.0 mm, 3.0 m) packed column was used for the separation of products in the gas phase such as CO_2, CH_4 and C_2H_6. The conversion, selectivity, carbon balance and formation rate (mmol h^{-1} g_{Cat}^{-1}) were defined on the carbon basis as shown below:

Conversion (%) = (1-(residual substrate amount (mol)) / (introduced substrate amount (mol)) × 100

Selectivity (%) = (carbon atom amount of a product (mol)) / (carbon atom amount of all products (mol)) × 100

Carbon balance (%) = (carbon atom amount of products and residual substrate (mol)) / (carbon atom amount of introduced substrate (mol)) × 100

Formation rate (mmol h^{-1} g_{Cat}^{-1}) = (produced amount of 1-octanol (mol)) / (reaction time (h) / (catalyst amount (g))

Products were also identified using GC–MS (QP-2020, Shimadzu). The carbon balance was also confirmed in each result and the difference in the mass balance was always in the range of the experimental error (±5%).

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded by a diffractometer (MiniFlex600; Rigaku). Cu K_α (λ = 0.154 nm, 45 kV, 40 mA) radiation was used as an X-ray source. The samples after the reaction or reduction were transferred to an atmosphere separator using a globe bag under N_2 atmosphere to avoid exposure to air. The XRD patterns were normalized by the area of SiO_2 patterns intensity. The particle size (d) on the catalysts was calculated by the Scherrer's equation. XRD patterns were fitted by some Gaussian and Lorentzian functions.

Field Emission-Scanning Transmission electron microscope (FE-STEM) images were taken with HD-2700 (Hitachi High-Technologies Corporation). The samples were dispersed in ethanol and placed on Cu grids under air atmosphere. Aver-age particle size was calculated by $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$ (d_i: particle size, n_i: number of particles with d_i).

Temperature-programmed reduction (TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector and frozen acetone trap using 5% H_2 diluted with Ar (30 mL/min). The amount of catalyst was ~0.05 g, and the temperature was increased from room temperature to 1173 K at a heating rate of 10 K/min.

Supporting Figures and Tables

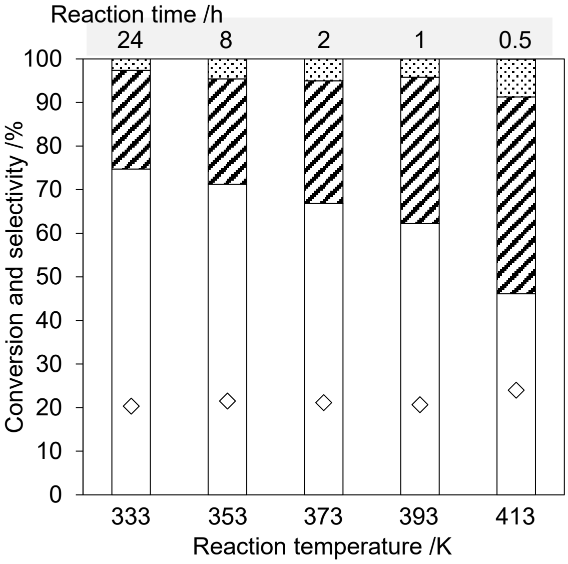

Figure S1 Effect of reaction temperatures in hydrogenation of *n*-octanoic acid. Diamond: Conversion, Bars: Selectivity (white: 1-octanol, stripe: octyl octanoate, dot: *n*-octane).

Reaction conditions: Mo-Pt/SiO_2 (Pt/Mo=0.05, 20 wt% Mo, H_2 1173 K reduction) 0.10 g, *n*-octanoic acid 2.0 g, H_2 8 MPa.

