Electronic Supplementary Information

Catalytic NH_3 Oxidation Affected by the Nanometric Roughness of the Platinum Overlayer

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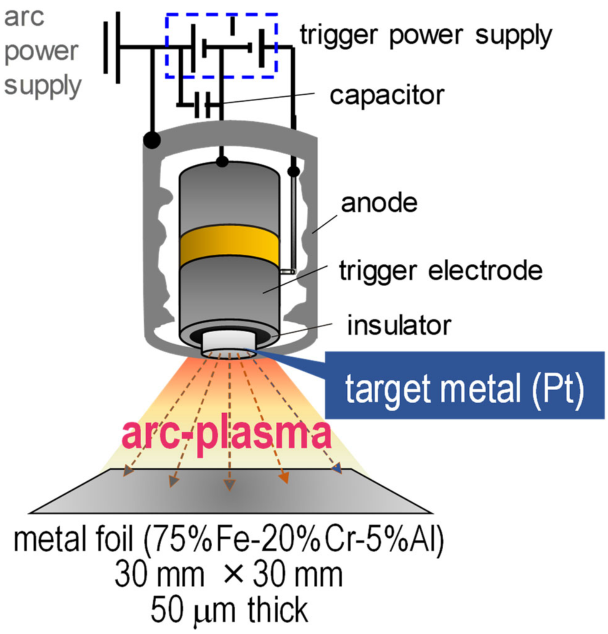

Figure S1. Schematic of the pulsed AP deposition of Pt on a Fe–Cr–Al foil. This figure is reproduced from a reference.[1]

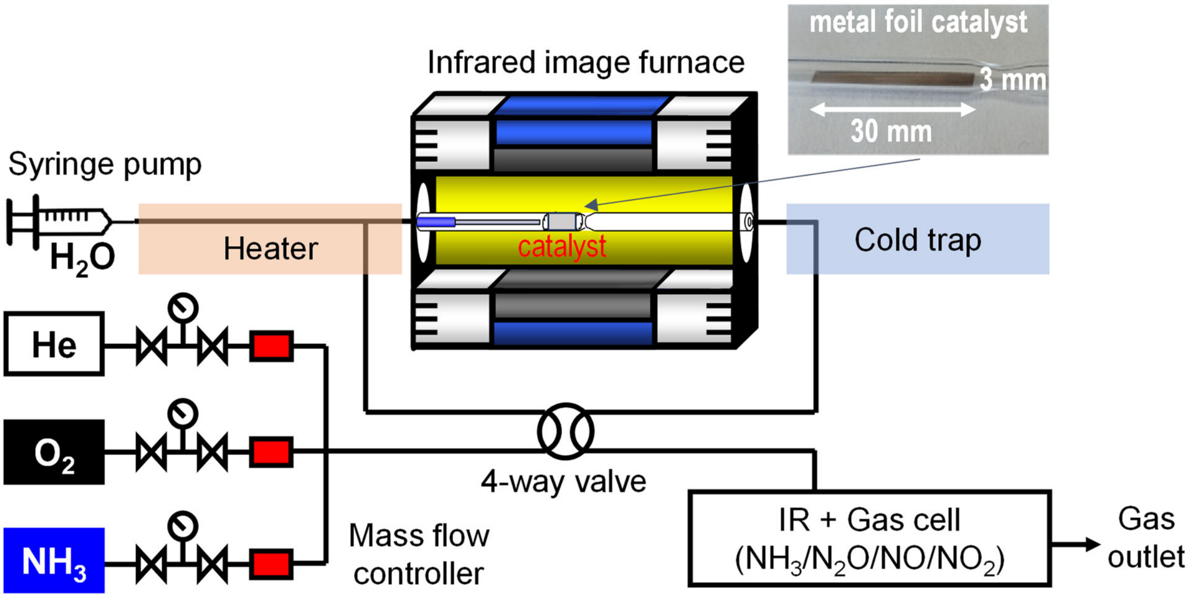

Figure S2. A schematic illustration of catalytic reaction experiments and gas analysis. This figure is reproduced from references.[2, 3]

