

Electronic Supplementary Information

Highly durable carbon-supported Pt catalysts prepared by hydrosilane-assisted nanoparticle deposition and surface functionalization

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Materials

Graphite (SP-1 grade) was purchased from BAY CARBON Inc. NaNO₃, KMnO₄, H₂SO₄, H₂O₂, SiO₂, Pt/C, methylene blue and hydrazine hydrate were purchased from Wako Pure Chemical Industries, Ltd. NaBH₄, Et₃SiH and 1,1,3,3-tetramethylsiloxane were purchased from Tokyo Chemical Industries Co., Ltd. Toluene, *n*-hexane and ethylene glycol were purchased from Kanto chemical Co., Ltd. Activated carbon was purchased from Aldrich Chemical Co. PtCl₂ was purchased from Tanaka Kikinzoku international k.k. EtOH was purchased from Kishida Chemical Co., Ltd. All reagents were used without further purification. Polymethylhydroxiloxane (PMHS) was purchased from Alfa Aesar.

Methods

Transmission Electron Microscope (TEM) images were collected from sample powder dispersed on a carbon-coated copper grid. A STEM microscope (JEOL JEM-2100F) equipped with a CEOS spherical aberration corrector (*C*_s-corrector) was operated at an acceleration voltage of 200 kV. X-ray

photoelectron spectroscopy (XPS; Kratos AXIS Ultra, Shimadzu) using a monochromatic Al K α X-ray source at 1486.6 eV and operated at 150 W, 15 kV and 10 mA with a base pressure in the XPS analysis chamber of 5×10^{-8} Torr. High resolution spectra (C1s and Pt4f) were acquired using pass energy of 20 eV and 0.1 eV energy steps. All binding energies were referenced to the hydrocarbon C1s peak at 284.5 eV. We acknowledge Mr. Tatsuya Murakami (Japan Advanced Institute of Science and Technology) for XPS measurements. X-ray diffraction (XRD) was measured by PANalytical Co. X'pert PRO using Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) in the 2θ range of $2.0-75^\circ$. The operating tube current and voltage were 40 mA and 40 kV, respectively. The data was collected at the step size of 0.017° and the type of scan was continuous. Energy dispersive X-ray spectroscopy (EDX) was measured by SHIMADZU. Co. Rayny EDX-700HS. The operating tube current and voltage were 100 μA and 15 kV, respectively. Rh was used as X-ray tube. X-ray absorption fine structure (XAFS) was measured at BL-27A of Photon Factory at High Energy Accelerator Research Organization. The X-rays were emitted from the bending magnet, and the photon energy was tuned by an InSb(111) double crystal monochromator. Gas chromatography (GC) analysis was performed by Shimadzu GC-2010 with TCD detector and Shincarbon-ST 50/80 mesh $2.0 \text{ m} \times 3.0 \text{ mm}$ packed column. Fourier-transfer infrared (FT-IR) spectroscopy was measured by SHIMADZU. Co. AIM-8800 complete with SHIMADZU. Co. IR Tracer-100. Thermo-gravimetric analysis (TGA) was carried out by Rigaku TG8120. UV-vis spectroscopy was measured by JASCO V-550 UV/vis spectrophotometer.

Preparation of Graphene oxide (GO)

GO was synthesized from modified Hummers method¹⁾. GO dispersion was dried for preparation of Si-modified GO by freezing dry.

Deposition of Pt on carbon supports

For preparation of Pt/SiGO and Pt/GO-NaBH₄, GO (200 mg) and PtCl₂ (5 - 6 mg) were dispersed in 50% aq. EtOH (40 mL). Then the reductant (Et₃SiH or NaBH₄, 100 equivalent amount of Pt) was added to the reaction mixture. The mixture was stirred in the autoclave at room temperature for 1 h, and then stirred at 95 °C for 6 h. After cooling to room temperature, the suspension was washed with

H₂O and acetone, and then dried at 50 °C under reduced pressure. Preparation of Pt/SiC, activated carbon was used in place of GO. When ethylene glycol was used as a reductant (Pt/GO-EG, Figure S1a), 50% aq. ethylene glycol (40 mL) was used in place of 50% aq. EtOH without any other reducing reagents.

