Supporting Information

Nanometric Platinum Overlayer to Catalyze NH$_3$ Oxidation with High Turnover Frequency

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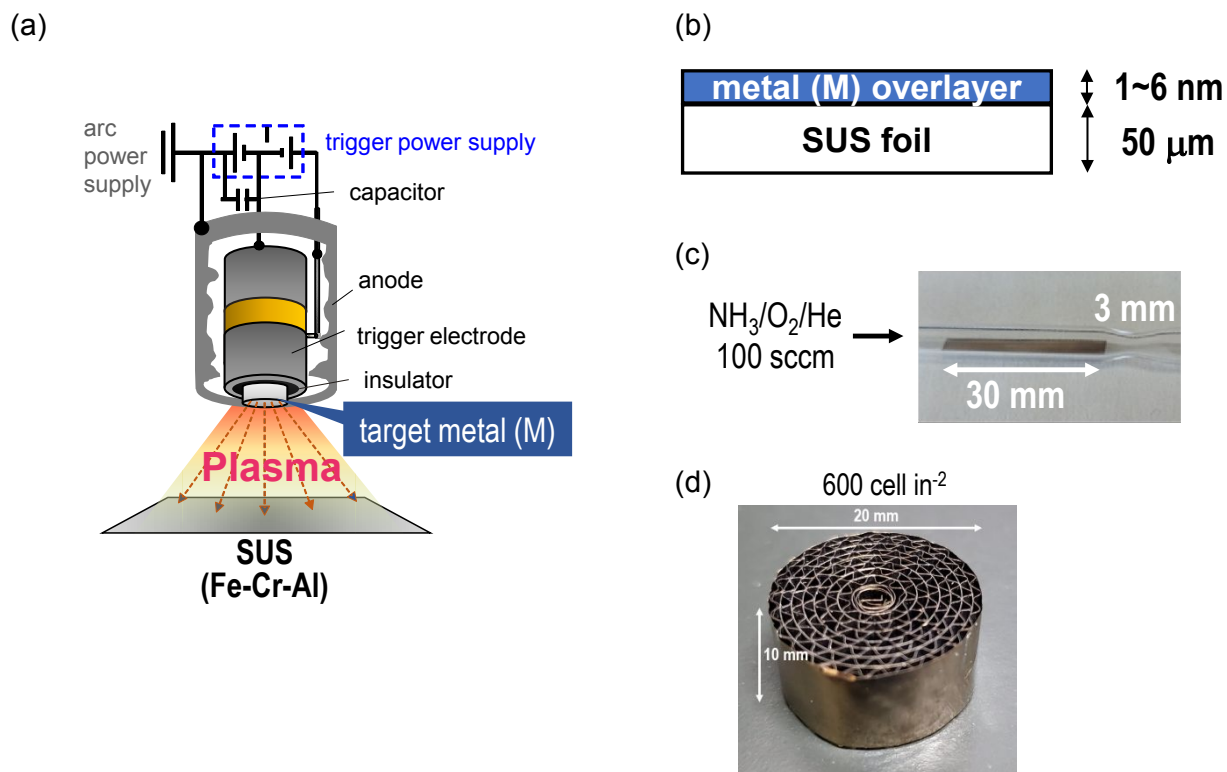