The catalytic NH_3 oxidation was conducted in a flow reactor comprising a gas-supplying system equipped with mass flow controllers, a water-supplying pump, a quartz tube reactor (6 mm in outer diameter and 4 mm in inner diameter), a water-cooled infrared image furnace (RHL-E25P, Ulvac Riko, Japan) and a cooling trap. A strip foil (3×30 mm^2) of an as-prepared film catalyst (coated on one side only) was set in a catalytic activity test tube. A simulated gas mixture comprising 300 ppm NH_3, 8% O_2, 10% H_2O and a He balance was supplied at a flow rate of 100 mL min^{-1}. Concentrations of NH_3, NO, N_2O and NO_2 were monitored using an online Fourier-transform infrared spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA) equipped with a temperature-controllable gas cell (2 m optical path length) maintained at 120°C.

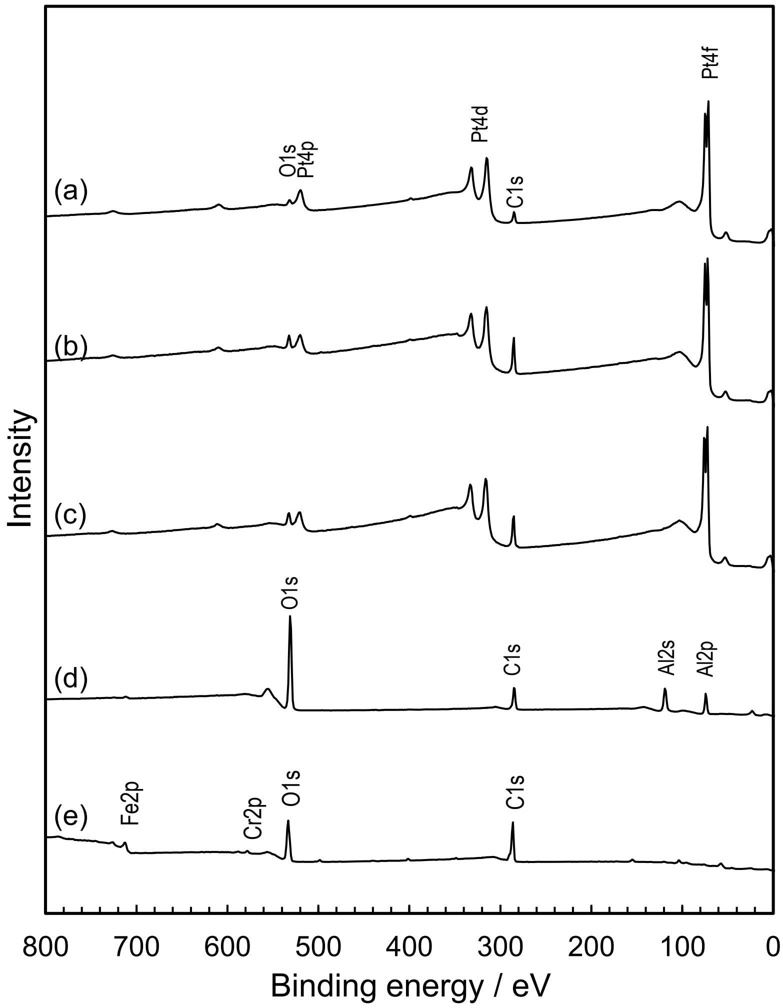

Figure S3. XPS Survey spectra of (a) Pt/p-SUS, (b) Pt/SUS, (c) Pt/Al_2O_3/SUS, (d) Al_2O_3/SUS, and (e) SUS. Pt was coated on SUS foils using 2,000-shot AP pulses.

The XPS data revealed that peaks assignable to the SUS components (Fe, Cr, and Al) disappeared almost completely after 2,000 shots of AP deposition, suggesting full coverage of the metal foil surface by a nanometric Pt overlayer.