Other hydrosilanes, such as Me₂SiHOSiHMe₂ and poly(methylhydro)siloxane (PMHS), could also form Pt nanoparticles (Fig S1c and S1d).

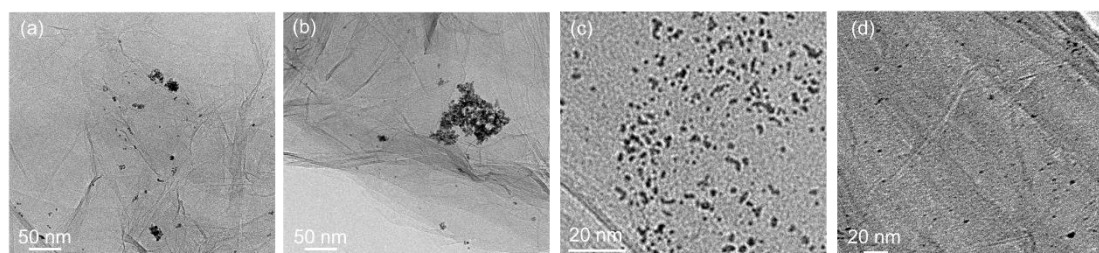


Fig. S1. TEM images of (a) Pt/GO-EG and (b) Pt/GO-NaBH₄ (c) Pt/SiGO with Me₂SiHOSiHMe₂, (d) Pt/SiGO with PMHS.

Table S1. Pt and Si contents of the composites determined by EDX.

Entry	Catalyst	Support	Pt (wt%)	Si (wt%)
1	Pt/SiGO	GO	4.2	1.5
2	Pt/SiC	Activated carbon	6.2	2.1
3	Pt/C with Et ₃ SiH	C	4.0	1.5

Preparation of Et₃Si-modified GO

Et₃Si-modified GO was carried out in the same way as the literature.²⁾ Et₃SiCl was used as silylation agent. Freeze dried GO (240 mg) and *n*-butylamine (2.5 mL) were added to the Schlenk tube under Ar atmosphere. Then, the mixture was sonicated for 1 h, and stirred at 60 °C for 1 h. After that, toluene (10 mL) and Et₃SiCl (5.0 mmol) were added to the mixture before sonication for 1 h. Then, the mixture was stirred at room temperature for overnight. The obtained product, Et₃Si-modified GO, was washed with toluene, *n*-hexane, EtOH and H₂O by centrifugation, and freeze dried.

Methylene blue (MB) adsorption ³⁾

The amount of MB adsorbed onto Pt composite was measured by UV-vis spectroscopy. To the solution of MB (100 mL, 62.1 mg / 1L) was added Pt composites (4 mg). The mixture was sonicated for 60 min, and then centrifugation. The absorbance of the resulting solution was measured at 246 nm.

Methane oxidation reaction at 400 °C

Pt/C or Pt/GO samples (100 mg) were filled into the quartz tube (φ 1.5 cm, 45 cm length) with glass wool. The quartz tube was replaced with CH₄/He (10/90) gas (20 mL/min) at room temperature for 30 min, and then the temperature was increased to 350 °C. Catalysts pretreatment was performed with a gas containing 7% methane, 33% O₂, and 60% He at 350 °C for 30 min, then the temperature was increased to 400 °C under He. The methane oxidation was performed with a gas containing 7% methane, 33% O₂, and 60% He at 400 °C. The flow rate was 30 mL/min and the conversion of methane was measured by gas chromatography (Fig. S2)