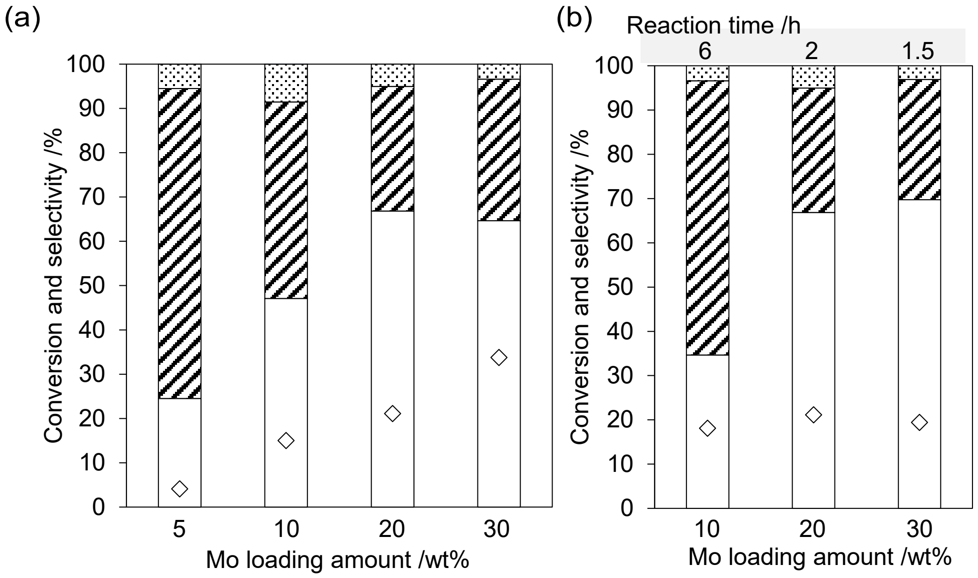

Figure S2 Effect of Mo loading amount in Mo-Pt/SiO_2 catalysts. (a) Conversion and selectivity at the same reaction time, (b) conversion and selectivity at a similar conversion level. ❋: Conversion, Bars: Selectivity (white: 1-octanol, stripe: ester, dot: octane).

Reaction conditions of (a): Mo-Pt/SiO_2 (2 wt% Pt, H_2 1173 K reduction) 0.10 g, *n*-octanoic acid 2.0 g, 373 K, H_2 8 MPa, 2 h.

Reaction conditions of (b): Mo-Pt/SiO_2 (2 wt% Pt, H_2 1173 K reduction) 0.10 g, *n*-octanoic acid 2.0 g, 373 K, H_2 8 MPa.

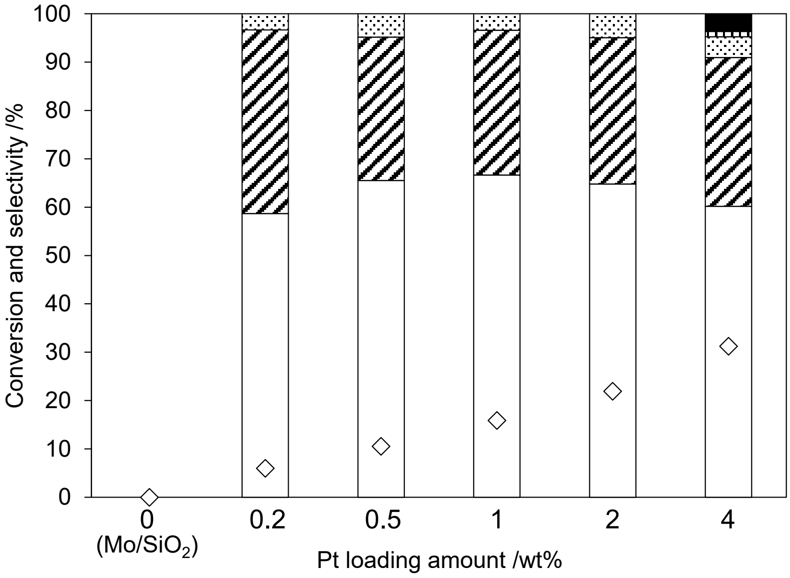

Figure S3 Effect of Pt loading amount in Mo-Pt/SiO_2 catalysts. Diamond: Conversion, Bars: Selectivity (white: 1-octanol, stripe: octyl octanoate, dot: *n*-octane, solid black: C1 gas products such as methane, CO and CO_2).

Reaction conditions: Mo-Pt/SiO_2 (Mo 20 wt%, H_2 1173 K reduction) 0.1 g or 20 wt% Mo/SiO_2, *n*-octanoic acid 2.0 g, 373 K, H_2 8 MPa, 2 h.

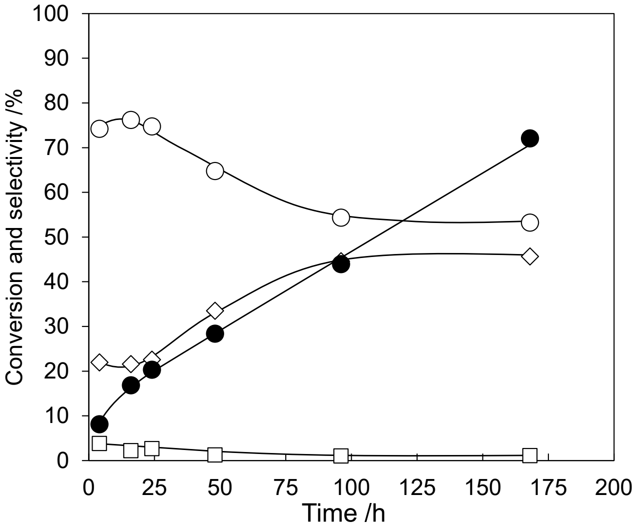

Figure S4 Time-course of hydrogenation of *n*-octanoic acid by Mo-Pt/SiO_2 catalyst at 333 K. ☙: Conversion, ❧: Selectivity to 1-octanol, ✵: selectivity to octyl octanoate, ⭘: selectivity to octane.