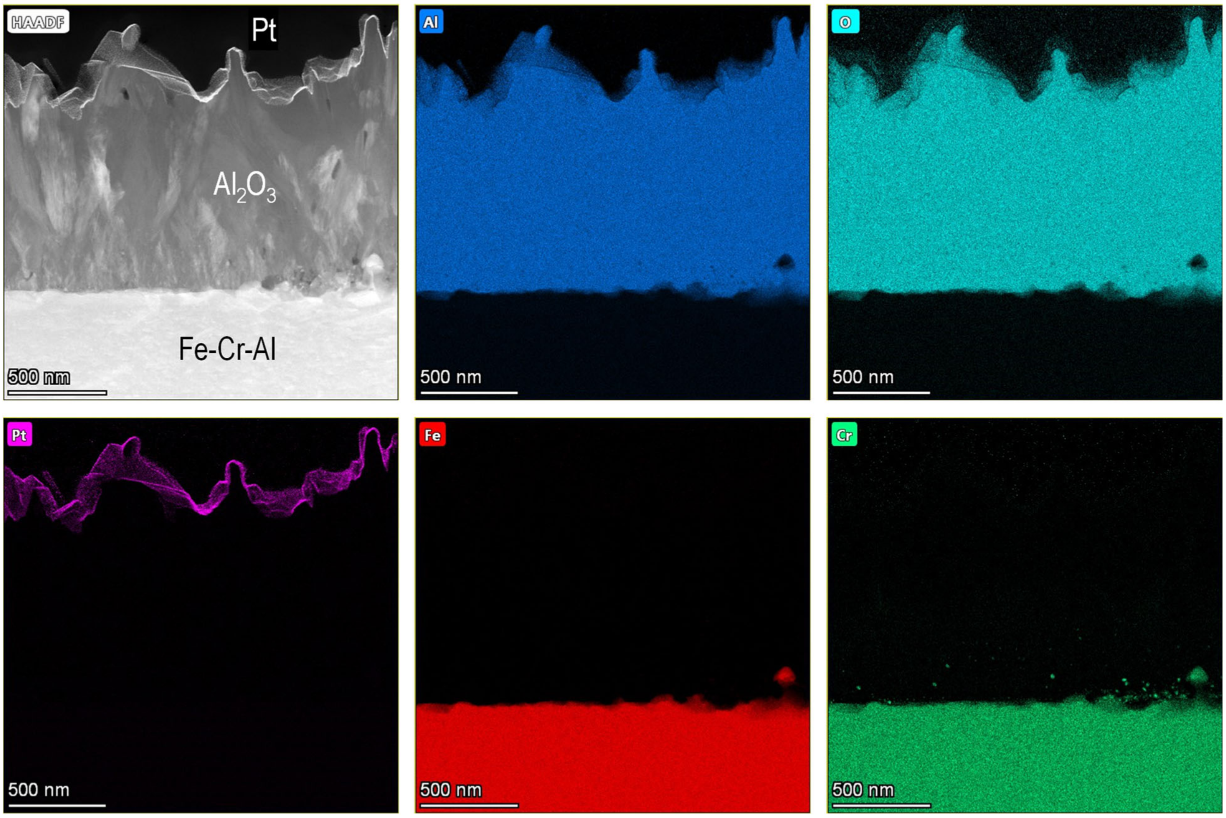

Figure S4. HAADF-STEM and X-ray images of cross-sectional $Pt/Al_2O_3/SUS$ foil catalyst.

