

Supporting Information

**Structure- and Temperature-Dependence of
Pt-Catalyzed Ammonia Oxidation Rates and
Selectivities**

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Free energies of ammonia oxidation

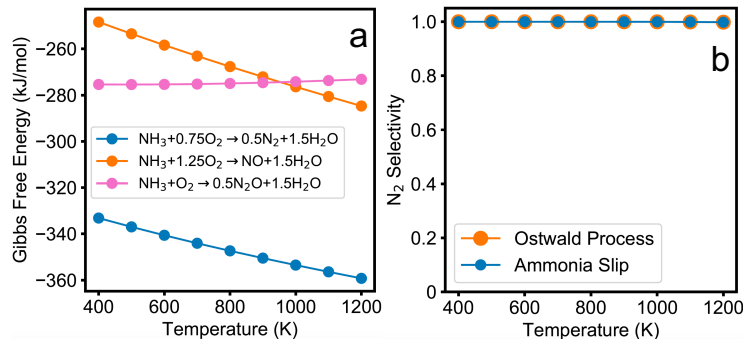


Figure S1: (a) Gibbs free energy of NO, N_2 and N_2O formation at standard pressure for each reactant and product.¹ (b) Equilibrium N_2 selectivity in reactors with constant overall pressures at Ostwald (10 bar) and ammonia slip (1 bar) conditions. The initial pressures of NH_3 , air and H_2O pressures are 0.9, 8.1 and 0.036 bar, respectively, for Ostwald process. The initial pressures of NH_3 , O_2 and H_2O are 0.001, 0.02 and 0.05 bar, respectively, for ammonia slip catalysis.

Binding strength of reaction intermediates

Table S1: Binding energies and the most favorable sites of intermediates in ammonia oxidation for Pt(211) and Pt(111). * represents a binding site. t, b, fcc and hcp represent an atop, bridge, fcc and hcp site, respectively.

Reaction	Pt(211)	Pt(111)
$\text{NH}_3(\text{g}) + * \rightleftharpoons \text{NH}_3^*$	-0.77 (t)	-0.69 (t)
$\text{NH}_3(\text{g}) + 0.25\text{O}_2(\text{g}) + * \rightleftharpoons \text{NH}_2^* + 0.5\text{H}_2\text{O}(\text{g})$	-1.81 (b)	-1.07 (b)
$\text{NH}_3(\text{g}) + 0.5\text{O}_2(\text{g}) + * \rightleftharpoons \text{NH}^* + \text{H}_2\text{O}(\text{g})$	-1.90 (hcp)	-2.02 (fcc)
$\text{NH}_3(\text{g}) + 0.75\text{O}_2(\text{g}) + * \rightleftharpoons \text{N}^* + 1.5\text{H}_2\text{O}(\text{g})$	-2.46 (hcp)	-2.50 (fcc)
$0.5\text{O}_2(\text{g}) + * \rightleftharpoons \text{O}^*$	-1.50 (b)	-1.24 (fcc)
$\text{NO}(\text{g}) + * \rightleftharpoons \text{NO}^*$	-2.33 (b)	-1.92 (fcc)
$\text{N}_2\text{O}(\text{g}) + * \rightleftharpoons \text{N}_2\text{O}^*$	-0.09 (b)	0.03 (t)
$\text{H}_2\text{O}(\text{g}) + * \rightleftharpoons \text{H}_2\text{O}^*$	-0.25 (t)	-0.19 (t)
$0.25\text{O}_2(\text{g}) + 0.5\text{H}_2\text{O}(\text{g}) + * \rightleftharpoons \text{OH}^*$	-1.12 (b)	-0.44 (b)

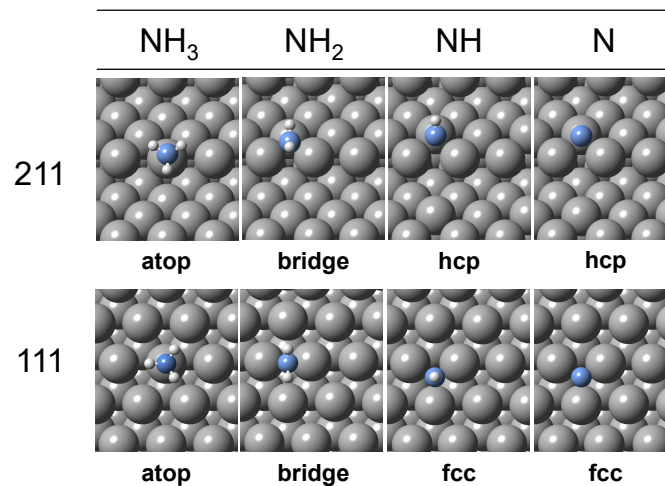


Figure S2: Most stable binding sites and configurations of NH_x intermediates on Pt(211) and Pt(111). Pt: silver; N: blue; H: white.