Reaction conditions: Mo-Pt/SiO_2 (Pt/Mo=0.05, 20 wt% Mo, H_2 1173 K reduction) 0.10 g, 333 K, *n*-octanoic acid 2.0 g, H_2 8 MPa.

Table S1 Summary of TPR analyses of Mo/SiO_2 (Mo: 20 wt%) and Pt-Mo/SiO_2 (Mo: 20 wt%, Pt: 2 wt%, Pt/Mo=0.05) catalysts

Catalyst	Mo-Pt/SiO_2(Mo: 20 wt%, Pt/Mo=0.05)		Mo/SiO_2 (Mo: 20 wt%)
Catalyst amount /mg	50.3		51.7
Mo amount /mmol	0.095		0.098
Pt amount /mmol	0.005		-
Calculation temperature range /K	r.t.-373	r.t.-1173	473-1173
Total H_2 consumption /mmol	0.079	0.288	0.318
H_2 consumption for Pt species /mmol	0.010	0.010	0.318
H_2 consumption for Mo species /mmol	0.069	0.278	-
Pt reduction degree /%	>99	>99	
Mo reduction degree /%	24	97	>99
Mo valence	4.6	0.2	0

Measurement conditions: 5% H_2/Ar 30 ml/min, 293-1673 K, 10 K /min

Assumption for estimation of metal reduction degrees: Pt is reduced near 293 K ($PtO_2 + 2H_2 \rightarrow Pt + 2H_2O$).

Mo reduction degree was determined by the following equation. $MoO_3 + 3H_2 \rightarrow 3Mo + 3H_2O$.

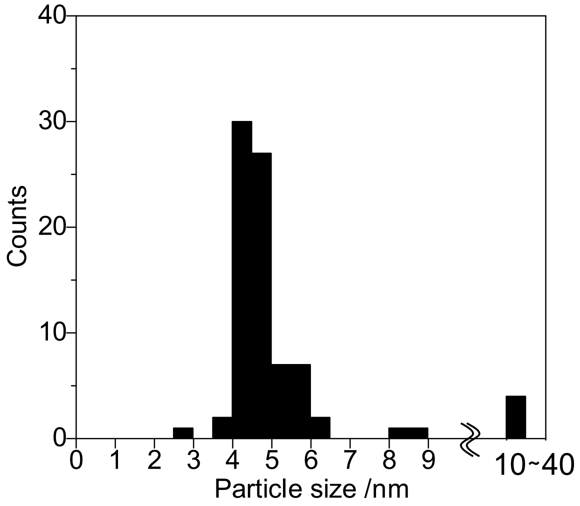

Figure S5 Particle distribution of TEM images (Figure 4(B)) of Mo-Pt/SiO_2 (Pt/Mo=0.05, 20 wt% Mo) after 1173 K H_2 reduction.