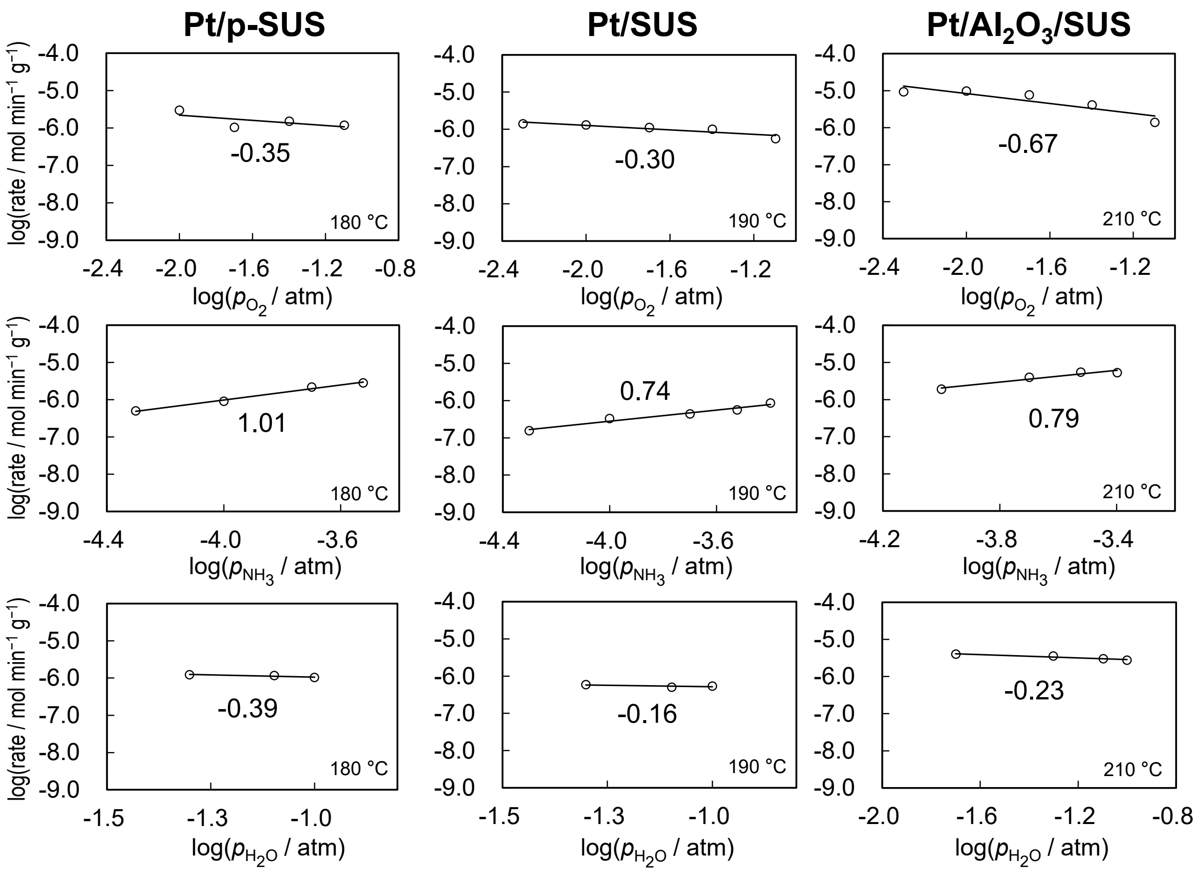

Figure S5. Dependence of NH_3 oxidation rate on partial pressures of O_2, NH_3, and H_2O for Pt/p-SUS (180°C), Pt/SUS (190°C) and Pt/Al_2O_3/SUS (210°C)

Table S1 Activity comparison between Pt/p-SUS, Pt/SUS and $Pt/Al_2O_3/SUS$ for NH_3 oxidation

Catalyst (strip size)	Pt surface area [a] (m^2)	Surface Pt (μmol)	NH_3 conv. [d] (%)	Reaction rate (μmol min^{-1})	TOF [e] (min^{-1})
Pt/p-SUS (3 × 10 mm^2)	3.0×10^{-5}	7.67×10^{-4} [b]	15.3	0.205	267
Pt/SUS (3 × 30 mm^2)	9.1×10^{-5}	2.33×10^{-3} [b]	18.7	0.250	107
$Pt/Al_2O_3/SUS$ (3 × 30 mm^2)	14.4×10^{-5}	3.69×10^{-3} [b]	6.2	0.083	22
		1.12×10^{-2} [c]	6.2	0.083	7

[a] Determined by a confocal laser scanning microscope.