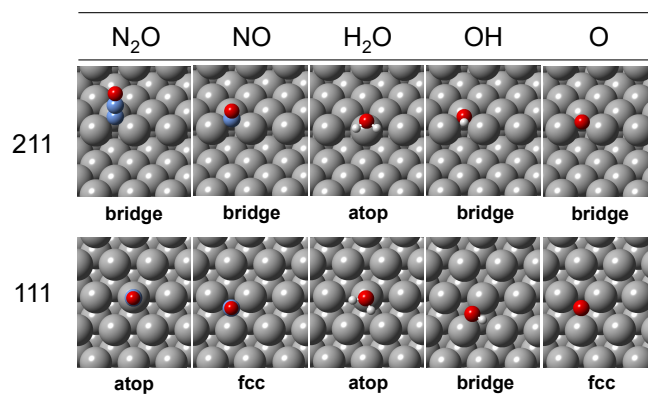


Figure S3: Most stable binding sites and configurations of oxygen containing intermediates on Pt(211) and Pt(111). Pt: silver; O: red; N: blue; H: white.

Initial, transition and final states of reaction steps

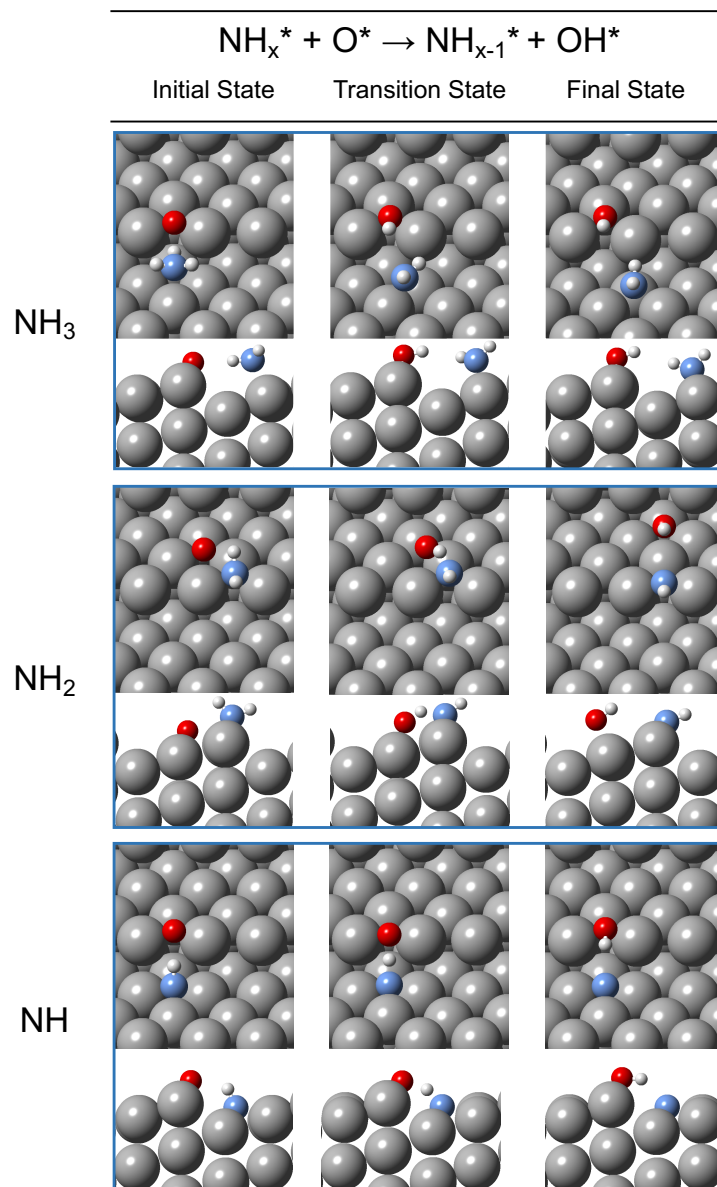


Figure S4: Initial, transition and final states of NH_x^* activation by O^* on Pt(211).

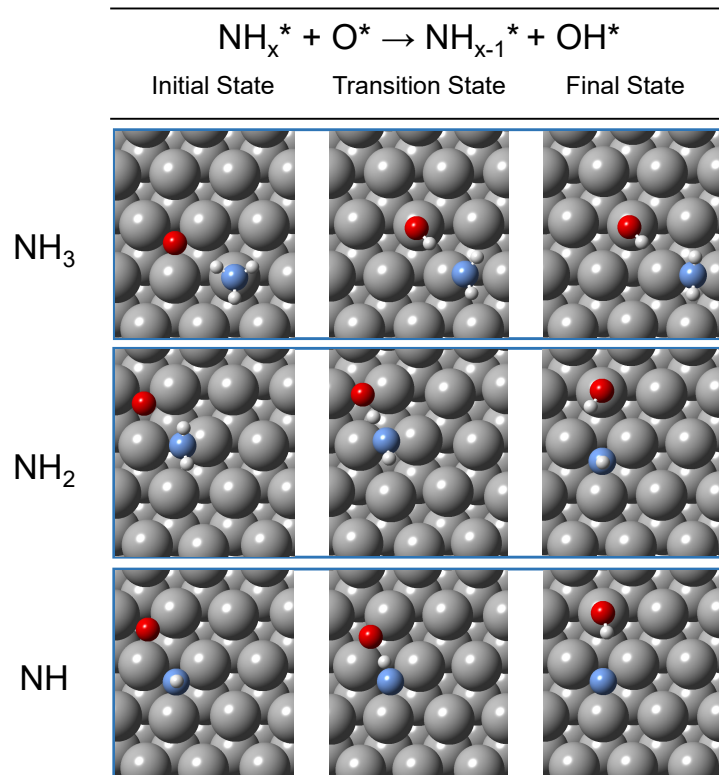


Figure S5: Initial, transition and final states of NH_x^* activation by O^* on Pt(111).