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Figure S1. (a) Schematic of the pulsed AP deposition of metal overlayer on a SUS foil and (b) the structure of as-prepared M/SUS. (c) A strip foil (3 × 30 mm²) of as-prepared M/SUS (coated on one side only) in a catalytic activity test tube. (d) A honeycomb catalyst consisting of Pt/SUS foils (ϕ20 mm × 10 mm, 600 cells in⁻², 2000 shot on both sides).
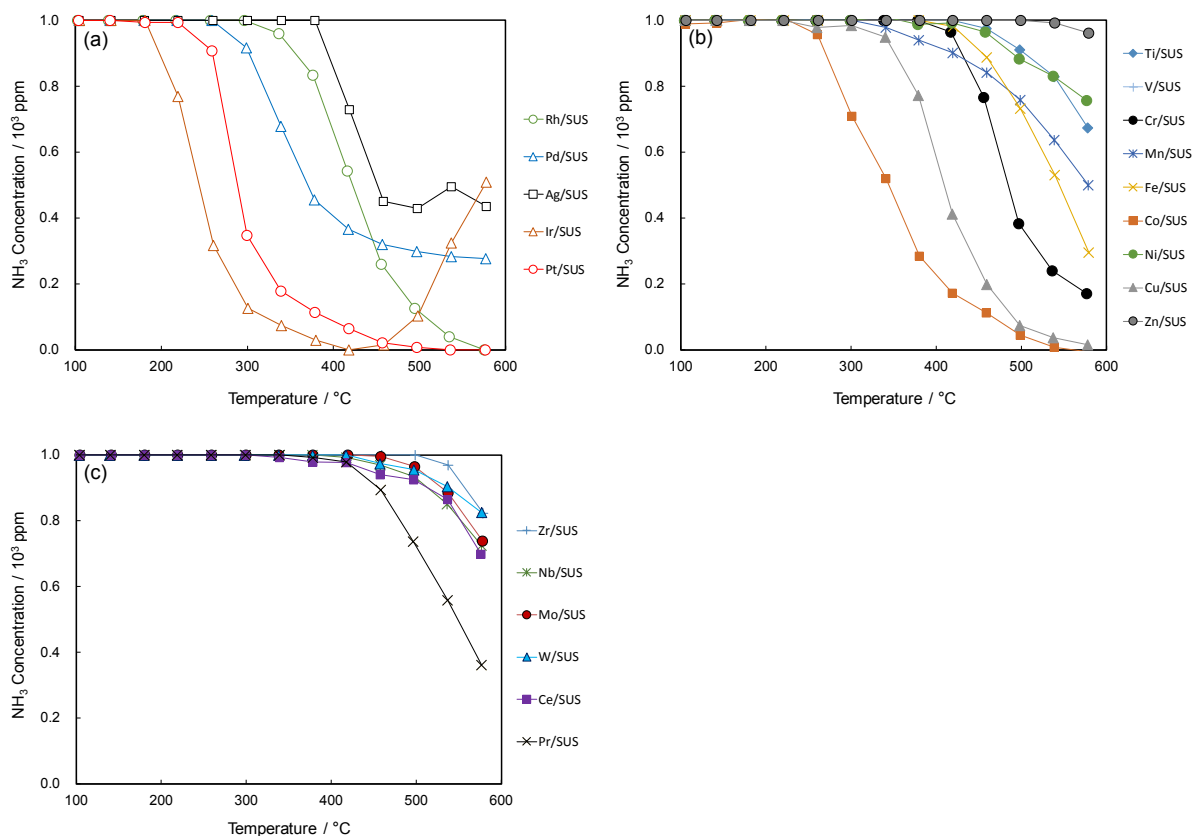
Figure S2. Light-off curves for NH$_3$ oxidation for a strip foil (3 × 30 mm^2) of as-prepared M/SUS. (a) M = precious metals, (b) M = 3d transition metals, and (c) M = other metals. Heating rate: 10 °C min^{-1}, Gas feed: 1000 ppm NH$_3$, 10% O$_2$, and He balance, 100 mL min^{-1}.