[b] Determined by the geometric area of the foil surface, surface coverage (100%), *Sdr* and surface atomic density of Pt (1.54×10^{19} atom m^{-2}) as shown below.

Pt/p-SUS:

[surface Pt] = [geometric area of foil] × [surface coverage] × [1 + *Sdr*] × [surface atomic density] = 3.0×10^{-5} (m^2) × 1 × 1.000 × 1.54×10^{19} atom m^{-2}/6.02×10^{23} (atom mol^{-1}) = 7.67×10^{-4} (μmol)

$$\mathrm{TOF} = \frac{[\text{reaction rate}]}{[\text{surface Pt}]} = 0.205 \times 10^{-6}\ (\mathrm{mol\ min^{-1}})/7.67 \times 10^{-10}\ (\mathrm{mol}) = 267\ (\mathrm{min^{-1}})$$

Pt/SUS:

[surface Pt] = [geometric area of foil] × [surface coverage] × [1 + *Sdr*] × [surface atomic density] = 9.0×10^{-5} (m^2) × 1 × 1.011 × 1.54×10^{19} atom m^{-2}/6.02×10^{23} (atom mol^{-1}) = 2.33×10^{-3} (μmol)

$$\mathrm{TOF} = \frac{[\text{reaction rate}]}{[\text{surface Pt}]} = 0.250\times10^{-6}\ (\mathrm{mol\ min^{-1}})/2.33\times10^{-9}\ (\mathrm{mol}) = 107\ (\mathrm{min^{-1}})$$

$Pt/Al_2O_3/SUS$:

[surface Pt] = [geometric area of foil] × [surface coverage] × [1 + *Sdr*] × [surface atomic density] = 9.0×10^{-5} (m^2) × 1 × 1.607 × 1.54×10^{19} atom m^{-2}/6.02×10^{23} (atom mol^{-1}) = 3.69×10^{-3} (μmol)

$$\mathrm{TOF} = \frac{[\text{reaction rate}]}{[\text{surface Pt}]} = 0.083 \times 10^{-6}\ (\mathrm{mol\ min^{-1}})/3.69 \times 10^{-9}\ (\mathrm{mol}) = 22\ (\mathrm{min^{-1}})$$

[c] Determined by the CO chemisorbed at 50°C assuming the stoichiometry of CO/Pt = 1.

[surface Pt] = [CO chemisorbed] = 1.12×10^{-2} (μmol)

$$\mathrm{TOF} = \frac{[\text{reaction rate}]}{[\text{surface Pt}]} = 0.083 \times 10^{-6}\ (\mathrm{mol\ min^{-1}})/1.12 \times 10^{-8}\ (\mathrm{mol}) = 7\ (\mathrm{min^{-1}})$$

[d] NH_3 conversion at 200°C (300 ppm NH_3, 8% O_2, 10% H_2O, and a He balance, 100 mL min^{-1}).

[e] Turnover frequency of the NH_3 conversion at 200°C.

REFERENCE

1. M. Machida, Y. Tokudome, A. Maeda, Y. Kuzuhara, T. Hirakawa, T. Sato, H. Yoshida, J. Ohyama, K. Fujii and N. Ishikawa, *ACS Catal.*, 2020, **10**, 4677-4685.
2. M. Machida, Y. Tokudome, A. Maeda, T. Koide, T. Hirakawa, T. Sato, M. Tsushida, H. Yoshida, J. Ohyama, K. Fujii and N. Ishikawa, *ACS Omega*, 2020, **5**, 32814–32822.
3. M. Machida, Y. Tokudome, A. Maeda, T. Sato, H. Yoshida, J. Ohyama, K. Fujii and N. Ishikawa, *Catal. Today*, 2022, **384-386**, 70-75.