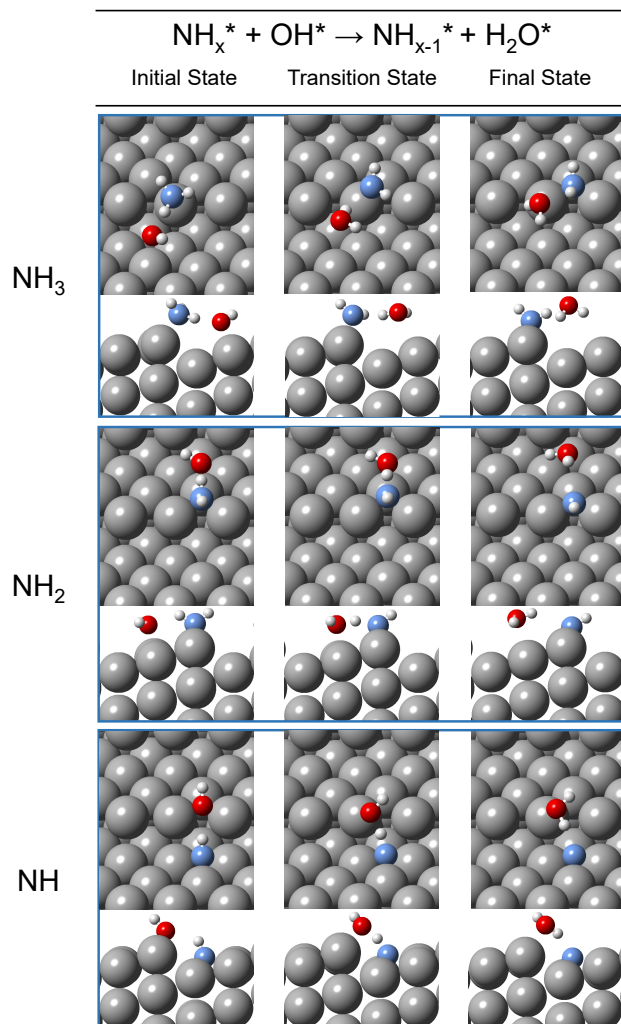


Figure S6: Initial, transition and final states of NH_x^* activation by OH^* on Pt(211).

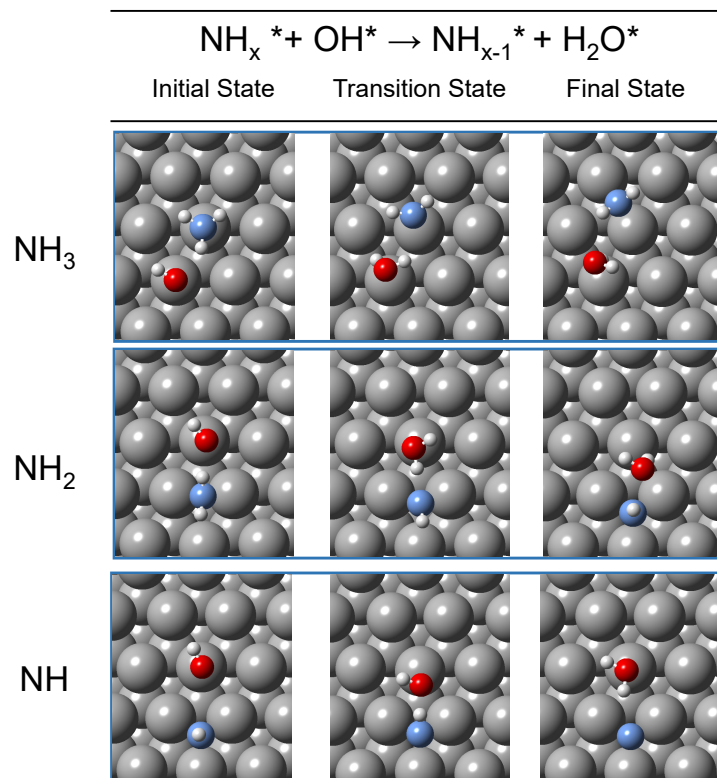


Figure S7: Initial, transition and final states of NH_x^* activation by OH^* on Pt(111).

