Supporting Information:
Ultra-small Mo-Pt subnanoparticles enable CO₂ hydrogenation at room temperature and atmospheric pressure


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Materials and Methods

Subnanoparticle Synthesis. The TPM-DPAG4 dendrimer template was synthesised according to the previous reports. All of the subnanoparticles were synthesised in three steps: (A) complexation of metal ions, (B) supporting of metal-dendrimer complex, and (C) reduction. (A) The complexation condition of TPM-DPAG4 vs MoCl$_5$ (and PtBr$_4$) was based on the previous reports.\(^2,3\) (B) The Mo$_{12}$O$_x$, Pt$_{12}$, and Mo$_4$Pt$_8$O$_x$ precursors (0.5 wt.% ) were then supported on TiO$_2$ and dried in vacuo for 1 h. (C) The obtained samples were reduced at 500 °C for 30 min under an H$_2$ (100 ml/min, 99.99999%) atmosphere on a quartz boat in a furnace at a heating rate of 24 °C/min. Before and after the reduction, the samples were handled under an Ar atmosphere.

HAADF-STEM Observation and Ultra-small EDS Analysis. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and ultra-small energy dispersive X-ray spectrometry (EDS) analysis were performed using a JEOL JEM-ARM200F ACCELARM (accelerating voltage: 80 kV) with a spherical aberration-corrected probe. The analytes were dispersed in THF, dropped onto micro Cu grids with carbon filaments (Nisshin EM), and dried for >12h in vacuo at room temperature.

XPS Analysis. X-ray photoelectron spectroscopy (XPS) was performed using a ULVAC PHI VersaProbe III. A monochromated Al 1486.6 eV at 49.5 W was used as an X-ray source (beam diameter 200.0 μm). The neutraliser parameter was set to 0.3 V, 3.0 μA. All samples were stored and prepared under an Ar atmosphere and transferred to XPS using a transfer vessel.

XAFS Studies (including in situ XAFS). X-ray absorption fine structure (XAFS) experiments were performed at KEK-IMSS-Photon Factory, Tsukuba, Japan. The beamline BL9C (ring energy: 2.5 GeV, 450 mA) was used for Pt L$_3$-edge measurement, and NW10A (ring energy: 6.5 GeV, 50 mA) was used for Mo K-edge measurement (including in situ experiments). X-rays were monochromated by channel-cut monochromators Si(111) at BL9C and Si(311) at NW10A. The ionisation chamber for $I_0$ was filled with Ar/N$_2$ 15/85 for BL9C and 50/50 for NW10A. The ionisation chamber for $I$ was filled with Ar 100% for BL9C and Kr 100% for NW10A. The fluorescence X-rays were detected using 3-element Si-SDD (BL9C) and 19-element Ge-MSSD (NW10A). MoO$_2$ and Mo$_2$C were pelletised by mixing with BN ($\phi$ 10 mm). The samples (Mo$_{12}$O$_x$/TiO$_2$, Pt$_{12}$/TiO$_2$, and Mo$_4$Pt$_8$O$_x$/TiO$_2$) were pelletised above the BN pellets. XAFS analyses were performed using REX2000 software (Rigaku Co., ltd., Japan).\(^4\)

In situ DRIFTS. In situ diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed using a JASCO FT/IR-6600 spectrometer with a Mercury-Cadmium-Tellurium (MCT) detector (resolution: 2cm$^{-1}$, 64 scans, DRIFT mode). Samples were pretreated with H$_2$ (100%, 20 ml/min) at 150 °C. After cooling to room temperature, CO$_2$ (100%, 20 ml/min) was introduced.
Low-temperature CO$_2$ hydrogenation evaluation. Low-temperature CO$_2$ hydrogenation (RT-150 °C) was conducted using a BELCAT-II instrument under atmospheric pressure. Samples (150 mg each) were packed into a continuous flow reactor and pretreated under H$_2$ gas flow (20 ml/min) at 150°C for 1 hour. After cooling to room temperature, the reactor was purged using Ar gas (20 ml/min) for 1 hour. Then, the gases (CO$_2$ 10 ml/min, H$_2$ 10 ml/min) were introduced. The reaction temperature was elevated by 10 °C per step until 150 °C (each step was held for 30 min). The gases were detected using a GC-FID (minimum detection 0.1 ppm) with Methanizer (Converting CO and CO$_2$ to CH$_4$ to be detectable by FID) (Carrier gas: Ar, column: Shincarbon ST 50-80 (6 m×1 mm ID), column temperature: 200 °C, FID temperature: 200 °C, Methanizer temperature: 400 °C). Calibration was performed using CO/Ar gas (10%). The mass spectrum of H$_2$O (m/z 18) was monitored using a quadrupole mass spectrometer (BELMASS II, Microtrac-Bel Japan Inc., detection limit: <1 ppm).