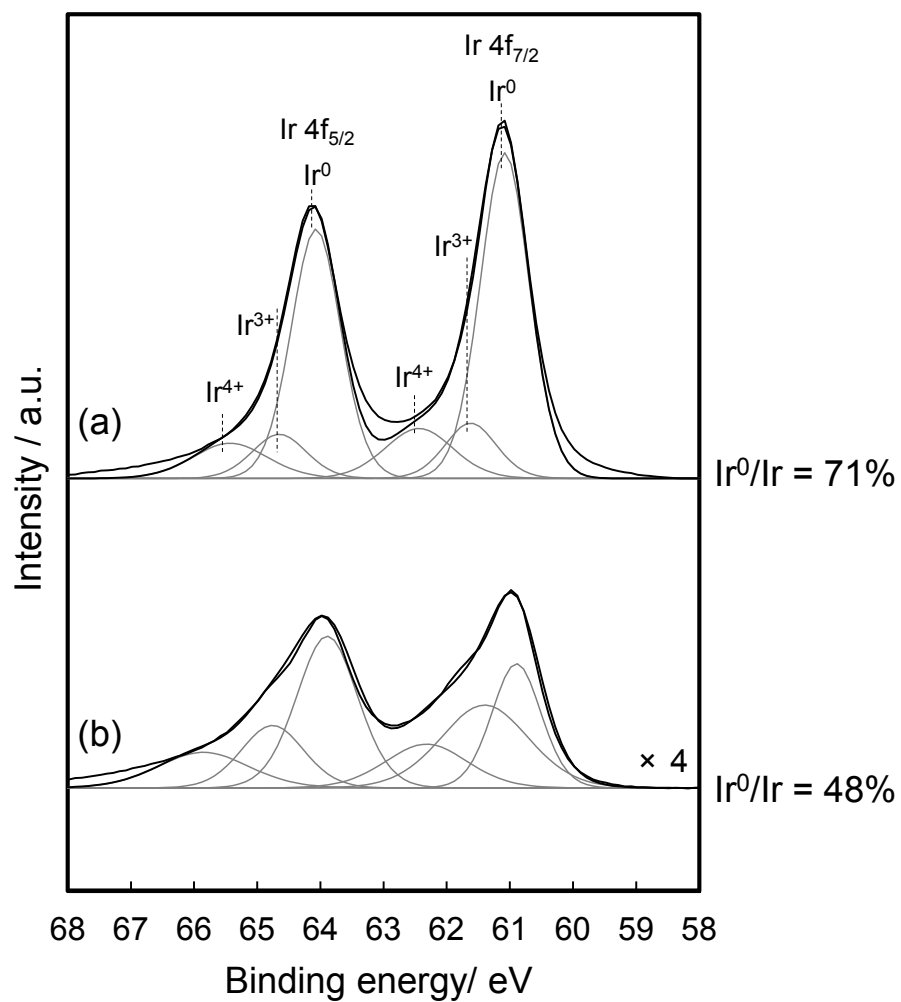
Figure S3. Ir4f XPS of (a) as-prepared Ir/SUS and (b) Ir/SUS after catalytic light-off test shown in Figure S2.
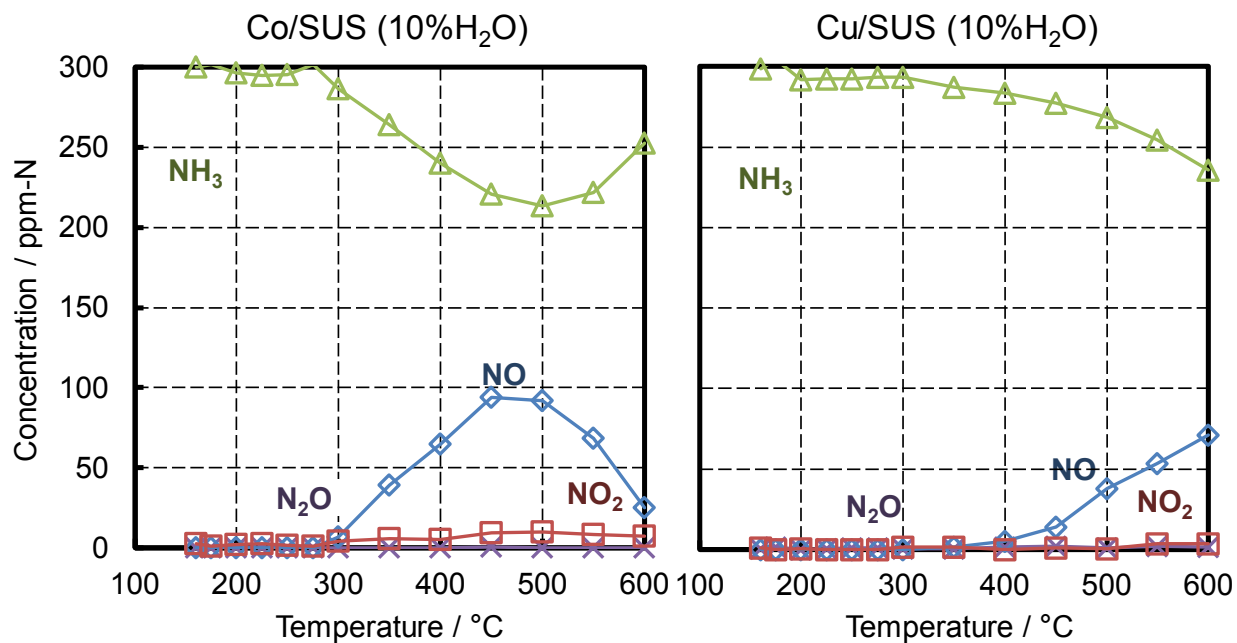
Figure S4. Temperature dependence of NH_3 oxidation and product selectivity over a strip foil (3 × 30 mm^2) of as-prepared M/SUS (M=Co and Cu, 2000 shot coated on one side only). Gas feed: 300 ppm NH_3, 8% O_2, 10% H_2O and He balance, 100 mL min^{-1}.
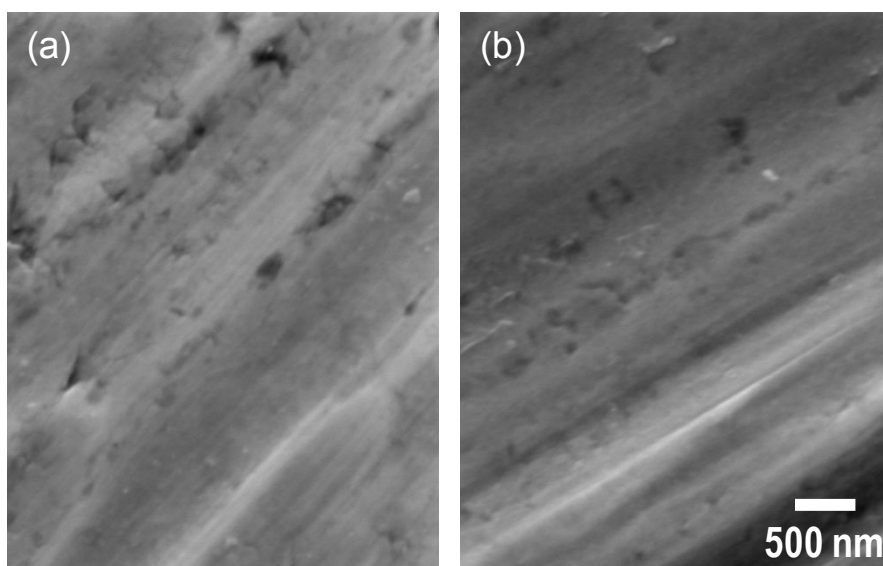
Figure S5. SEM photographs of the surfaces of (a) a SUS foil and (b) a Pt/SUS foil.
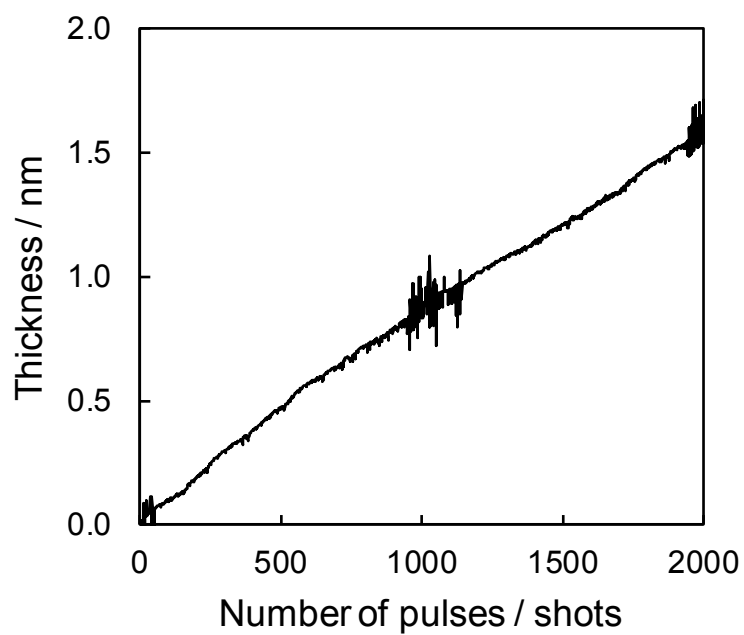