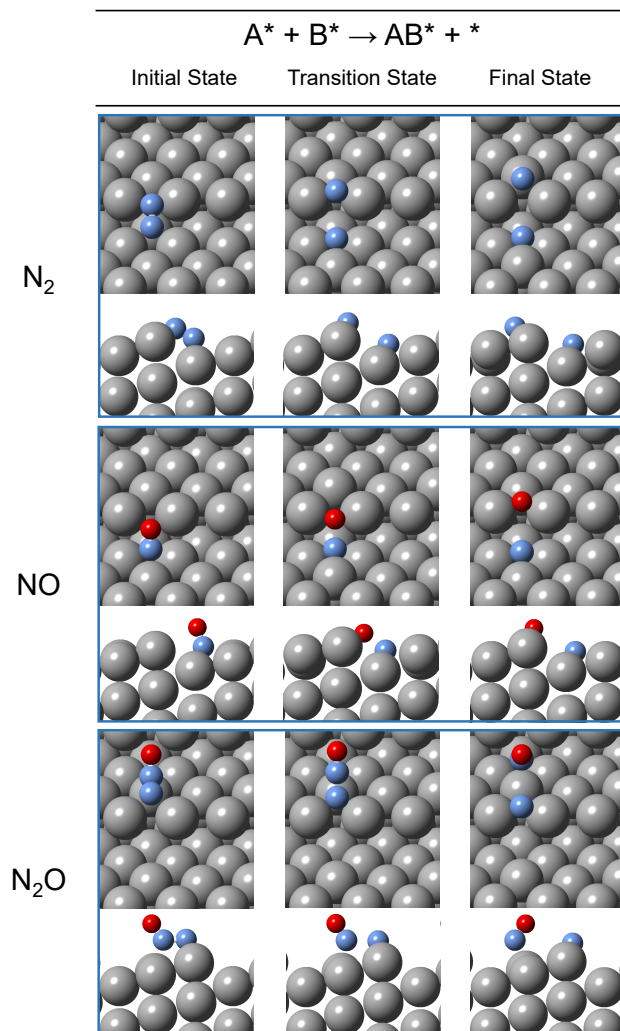


Figure S8: Initial, transition and final states of products formation on Pt(211).

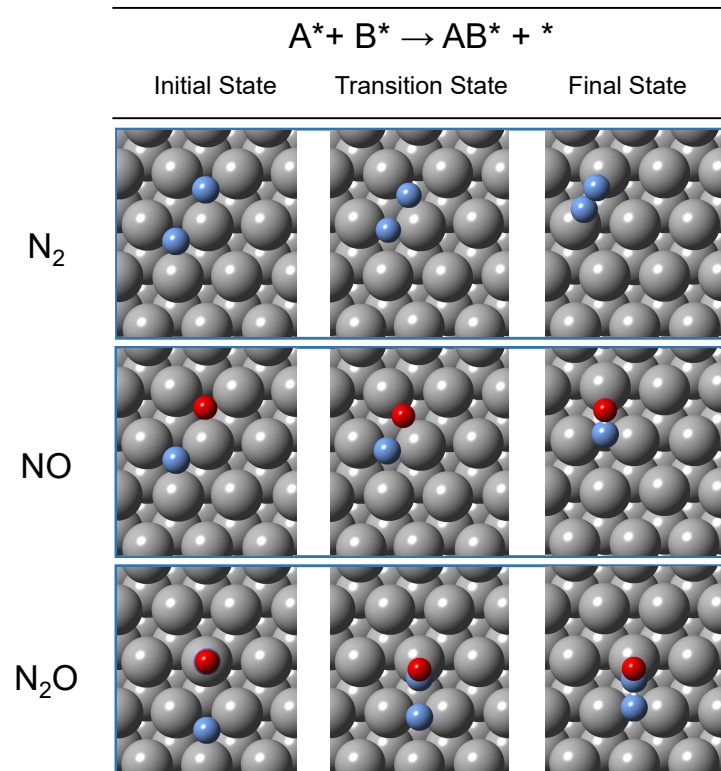


Figure S9: Initial, transition and final states of products formation on Pt(111).

