SUPPORTING INFORMATION

Dynamic nitroxyl formation in the ammonia oxidation on platinum via Eley-Rideal reactions

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Supplemental Figs. S1-S7
Fig. S1 Beam current of $\text{O}^+$ and $\text{O}_2^+$ beams as a function of incidence energy.
Fig. S2 Mass resolution setting for the quadrupole mass spectrometer. Collision-induced dissociation of $\text{H}_2\text{O}^+$ on Au surfaces produces strong signals of scattered ions at 17 amu ($\text{OH}^+$) and 16 amu ($\text{O}^+$). The resolution is set to be less than 0.5 amu to prevent signal interference between adjacent mass numbers, which is verified by the zero signal present at 16.5 amu.
Fig. S3 Surface sputtering products (positive ions). Energy distributions of: (a) $\text{O}^+$, (b) $\text{OH}^+$ and (c) $\text{H}^+$ from $\text{O}^+$ bombardment of Pt exposed to $1 \times 10^{-7}$ Torr NH$_3$ at various $\text{O}^+$ incidence energies, as indicated.
Fig. S4 Surface temperature dependence of the HNO⁻ signal. Energy distributions for HNO⁻ from O⁺ ion-scattering experiments on Pt exposed to 1×10⁻⁷ Torr NH₃ at E₀ = 67 eV, as a function of surface temperature from 420 to 310 K. HNO⁻ signal appears at surface temperatures below 360 K.
Fig. S5 Scattering at elevated surface temperature (420K). Energy distributions of: (a) O\(^-\), (b) OH\(^-\) and (c) NO\(^-\) from O\(^+\) bombardment of Pt exposed to 1\(\times\)10\(^{-7}\) Torr NH\(_3\) at various O\(^+\) incidence energies, as indicated.
Fig. S6 Kinematic analysis for scattering at 420 K. Exit energies of O\(^-\), OH\(^-\), and NO\(^-\) from O\(^+\)/Pt(NH\(_3\)) as a function of O\(^+\) incidence energy. The data points are obtained from the distributions of Fig. S5. The solid line for O\(^-\) is linear fitting with a slope calculated from standard BCT. The lines for OH\(^-\) and NO\(^-\) are linear fittings with slopes predicted from a modified BCT for Eley-Rideal reactions. The kinematic behavior is similar to that found at room temperature, with one exception. The inelastic energy loss for OH\(^-\) and NO\(^-\) ion exits at 420 K is about 2-3 eV lower than that observed at room temperature, which may be caused by Pt work function change upon surface annealing.
Fig. S7 Oxidation with molecular O$_2^+$ projectiles. Exit energies of O$_2^-$, HO$_2^-$, O$^-$, OH$^-$, NO$^-$ and HNO$^-$ from O$_2^+/\text{Pt(NH}_3\text{)}$ as a function of O$_2^+$ incidence energy. The data points are obtained from the distributions of Fig. 4. The solid line for O$_2^-$ is linear fitting with a slope calculated from BCT assuming consecutive collisions of the two oxygen atoms with the same surface atom. The HO$_2^-$ exit data can be captured by the O$_2^-$ kinematic factor with $\sim$3.8 eV larger inelastic energy loss. The exit energy of O$^-$ is roughly half of that for O$_2^-$ exit, though it cannot be fitted linearly. The OH$^-$, NO$^-$ and HNO$^-$ exit energy cannot be described by Eley-Rideal reactions between dissociated O and adsorbed H, N and NH species. There must be additional surface interactions, currently not understood (possibly similar to hot-atom reactions).