Figure S6. Thickness of Pt overlayer formed on a SUS foil as a function of number of AP pulses.
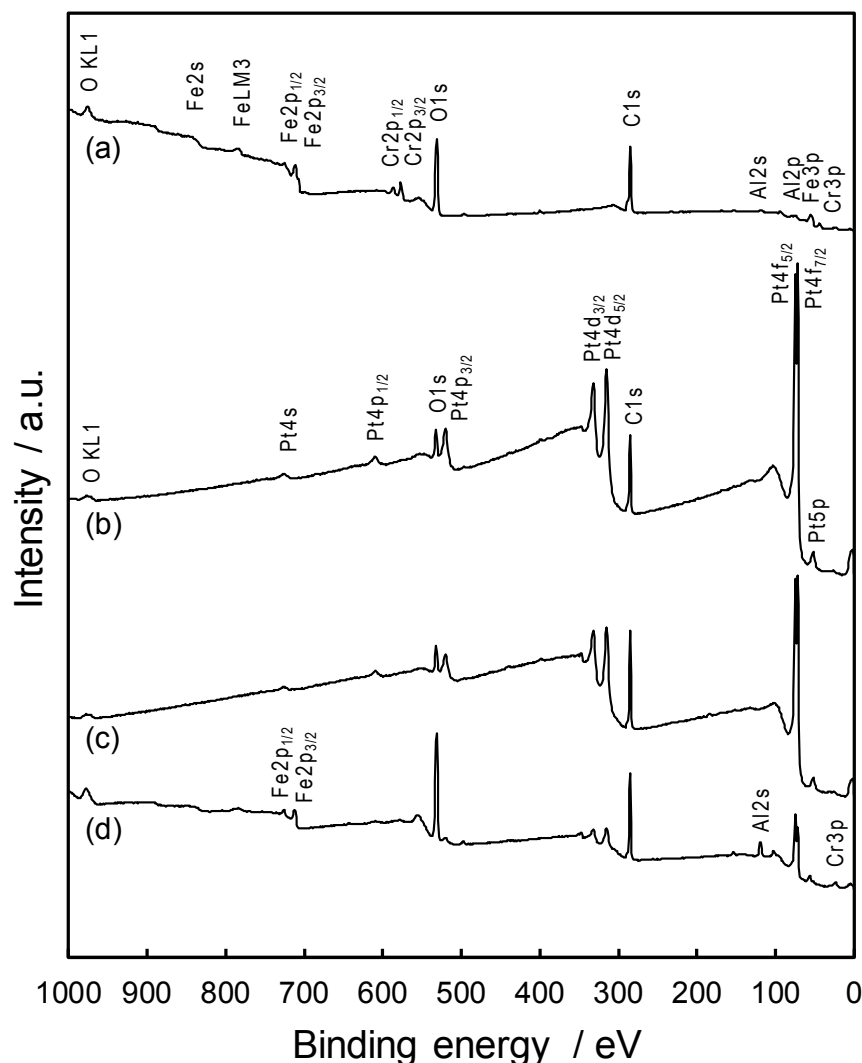
Figure S7. XPS Survey spectra of (a) Fe−Cr−Al (SUS) foil, (b) as-prepared Pt/SUS, (c) as-prepared Pt/Zr/SUS, and (d) Pt/SUS after thermal aging at 650 °C for 24 h. AP pulses: 2000 shot Pt, 20000 shot Zr.