Energy diagrams for O_2 dissociative adsorption and OH^* reaction

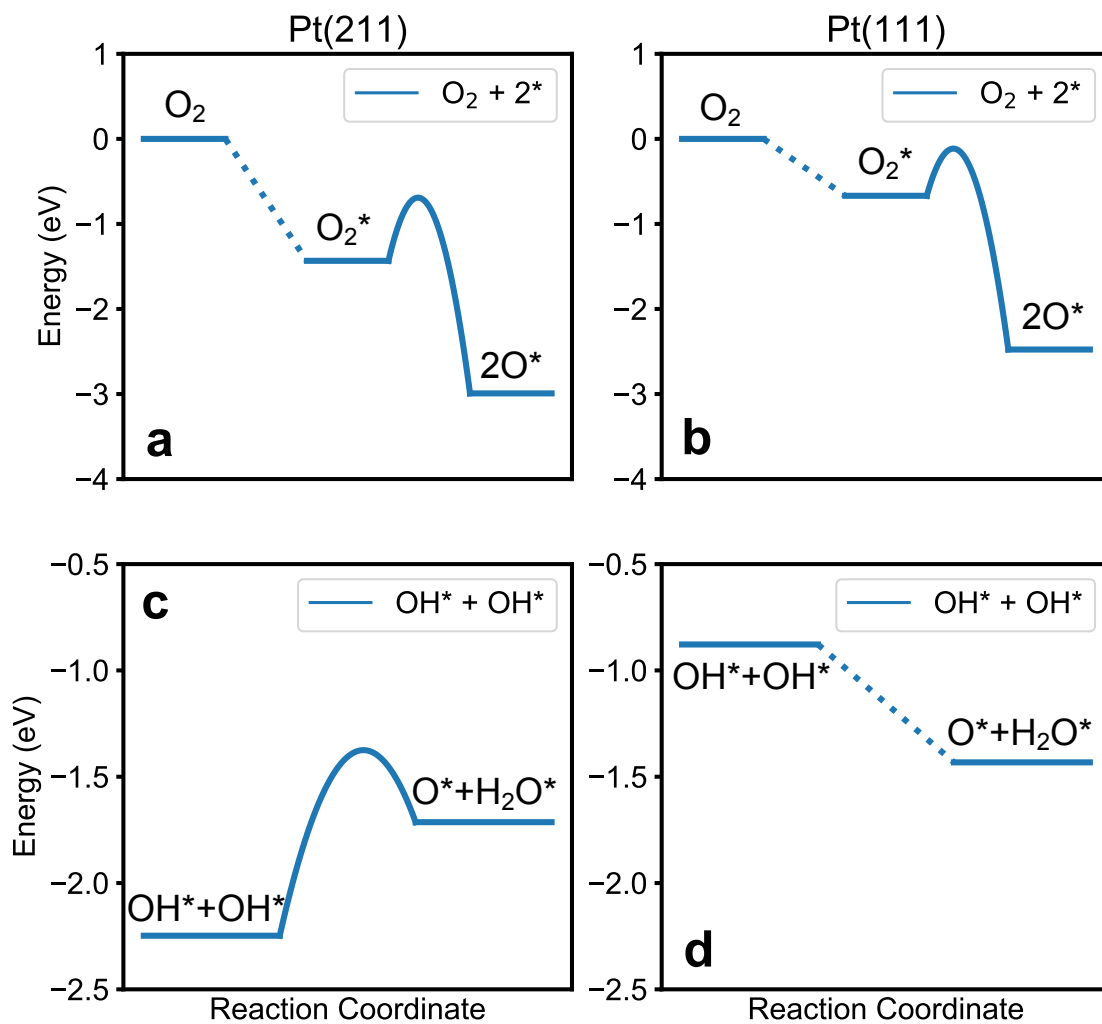


Figure S10: Energy diagrams for O_2 dissociative adsorption and OH^* reaction on Pt(211) and Pt(111).

Reaction energies and barriers of ammonia oxidation on Pt (211) and Pt(111)

Table S2: Reaction pathways, energies and barriers of ammonia oxidation on Pt(211) and Pt(111). (*) represents a binding site. The barriers are the energy differences between the transition states and the initial states at infinite separation. If the value is negative, we treat it as barrierless. For non-activated adsorption, the barriers are assumed to be 0.

Reaction	Pt(211) ΔE	Pt(211) E_a	Pt(111) ΔE	Pt(111) E_a
(1) $\text{O}_2(\text{g}) + 2^* \longleftrightarrow 2\text{O}^*$	-2.99	0.00	-2.47	0.00
(2) $\text{NH}_3(\text{g}) + ^* \longleftrightarrow \text{NH}_3^*$	-0.77	0.00	-0.69	0.00
(3) $\text{NH}_3^* + \text{O}^* \longleftrightarrow \text{NH}_2^* + \text{OH}^*$	-0.70	0.58	0.41	0.70
(4) $\text{NH}_2^* + \text{O}^* \longleftrightarrow \text{NH}^* + \text{OH}^*$	0.25	1.45	-0.15	0.81
(5) $\text{NH}^* + \text{O}^* \longleftrightarrow \text{N}^* + \text{OH}^*$	-0.22	0.47	0.33	1.60
(6) $\text{NH}_3^* + \text{OH}^* \longleftrightarrow \text{NH}_2^* + \text{H}_2\text{O}^*$	-0.16	0.83	-0.14	0.35
(7) $\text{NH}_2^* + \text{OH}^* \longleftrightarrow \text{NH}^* + \text{H}_2\text{O}^*$	0.78	0.79	-0.70	0.01
(8) $\text{NH}^* + \text{OH}^* \longleftrightarrow \text{N}^* + \text{H}_2\text{O}^*$	0.31	0.84	-0.23	0.41
(9) $\text{OH}^* + \text{OH}^* \longleftrightarrow \text{O}^* + \text{H}_2\text{O}^*$	0.53	0.84	-0.55	0.00
(10) $\text{H}_2\text{O}^* \longleftrightarrow \text{H}_2\text{O}(\text{g}) + ^*$	0.25	0.25	0.19	0.19
(11) $\text{N}^* + \text{N}^* \longleftrightarrow \text{N}_2(\text{g}) + 2^*$	-0.63	1.18	-0.54	2.53
(12) $\text{N}^* + \text{O}^* \longleftrightarrow \text{NO}^* + ^*$	-0.20	1.46	0.04	2.21
(13) $\text{NO}^* \longleftrightarrow \text{NO}(\text{g}) + ^*$	2.33	2.33	1.91	1.91
(14) $\text{N}^* + \text{NO}^* \longleftrightarrow \text{N}_2\text{O}^*$	1.18	1.62	0.93	1.71
(15) $\text{N}_2\text{O}^* \longleftrightarrow \text{N}_2\text{O}(\text{g}) + ^*$	0.10	0.10	-0.03	0.00

Table S3: Reaction energies and barriers of ammonia decomposition² and hydrogen oxidation³ on Pt(211) and Pt(111). (*) represents a binding site. The barriers are the energy differences between the transition states and the initial states at infinite separation.