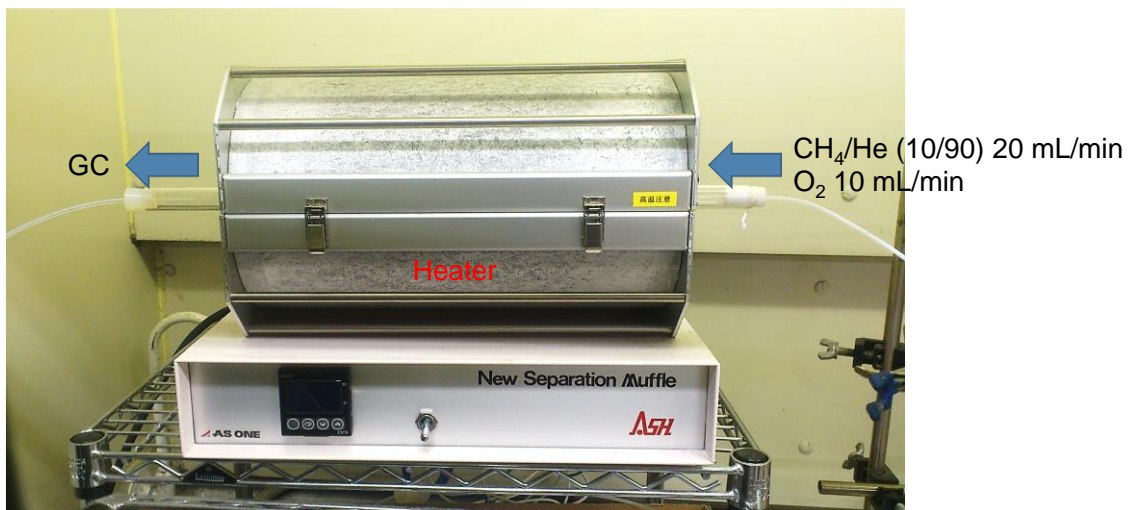


Fig. S2. Flow reactor for methane oxidation.

Scanning transmission electron microscopy (STEM)-EDX mapping of Pt/SiGO before and after methane oxidation.

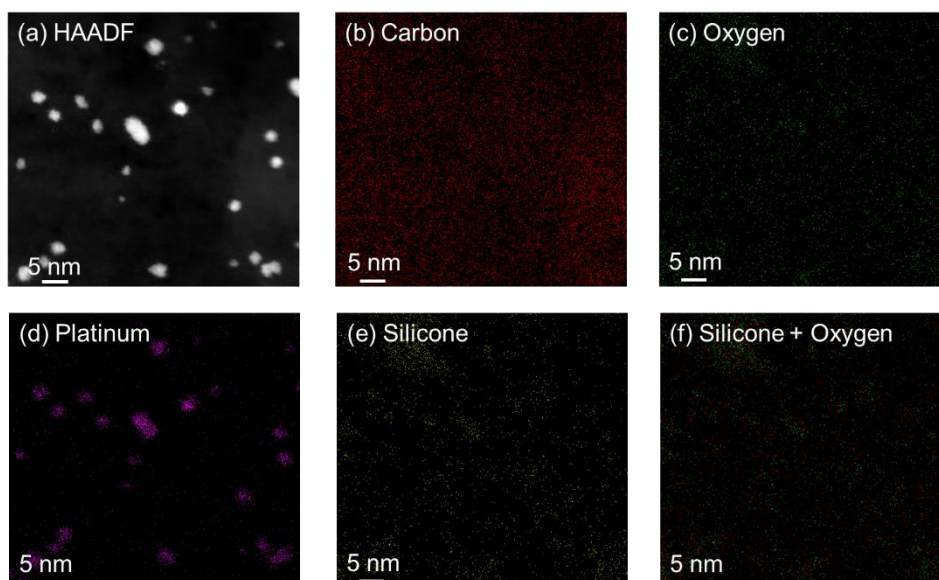


Fig. S3a. STEM-EDX mapping of Pt/SiGO before methane oxidation.