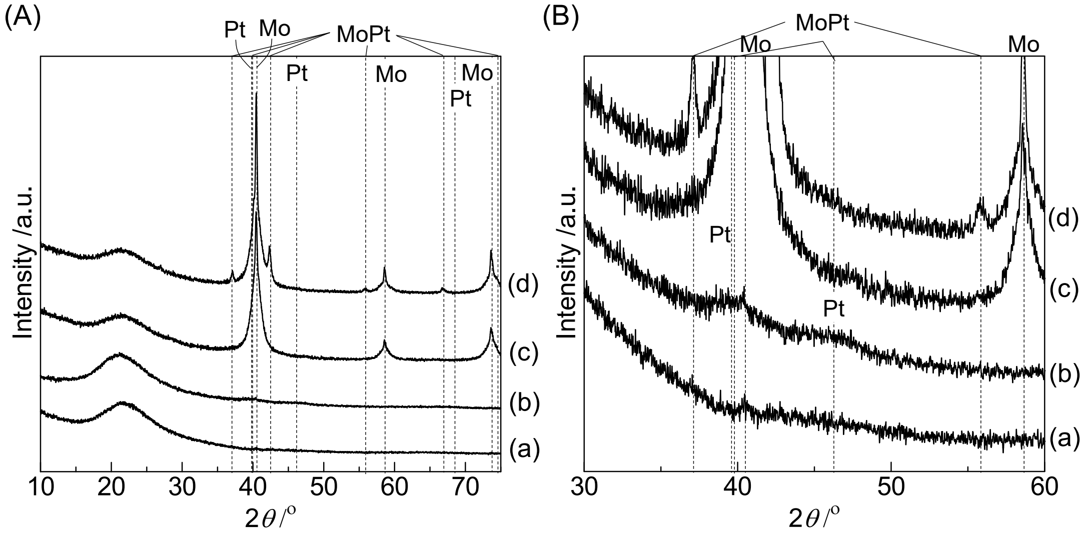

Figure S6 XRD patterns of Mo-Pt/SiO_2 (Pt/Mo=0.05, 20 wt% Mo), Mo/SiO_2 (20 wt% Mo), Pt/SiO_2 (2 wt% Pt) after reduction and SiO_2 (A) and expanded figure (B). (a) SiO_2, (b) Pt/SiO_2, (c) Mo/SiO_2, (d) Mo-Pt/SiO_2 (1173 K). The number in the parenthesis after catalyst is the H_2 reduction temperature.

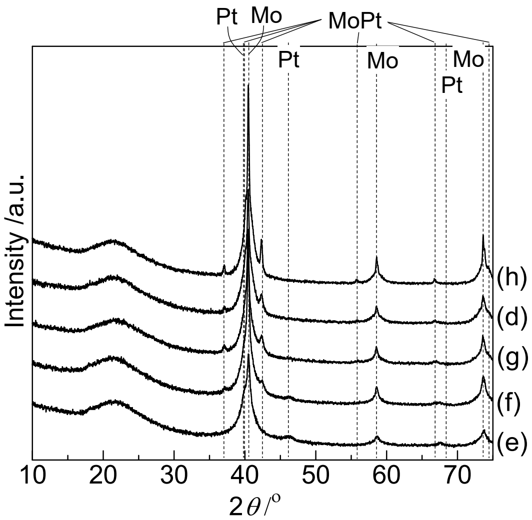

Figure S7 XRD patterns of Mo-Pt/SiO$_2$ (Pt/Mo=0.05, 20 wt% Mo) with different reduction temperatures. (d) Mo-Pt/SiO$_2$ (1173 K), (e) Mo-Pt/SiO$_2$ (873 K), (f) Mo-Pt/SiO$_2$ (973 K), (g) Mo-Pt/SiO$_2$ (1073 K), (h) Mo-Pt/SiO$_2$ (1273 K).

The number in the parenthesis after catalysts is the H$_2$ reduction temperature.

Table S2 The summary of the deconvolution of the XRD patterns of Mo-Pt/SiO_2 catalyst with different reduction temperatures and conversion.

Reduction temperature	Conv. [a] /%	XRD intensity[b]				
		MoPt alloy (~42.3°)	Pt + MoPt alloy (~39.5 °)	Mo small (~40.5 °)	Mo large (~40.5 °)	MoPt alloy (~37.1 °)
1173 K	20	384	167	3422	670	77
1073 K	18	287	384	2316	420	61
973 K	9	168	388	2348	454	35
873 K	6	93	451	2341	197	17

[a] The data are from Figure 2.

[b] The intensity is the area of the corresponding peak.

Reaction conditions: Mo-Pt/SiO_2 (Pt/Mo=0.05, Mo 20 wt%, H_2 reduction) 0.10 g, *n*-octanoic acid 2.0 g, 333 K, H_2 8 MPa, 24 h.

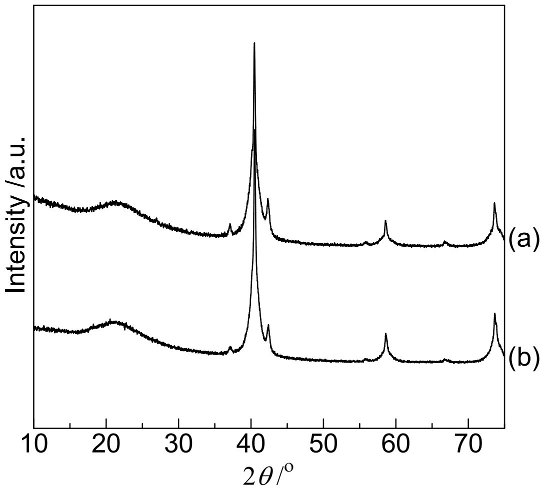

Figure S8 XRD patterns of (Pt/Mo=0.05, 20 wt% Mo, H_2 1173 K reduction) before (after reduction, (a)) and after the reaction (b).

Reaction conditions: Mo-Pt/SiO_2 (Pt/Mo=0.05, Mo 20 wt%, H_2 reduction) 0.10 g, *n*-octanoic acid 2.0 g, 333 K, H_2 8 MPa, 20 h.