Reaction	Pt(211) ΔE	Pt(211) E_a	Pt(111) ΔE	Pt(111) E_a
(1) $\text{NH}_3^* + ^* \longleftrightarrow \text{NH}_2^* + \text{H}^*$	-0.22	1.15	0.53	1.16
(2) $\text{NH}_2^* + ^* \longleftrightarrow \text{NH}^* + \text{H}^*$	0.73	1.61	-0.04	1.36
(3) $\text{NH}^* + ^* \longleftrightarrow \text{N}^* + \text{H}^*$	0.64	1.30	0.41	1.39
(4) $\text{H}^* + \text{O}^* \longleftrightarrow \text{OH}^* + ^*$	-0.53	0.50	0.15	1.09
(5) $\text{H}^* + \text{OH}^* \longleftrightarrow \text{H}_2\text{O}^* + ^*$	0.32	0.96	-0.57	0.21

Imaginary frequencies of transition states and prefactors of the reactions

Table S4: Imaginary frequencies (f/i) of transition states and prefactors at 300 K of surface reactions on Pt(211) and Pt(111). (*) represents a binding site

Reaction	Pt(211)			Pt(111)		
	f/i (cm ⁻¹)	$A_f(s^{-1})$	$A_b(s^{-1})$	f/i (cm ⁻¹)	$A_f(s^{-1})$	$A_b(s^{-1})$
(1) O ₂ (g) + 2* \longleftrightarrow 2O*	96	$1.8 \times 10^3 Pa^{-1}$	1.7×10^{17}	289	$1.8 \times 10^3 Pa^{-1}$	4.7×10^{17}
(2) NH ₃ (g) + * \longleftrightarrow NH ₃ *	NA	$2.5 \times 10^3 Pa^{-1}$	2.9×10^{16}	NA	$2.5 \times 10^3 Pa^{-1}$	5.2×10^{16}
(3) NH ₃ * + O* \longleftrightarrow NH ₂ * + OH*	311	4.1×10^{12}	1.0×10^{13}	228	5.2×10^{12}	8.4×10^{12}
(4) NH ₂ * + O* \longleftrightarrow NH* + OH*	1248	4.7×10^{12}	6.0×10^{12}	1147	5.5×10^{12}	4.2×10^{12}
(5) NH* + O* \longleftrightarrow N* + OH*	786	3.4×10^{12}	2.5×10^{12}	1240	7.8×10^{12}	3.8×10^{12}
(6) NH ₃ * + OH* \longleftrightarrow NH ₂ * + H ₂ O*	148	8.2×10^{12}	3.5×10^{12}	257	4.9×10^{13}	3.2×10^{13}
(7) NH ₂ * + OH* \longleftrightarrow NH* + H ₂ O*	785	3.9×10^{12}	8.7×10^{11}	198	1.5×10^{13}	4.7×10^{12}
(8) NH* + OH* \longleftrightarrow N* + H ₂ O*	693	5.3×10^{12}	6.8×10^{11}	1058	5.9×10^{12}	1.2×10^{12}
(9) OH* + OH* \longleftrightarrow O* + H ₂ O*	477	4.2×10^{12}	7.1×10^{11}	554	3.1×10^{12}	1.3×10^{12}
(10) H ₂ O* \longleftrightarrow H ₂ O(g) + *	NA	3.7×10^{15}	$2.4 \times 10^3 Pa^{-1}$	NA	5.9×10^{15}	$2.4 \times 10^3 Pa^{-1}$
(11) N* + N* \longleftrightarrow N ₂ (g) + 2*	343	5.3×10^{12}	$4.7 \times 10^{-2} Pa^{-1}$	552	9.2×10^{12}	$6.8 \times 10^{-2} Pa^{-1}$
(12) N* + O* \longleftrightarrow NO* + *	467	3.8×10^{12}	9.6×10^{11}	443	8.3×10^{12}	2.7×10^{12}
(13) NO* \longleftrightarrow NO(g) + *	NA	1.3×10^{17}	$1.9 \times 10^3 Pa^{-1}$	NA	2.6×10^{17}	$1.9 \times 10^3 Pa^{-1}$
(14) N* + NO* \longleftrightarrow N ₂ O*	231	6.1×10^{12}	6.5×10^{12}	332	4.3×10^{12}	4.0×10^{11}
(15) N ₂ O* \longleftrightarrow N ₂ O(g) + *	NA	1.5×10^{17}	$1.6 \times 10^3 Pa^{-1}$	NA	1.4×10^{16}	$1.6 \times 10^3 Pa^{-1}$

Surface coverages of Pt(211) and Pt(111)

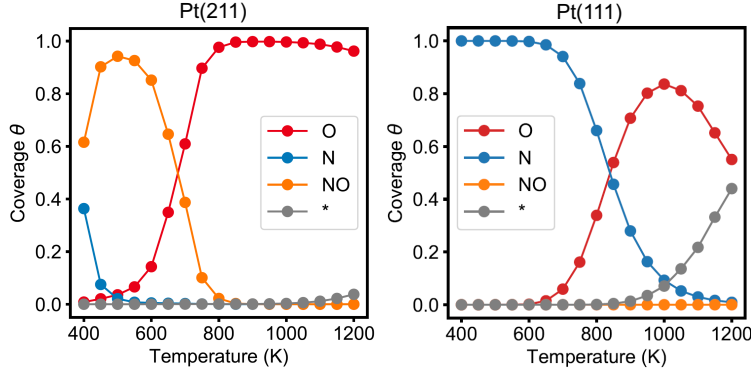


Figure S11: Surface coverages of major surface species and vacancies on Pt(211) and Pt(111) at ammonia slip control conditions. The partial pressures of NH_3 , O_2 and H_2O are 0.001, 0.02 and 0.05 bar, respectively.