The XPS data reveal that peaks assignable to the SUS components (Fe, Cr, and Al) disappeared almost completely after 2000 shots of AP deposition and suggest full coverage of the metal foil surface by a nanometric Pt overlayer. A relatively strong C 1s peak is observed in the all samples. This is likely attributed to contamination from the residual gas in the vacuum chamber during the XPS analysis duration but not to contamination in the pulsed arc-plasma deposition process.
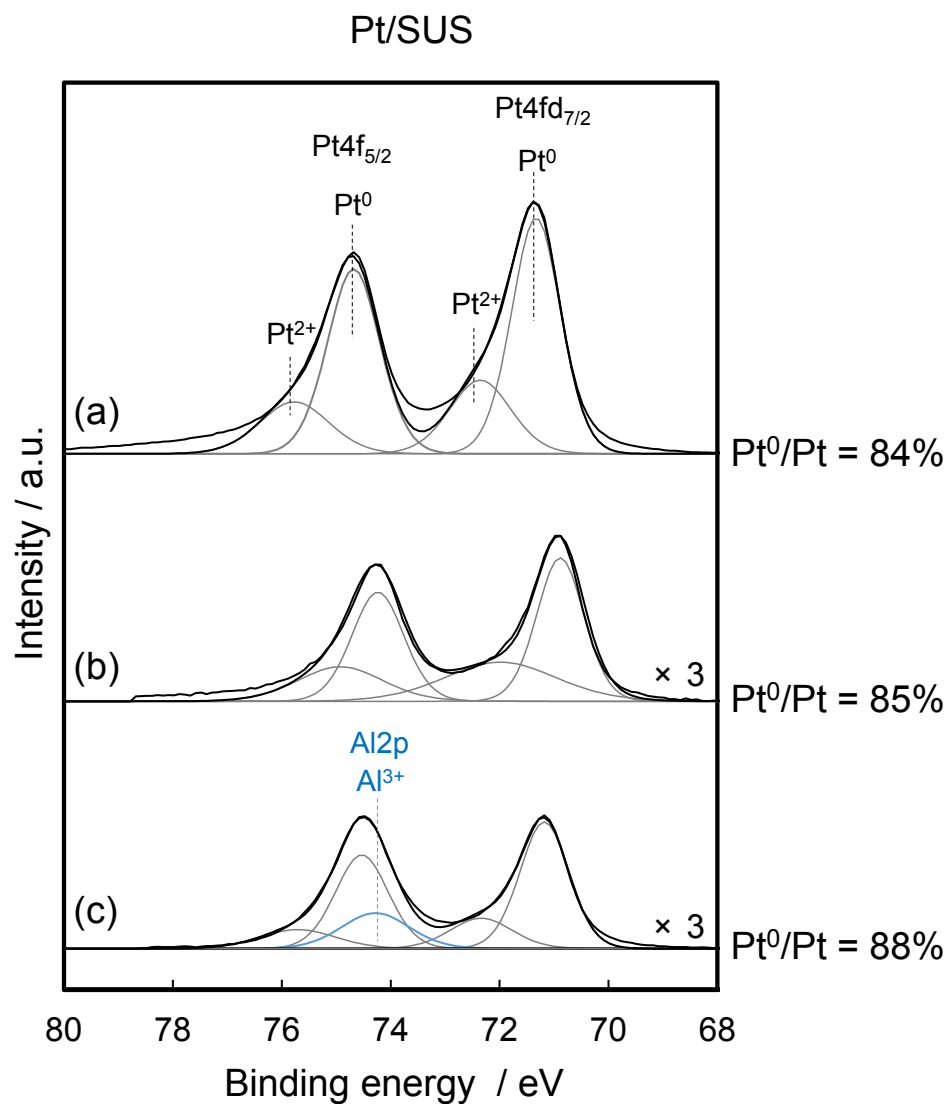