DFT calculation. In order to analyse the adsorption mechanism of CO of each subnanoparticle on the TiO$_2$ surface, we performed ab-initio calculation based on density functional theory (DFT) calculation. We obtained the most stable unit cell structure from the Materials Project database to construct a slab model of the TiO$_2$(101) surface. The program package used was the Vienna ab initio simulation package (VASP 5.4.1). The projector-augmented wave (PAW) method was used for solving the Kohn-Sham equations, and the generalised gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) was used for calculating exchange and correlation energies. The system must satisfy periodic boundary conditions for calculations using plane wave basis sets. The coordinates of the lower atoms in the slab model are fixed. A vacuum space of 25 Å length is placed on the surface. The k-point spacing was set to $2\pi \times 0.05$ Å$^{-1}$. The cutoff energy of the plane-wave basis set was 500 eV, and the convergence condition for the self-consistent field (SCF) loop was set to $1 \times 10^{-6}$ eV. As the convergence condition for structural optimisation, the threshold of the forces on each atom was set to $5 \times 10^{-2}$ eV/Å. Spin-polarised calculations are performed. We performed all calculations taking collinear spin polarisation into account.
Supplementary Figures

**Fig. S1** HAADF-STEM observation of the Pt nanoparticles prepared from Pt$_{12}$ subnanoparticles supported on TiO$_2$ (**left**) and size distribution comparison of Pt nanoparticles and Pt$_{12}$ subnanoparticles supported on TiO$_2$ (**right**).

**Fig. S2** An example of ultra-small STEM-EDS analyses of one particle region. The average single-particle composition was determined to be Mo: Pt = 1:(2.1±0.2) by the analyses on more than 30 particles.
Fig. S3 XPS analysis of Pt4f of Mo4Pt8Ox, Pt12 subnanoparticles (A), and Mo3d of Mo4Pt8Ox, Mo12Ox subnanoparticles (B) supported on TiO2 (All spectra were calibrated using Ti2p3/2 459.5 eV and the estimated error was estimated to be ±0.1 eV). Pt L3-edge XANES spectra of Mo4Pt8Ox & Pt12 subnanoparticles (C), Mo K-edge XANES spectra of Mo4Pt8Ox & Mo12Ox subnanoparticles (D) supported on TiO2. A linear interpolation result of Mo K-edge XANES spectra to obtain the average valence states of Mo species inside the subnanoparticles (E).
**Fig. S4** CO$_2$ hydrogenation over Mo$_{12}$O$_x$ subnanoparticles supported on TiO$_2$ (A). CO$_2$ hydrogenation with a temperature range from 200-250 °C (B). Reaction condition: Catalyst used 150 mg (0.4 wt.%), CO$_2$ 10 ml/min, H$_2$ 10 ml/min, 1 bar (pre-treatment H$_2$ 20 ml/min, 150 °C, 1 h.)

**Fig. S5** Operando DRIFTS spectra of CO$_2$ hydrogenation at room temperature and atmospheric pressure employing Mo$_4$Pt$_8$O$_x$ subnanoparticles on TiO$_2$. The increase of the OH group bands indicates the generated H$_2$O adsorbs on the catalyst surface (TiO$_2$). Reaction condition: CO$_2$ 10 ml/min, H$_2$ 10 ml/min (pre-treatment H$_2$ 20 ml/min, 150 °C, 1 h.)
**Fig. S6** *In situ* Pt L₃-edge XANES spectra of Mo₄Pt₈Oₓ subnanoparticles supported on TiO₂ at room temperature.

**Fig. S7** The desorbed H₂O signals monitored using a quadrupole mass spectrometer. At slightly higher temperature like 40 °C, the m/z 18 intensity increased, indicating the detection of generated H₂O from reaction.
Fig. S8 *In situ* DRIFTS spectra comparison between Mo₄Pt₈Oₓ (A, B) and Pt₁₂ (C, D) subnanoparticles supported on TiO₂.
**Fig. S9** DFT calculations of Pt-CO adsorption energies on Mo₄Pt₈O₈/TiO₂(101) (Mo: purple, Pt: silver, C: brown, O: red, Ti: blue).
Fig. S10 DFT calculations of Pt-CO adsorption energies on Pt$_{12}$/TiO$_2$(101) (Mo: purple, Pt: silver, C: brown, O: red, Ti: blue).
REFERENCES