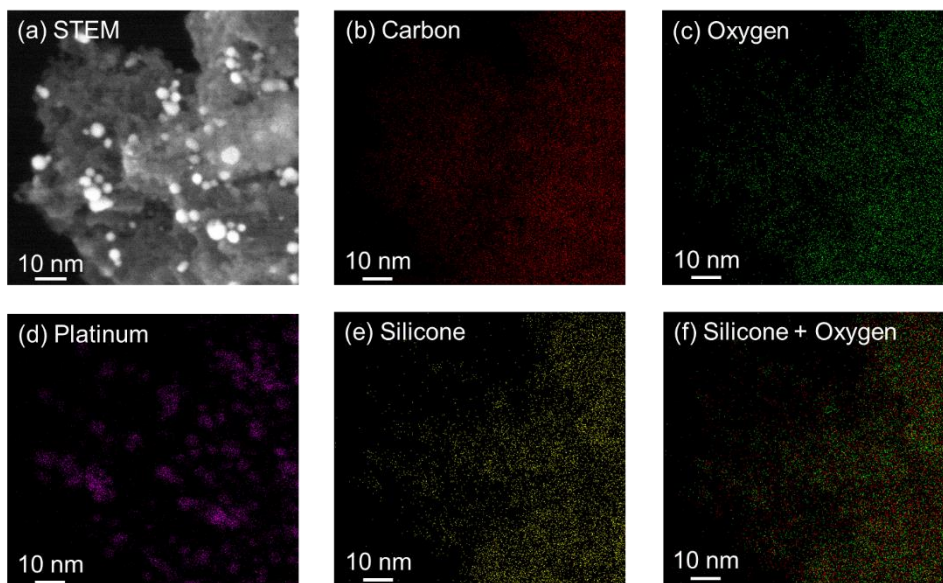


Fig. S3b. STEM-EDX mapping of Pt/SiGO after methane oxidation.

DTA of Pt/C, Pt/SiGO, and Pt/GO-NaBH₄

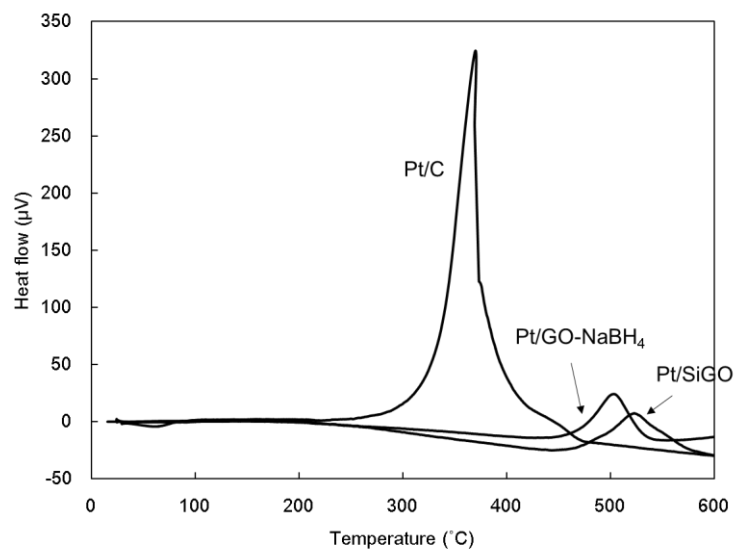


Fig. S4. DTA analysis of Pt/C, Pt/SiGO, and Pt/GO-NaBH₄.

IR analysis of Pt/SiGO after methane oxidation

After the methane oxidation, the alkyl groups of Pt/SiGO were disappeared.

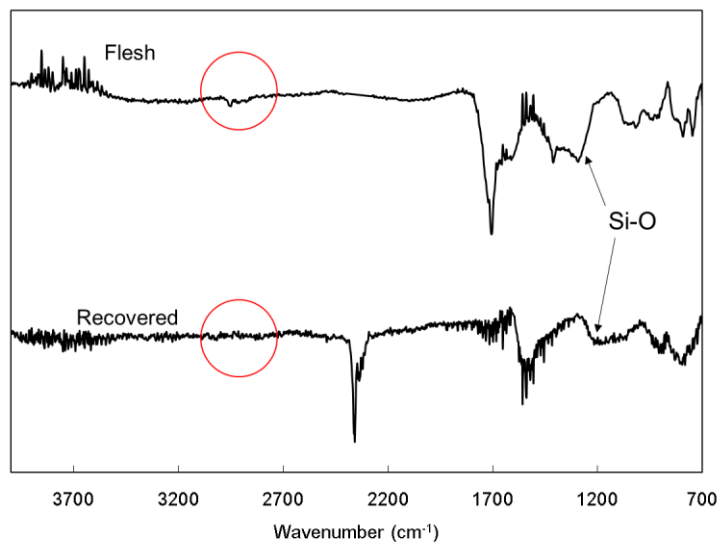


Fig. S5. IR analysis of the catalysis before and after methane oxidation.