Figure S8. Pt4f XPS of (a) as-prepared Pt/SUS, (b) Pt/SUS after catalytic test in Figure 2, and (c) Pt/SUS after thermal aging at 650 °C for 24 h. AP pulses: 2000 shot Pt.
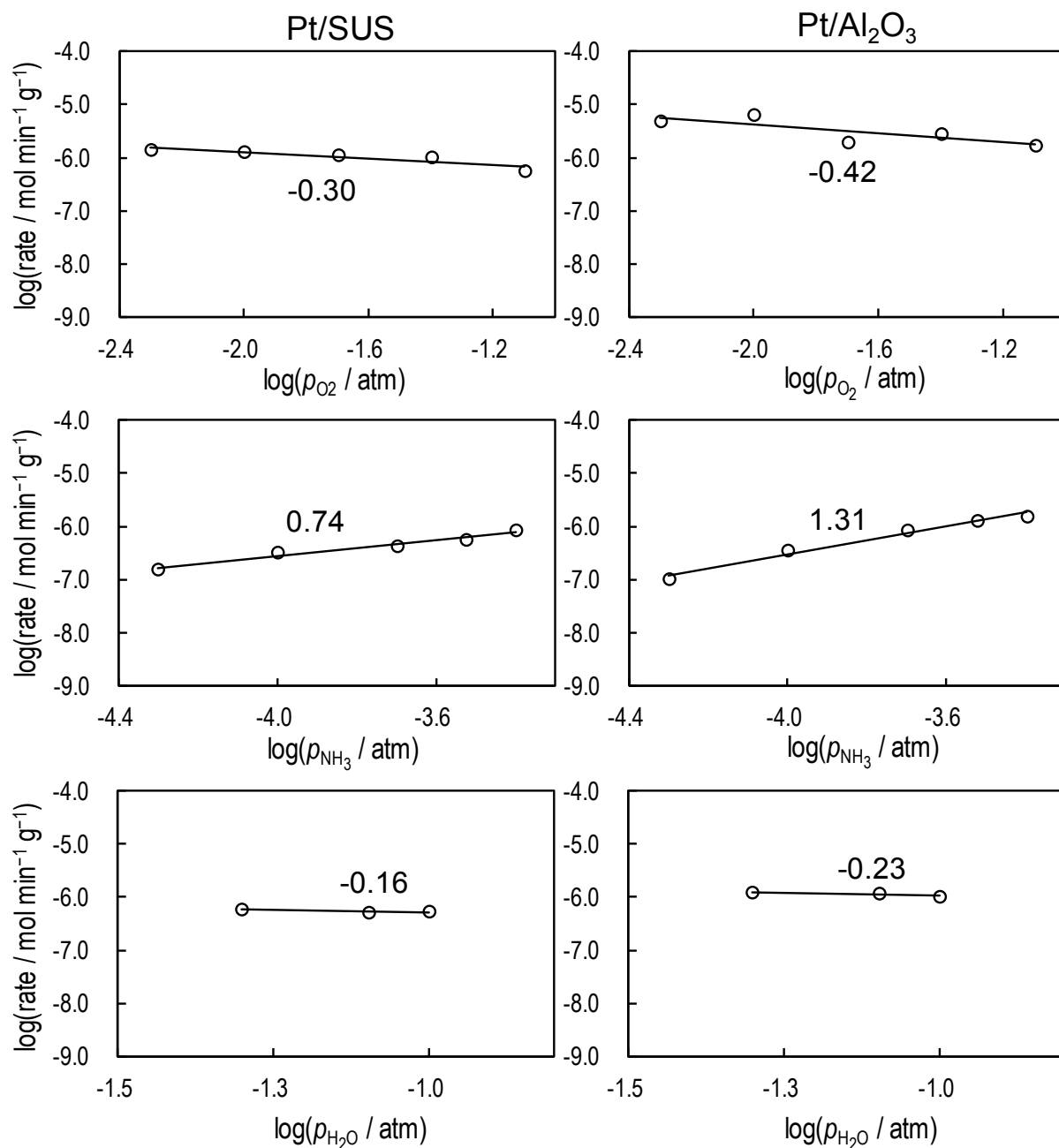
Figure S9. Dependence of NH$_3$ oxidation rate on partial pressures of NH$_3$, O$_2$, and H$_2$O for Pt/SUS (190 °C) and Pt/Al$_2$O$_3$ (180 °C).
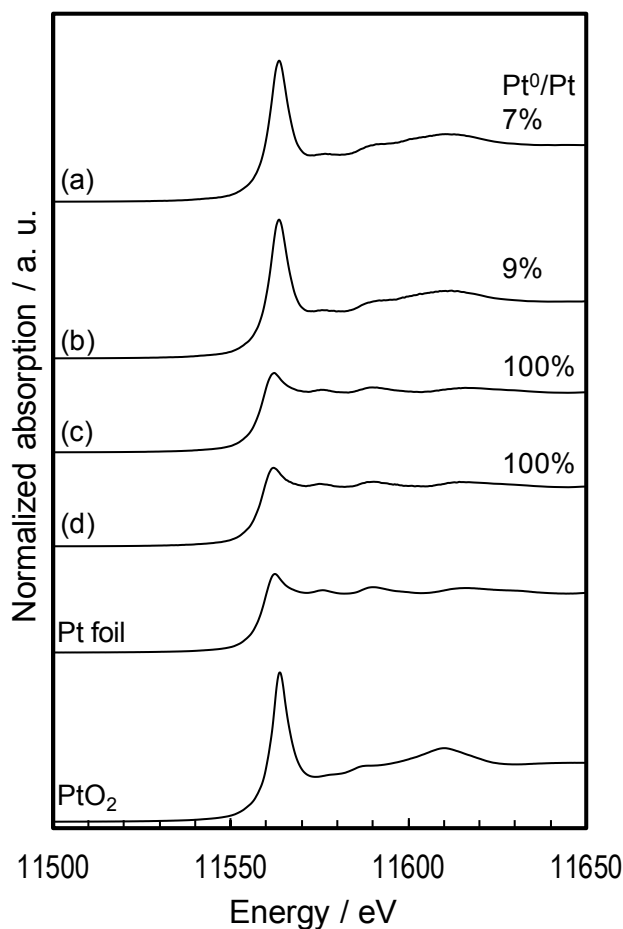
Figure S10. Pt L_{III}-edge XANES of Pt/Al_2O_3 (a) as-prepared and (b) after the catalytic activity test (Figure 2), and Pt/SUS (c) as-prepared and (d) after the catalytic activity test. Pt foil and PtO_2 are shown as references.