Rate and selectivity temperature-dependence in a CSTR

In a continuous stirred-tank reactor (CSTR), the partial pressures of gaseous species are governed by Equation S1, where P_i is the partial pressure of a gaseous species, t is time, τ is residence time, $P_{i,0}$ is the inlet pressure of P_i , R is gas constant, T is temperature, TOF is turnover frequency of an active site and S is the active site number normalized to the volume of the reactor. When a CSTR reaches steady-state, $\frac{\partial P_i}{\partial t} = 0$. The steady-state pressures are solved for both Pt(211) and Pt(111) at ammonia slip conditions. The conversion of ammonia on Pt(211) increases from 0.04% to 95% and from 4×10^{-20} to 93% on Pt(111) when temperature increases from 400 to 1200K.

$$\frac{\partial P_i}{\partial t} = \frac{1}{\tau}(P_{i,0} - P_i) + R \times T \times S \times \text{TOF} \quad (\text{S1})$$

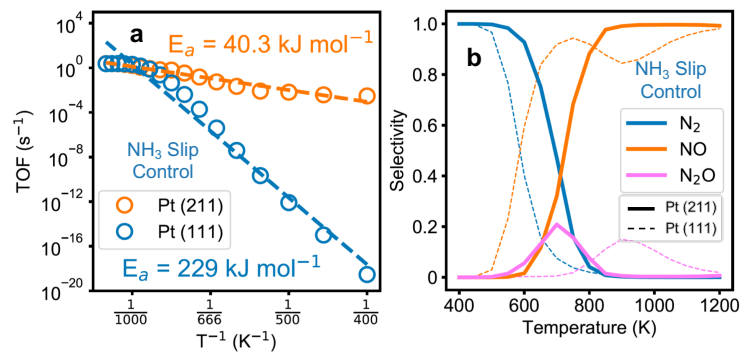


Figure S12: (a) Reaction rate against reciprocal temperature on Pt(211) and Pt(111) surfaces at ammonia slip catalysis conditions in a continuous stirred-tank reactor, where the inlet pressures of NH₃, O₂ and H₂O are 0.001, 0.02 and 0.05 bar, respectively. The concentration of active sites is 0.001 mol m⁻³ and the residence time is 4 s. (b) Selectivities of reaction products on Pt(211) and Pt(111) surfaces at the same conditions of (a). The selectivity is calculated from the product pressures in the reactor.

Rate at low pressure

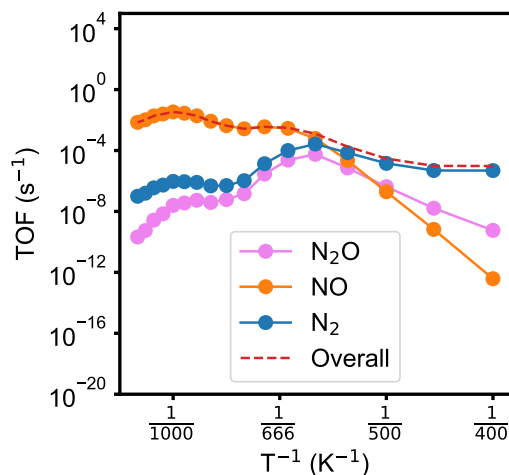


Figure S13: Reaction rate against reciprocal temperature on Pt(211) at low pressures. Pressures of NH₃ and O₂ are both 10^{-7} bar.

Rate and selectivity temperature-dependence in with *-assisted dehydrogenation of NH₃

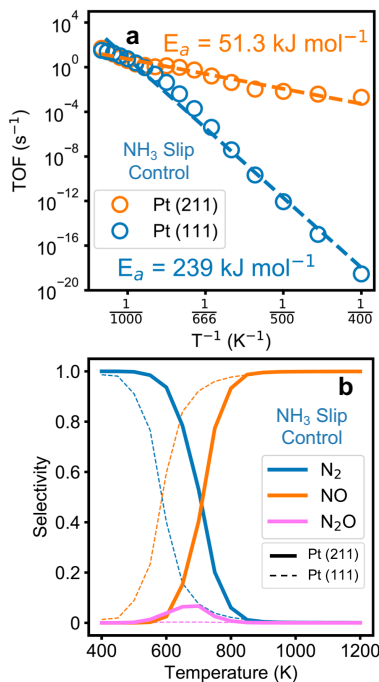


Figure S14: (a) Reaction rate against reciprocal temperature on Pt(211) and Pt(111) at ammonia slip catalysis conditions including the pathways of N-H dissociation and hydrogen oxidation on metal sites. (b) Selectivities to reaction products on Pt(211) and Pt(111). Pressures of NH₃, O₂ and H₂O are 0.001, 0.02 and 0.05bar, respectively.