Recycle of Pt/SiGO composites

To investigate the recycle of the catalyst, the methane oxidation was performed at 350 °C (providing moderate catalytic activity). Activity of Pt/C was dramatically decreased after reaction at 400 °C, however, Pt/SiGO maintained the activity.

Table S2. Reuse of the catalyst.

	Before methane oxidation at 400 °C	After methane oxidation at 400 °C
Pt/C	97	7.6
Pt/SiGO	55	52

X-ray diffraction (XRD)

The peaks are at $2\theta = 39.7$, 46.2 , and 67.6° and these correspond to the (111), (200), and (220) planes of a face-centered cubic (fcc) Pt crystal, respectively. When ethylene glycol (EG) was used as the reductant, the peak of GO remained at $2\theta = 10.5^\circ$.

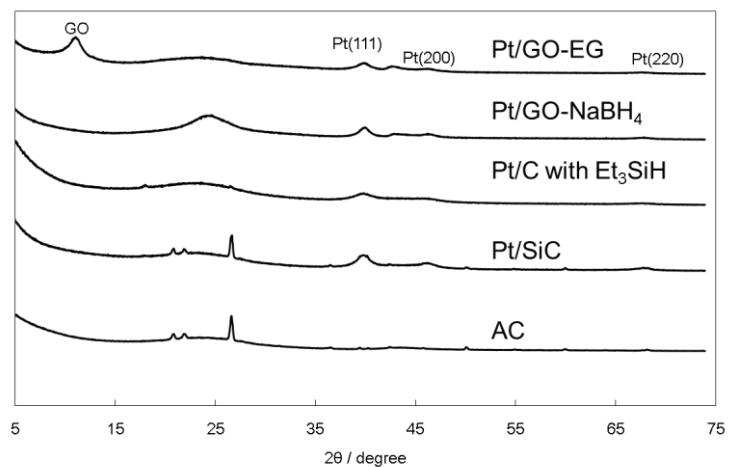
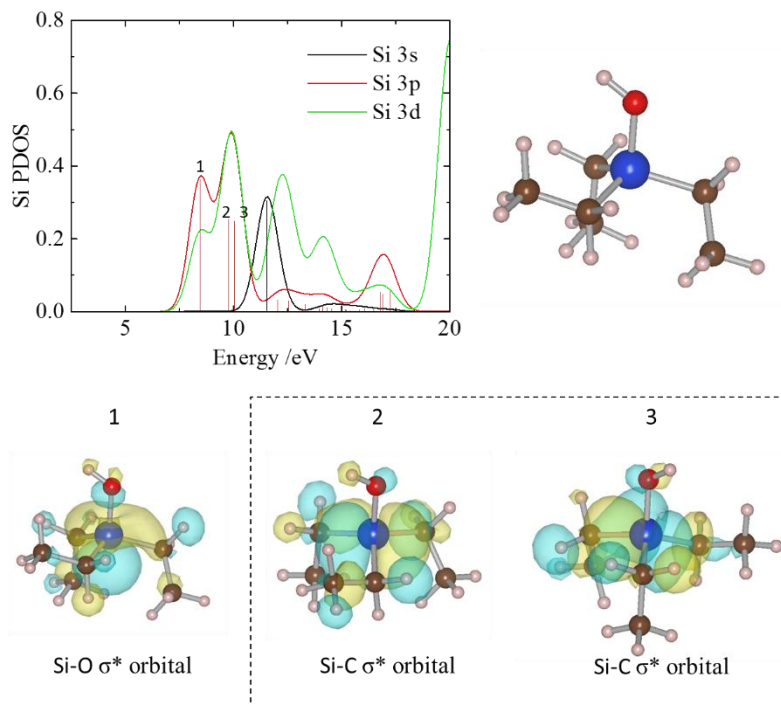


Fig. S6. XRD spectra of Pt/GO prepared by different reductants, Pt/GO-EG, Pt/GO-NaBH₄, Pt/C with Et₃SiH, Pt/SiC, and activated carbon.

Simulation of Si K-edge XANES with DV-X α molecular-orbital calculation



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