Pt L_{III}-edge XANES was recorded on the SPring-8 BL14B2 of the Japan Synchrotron Radiation Research Institute. The spectral data were recorded at room temperature in a transmission mode using a Si(111) double-crystal monochromator, or in a fluorescence mode using a solid-state detector. In addition, a grazing incidence technique was employed for the Pt/SUS samples. The obtained XAFS data were processed using the Athena program. The oxidation state of the samples was analyzed by linear combination fitting of the sample spectra with the reference spectra of Pt foil and PtO_2. More than 90% Pt in Pt/Al_2O_3 was oxidized before and after the catalytic activity test. By contrast, metallic Pt was dominant in as-prepared Pt/SUS and remained unchanged after the catalytic test. Metallic Pt was found to be more stable in Pt/SUS.
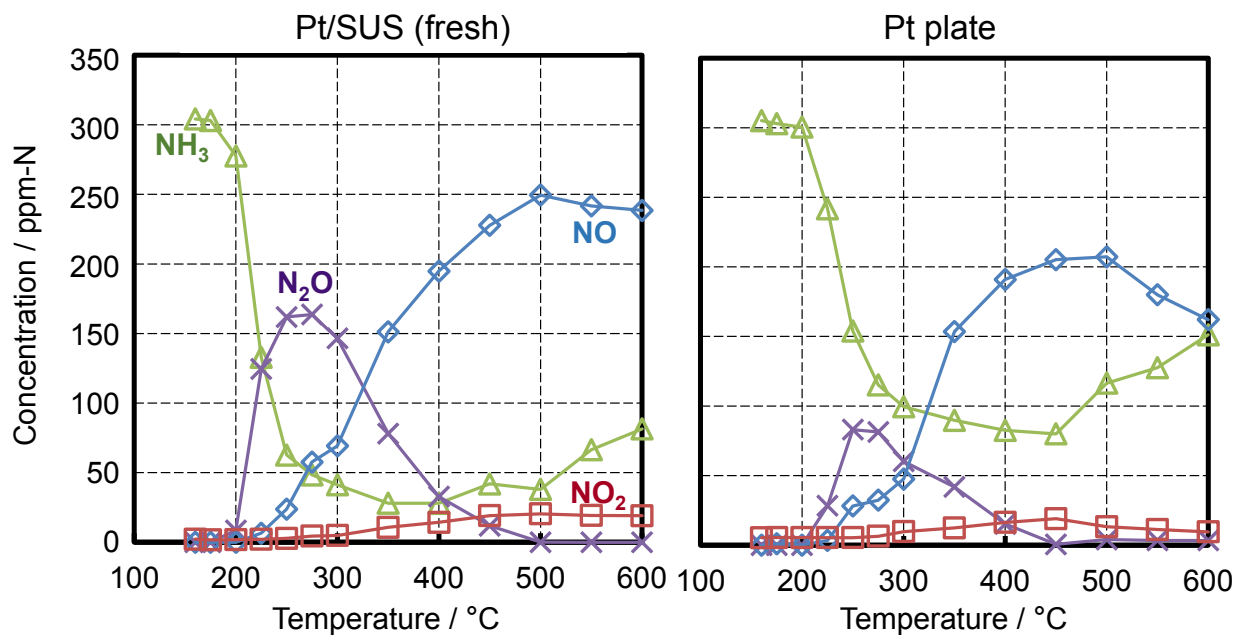
Figure S11. Temperature dependence of NH_3 oxidation and product selectivity over as-prepared Pt/SUS (3×30 mm^2 strip foil, 2000 shot on one side only) and a Pt plate (97.2 mm^2 strip). Gas feed: 300 ppm NH_3, 8% O_2, 10% H_2O and He balance, 100 mL min^{-1}.
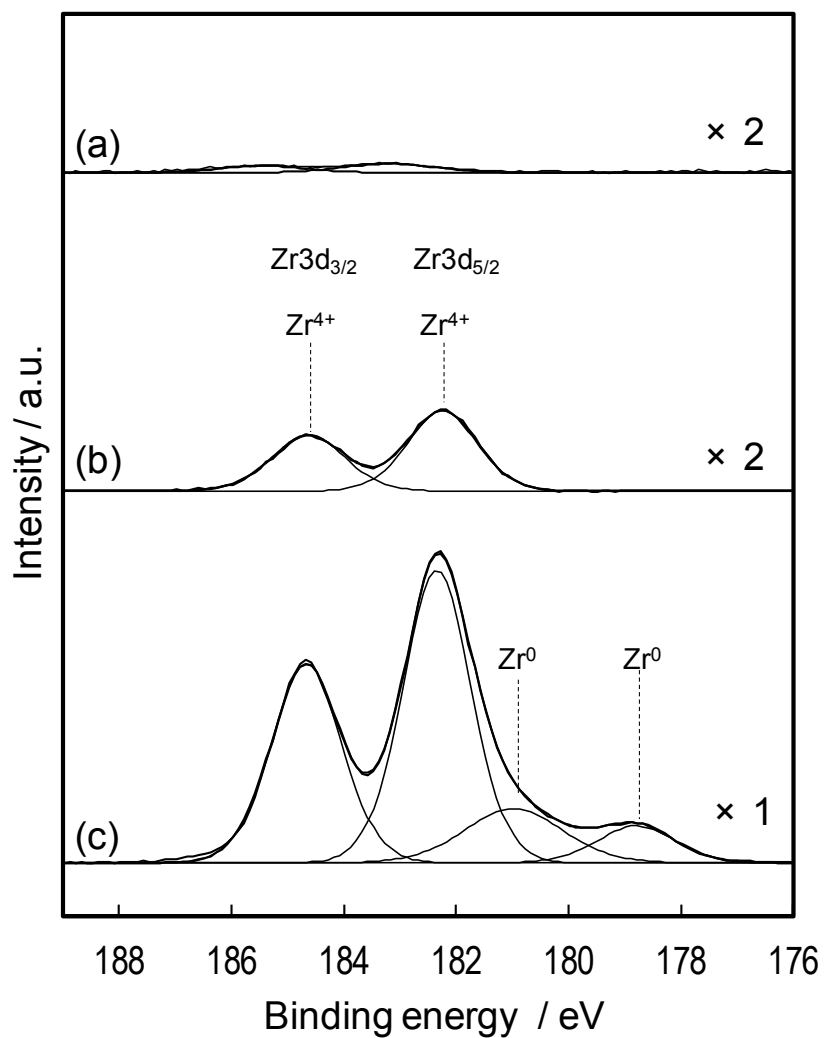
Figure S12. Zr3d XPS of (a) as-prepared Pt/Zr/SUS, (b) Pt/Zr/SUS after thermal aging at 650 °C for 24 h, and (c) as prepared Zr/SUS. AP pulses: 4000 shot Pt, 20000 shot Zr.
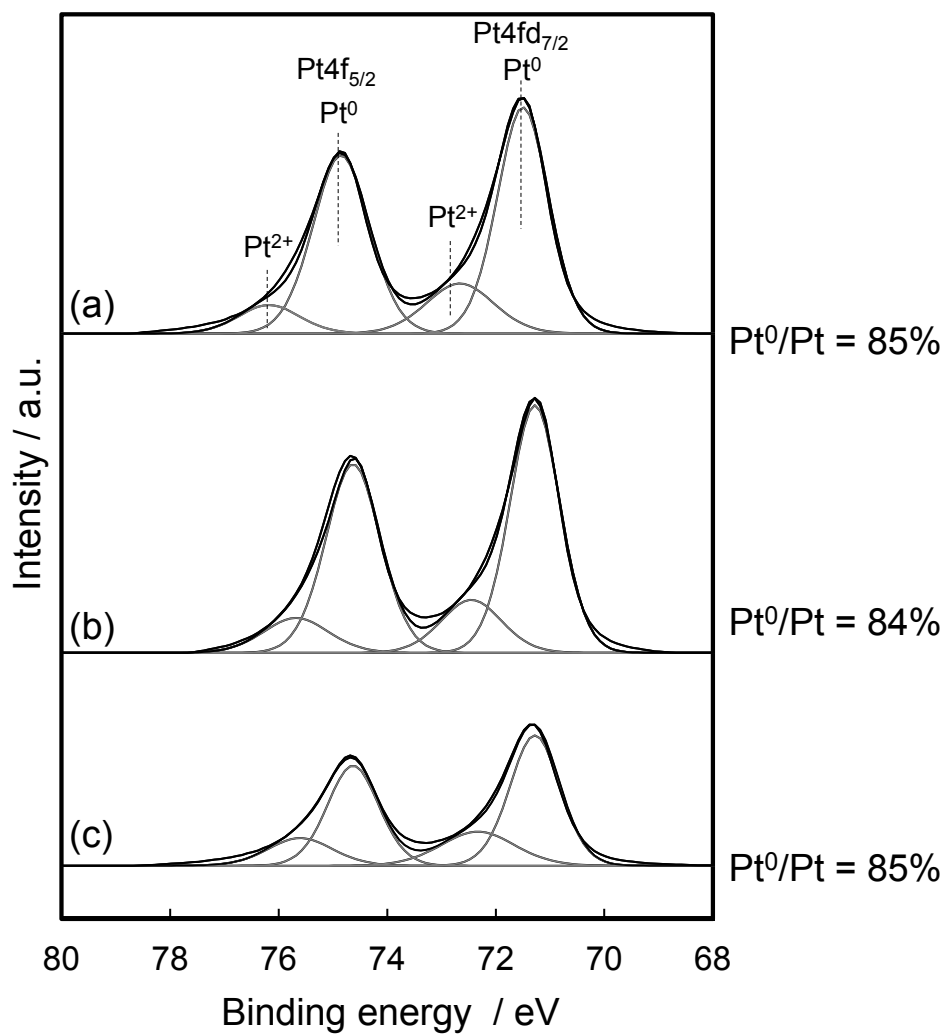
Figure S13. Pt4f XPS of (a) as-prepared Pt/Zr/SUS, (b) Pt/Zr/SUS after catalytic test, and (c) Pt/Zr/SUS after thermal aging at 650 °C for 24 h. AP pulses: 4000 shot Pt, 20000 shot Zr.