Rate and selectivity sensitivity to sticking coefficient

The sticking coefficient is irrelevant for equilibrated processes. All molecular adsorption events are equilibrated in the models here. Nonetheless, we tested this assumption by introducing a 0.01 sticking coefficient on molecular adsorption and resolved the models for ammonia slip conditions; results are unchanged. O₂ adsorption rates do influence overall kinetics. To test the sensitivity of our conclusions to this assumption, we assume sticking coefficients as 0.01 and 0.1 and 0.01, and resolve. We show the conclusions are insensitive to sticking coefficient.

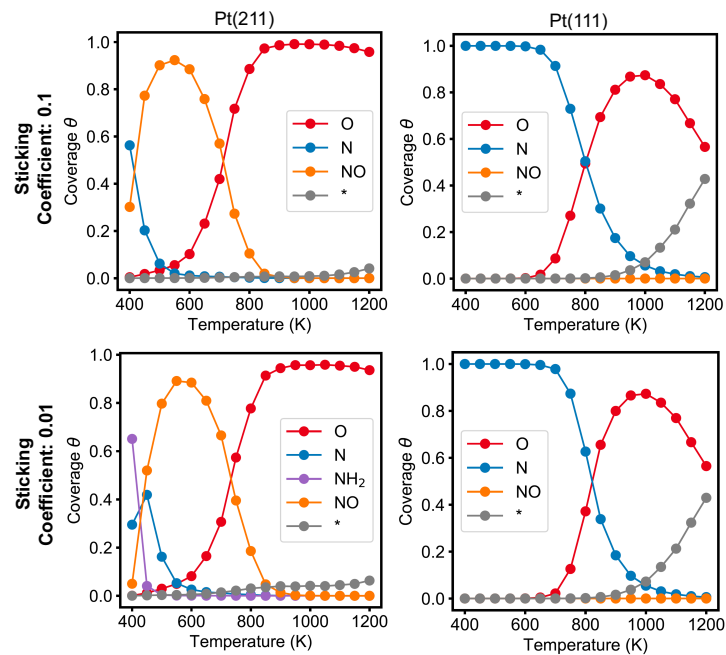


Figure S15: Surface coverages of major surface species and vacancies on Pt(211) and Pt(111) at ammonia slip control conditions with different sticking coefficients. The partial pressures of NH₃, O₂ and H₂O are 0.001, 0.02 and 0.05 bar, respectively.

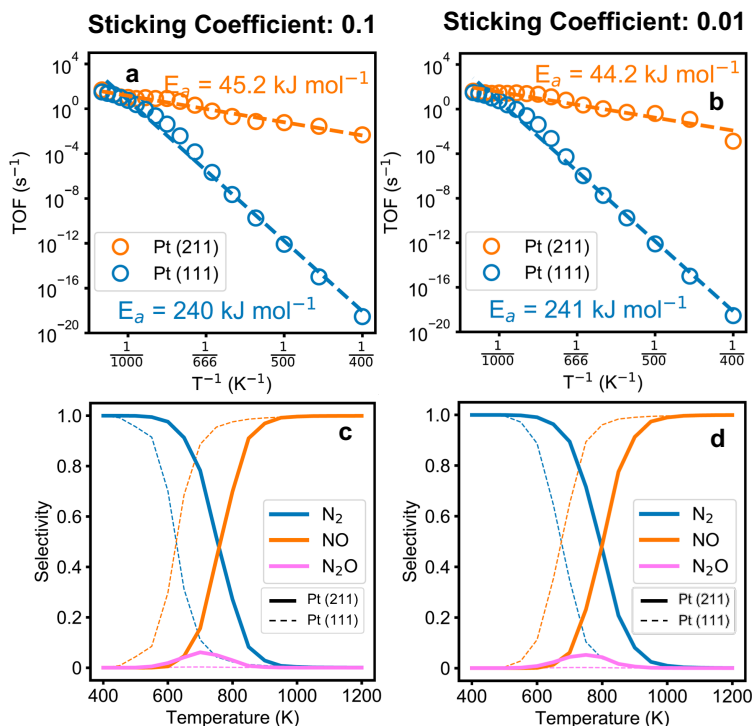


Figure S16: Reaction rate against reciprocal temperature on Pt(211) and Pt(111) at ammonia slip catalysis conditions with sticking coefficient as (a) 0.1 and (b) 0.01. Selectivities to reaction products on Pt(211) and Pt(111) with sticking coefficient as (c) 0.1 and (d) 0.01. Pressures of NH₃, O₂ and H₂O are 0.001, 0.02 and 0.05bar, respectively.

References

- (1) Chase Jr, M. W. NIST-JANAF Thermochemical Tables. *J. Phys. Chem. Ref. Data, Monograph* **1998**, *9*.
- (2) Offermans, W.; Jansen, A.; Van Santen, R.; Novell-Leruth, G.; Ricart, J.; Perez-Ramirez, J. Ammonia Dissociation on Pt {100}, Pt {111}, and Pt {211}: A Comparative Density Functional Theory Study. *J. Phys. Chem. C* **2007**, *111*, 17551–17557.
- (3) Stamatakis, M.; Chen, Y.; Vlachos, D. G. First-Principles-Based Kinetic Monte Carlo Simulation of the Structure Sensitivity of the Water–Gas Shift Reaction on Platinum Surfaces. *J. Phys. Chem. C* **2011**, *115*, 24750–24762.