Table S1 Details of the TOF calculation for catalytic NH_3 oxidation

catalyst	Pt surface area/m^2	surface Pt /μmol	NH_3 conv. [c] /%	reaction rate /mol min^{-1}	TOF [d] / min^{-1}
Pt/SUS (2000 pulse, 3 mm×30 mm)	0.90×10^{-4}	0.0023 [a]	8.9	11.9×10^{-8}	51.7
Pt plate (3 mm×30 mm×0.2 mm)	0.97×10^{-4}	0.0025 [a]	1.6	2.2×10^{-8}	8.8
Pt/Al$_2$O$_3$ (0.13 wt%, 52.3 mg)	65.2×10^{-4}	0.135 [b]	2.8	3.8×10^{-8}	0.28

[a] Determined by the geometric area of the foil surface, surface coverage (100%), and surface atomic density of Pt (111) ($1.54×10^{19}$ atom m^{-2}).

[b] Determined by the Pt loading (68.0 μg) and Pt metal dispersion (38.8%).

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

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

(i) Pt/SUS

[surface Pt] = [geometric area of foil] × [surface coverage] × [surface atomic density]

$$= 0.90×10^{-4} \text{ (m}^2\text{)} × 1 × 1.54×10^{19} \text{ atom m}^{-2} / 6.02×10^{23} \text{ (atom mol}^{-1}\text{)} = 2.3×10^{-9} \text{ (mol)}$$

$$\text{TOF} = \frac{\text{[reaction rate]}}{\text{[surface Pt]}} = 11.9×10^{-8} \text{ (mol min}^{-1}\text{)} / 2.3×10^{-9} \text{ (mol)} = 51.7 \text{ (min}^{-1}\text{)}$$

(ii) Pt plate

[surface Pt] = [geometric area of plate] × [surface atomic density]

$$= 0.97×10^{-4} \text{ (m}^2\text{)} × 1.54×10^{19} \text{ atom m}^{-2} / 6.02×10^{23} \text{ (atom mol}^{-1}\text{)} = 2.48×10^{-9} \text{ (mol)}$$

$$\text{TOF} = \frac{\text{[reaction rate]}}{\text{[surface Pt]}} = 2.2×10^{-8} \text{ (mol min}^{-1}\text{)} / 2.5×10^{-9} \text{ (mol)} = 8.8 \text{ (min}^{-1}\text{)}$$

(iii) Pt/Al$_2$O$_3$

[surface Pt] = [Pt loading] × [Pt metal dispersion]

$$= 68.0 \text{ (μg)} × 0.388 / 195.084 \text{ (g mol}^{-1}\text{)} = 0.135×10^{-6} \text{ (mol)}$$

$$\text{TOF} = \frac{\text{[reaction rate]}}{\text{[surface Pt]}} = 3.8×10^{-8} \text{ (mol min}^{-1}\text{)} / 0.135×10^{-6} \text{ (mol)} = 0.28 \text{ (min}^{-1}\text{)}$$