Mechanism of N$_2$O formation in catalytic aftertreatment systems of ammonia/hydrogen-fueled engines

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Table S1 Energy barriers for dissociation and dimerization pathways for N$_2$O formation

Pathways	Energy barriers [kJ/mole]	catalyst
Dissociation pathway		
NO* → N* + O*	263.40	Ru(0001) surface[1]
NO* → N* + O*	299.10	Ru(0001) steps[1]
NO* → N* + O*	381.12	Au(111)[2]
NO* → N* + O*	373.40	Au(111)[2]
NO* → N* + O*	116.73	Pt(100)[3]
NO* → N* + O*	154.37	Pd steps[4]
NO* → N* + O*	457.56	Pt$_1$@γ-Al2O3 N-Down
NO* → N* + O*	347.82	Pt$_1$@γ-Al2O3 Bridge
Dimerization pathway		
NO* + NO* → N$_2$O* + O*	32.81	Au(111)[2]
NO* + NO* → N$_2$O* + O*	15.05	Silicene [5]
NO* + NO* → N$_2$O* + O*	67.54	N-doped graphene [6]
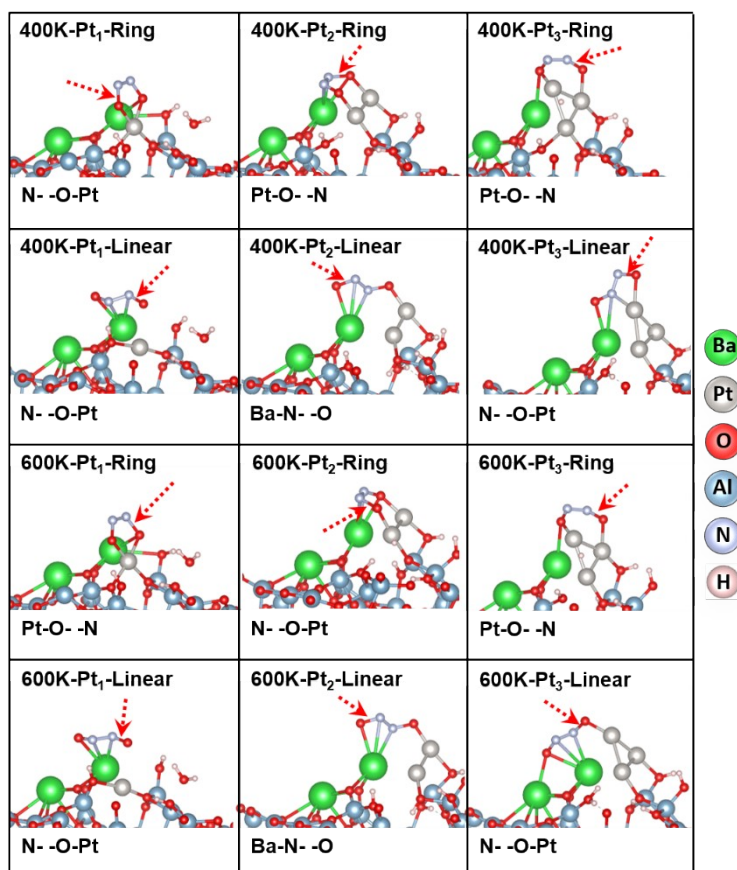
Figure S1. Initial adsorption configurations of NO dimer on Pt_{1-3}-$(BaO)_2$@γ-Al_2O_3(100)

(The 3-dimensional model of the atomic structure of Pt_{1-3}-$(BaO)_2$@γ-Al_2O_3(100) is shown in the Appendix

PCCPPtcluster@Al2O3_vasp_CONTCAR.rar)

The SG-FPMD method for obtaining the free energy barriers of N_2O formation

In the FPMD process in this paper, the Slow-growth approach[7] (SG) is used to capture the free energy (A) trend of the N-O bond breaking (corresponding to a specific structural parameter ξ) in the reaction ONNO* - NNO* + O*. The work done ($w_{1 \to 2}$) to change slowly and linearly from state 1 to state 2 at a transition rate of $\dot{\xi}$ can be expressed as:

$$w_{1 \to 2} = \int_{\xi_1}^{\xi_2} \left(\frac{\partial A}{\partial \xi} \right) \cdot \dot{\xi} dt$$

where $\partial A / \partial \xi$ can be obtained from the trajectory of the restricted FPMD of the blue-moon ensemble[8] by the SHAKE algorithm[9]. When the transition rate $\dot{\xi}$ is sufficiently small, the work required to move from state 1 to state 2 is representative of the free energy difference corresponding to the two states, and thus the value of $\dot{\xi}$ used in this paper is 0.0005 Å/fs. Since the two N-O bonds of the NO dimer (labelled *d1* and *d2*, respectively) in the reaction ONNO* - NNO* + O* both have the possibility of breaking, so the collective variable (CV) was chosen as the difference between the two (CV = *d1 - d2*), as shown in Figure S2(a). Figure S2(b) is a schematic of the CV setting for the 600K-Pt_3-Ring initial adsorption configuration as an example, and the rest of the 11 initial adsorption configurations are used as an analogy. Since the tethering system is adopted as the canonical tethering system (NVT). Therefore, the final free energy obtained by the SG-FPMD approach is the Helmholtz free energy.
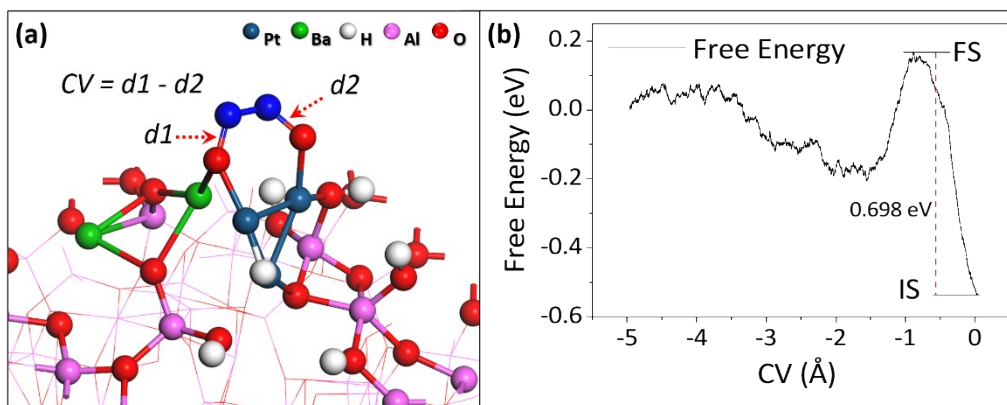
Figure. S2 Schematic of CV setting for structure 600K-Pt$_3$-Ring (a) with free energy profile (b)
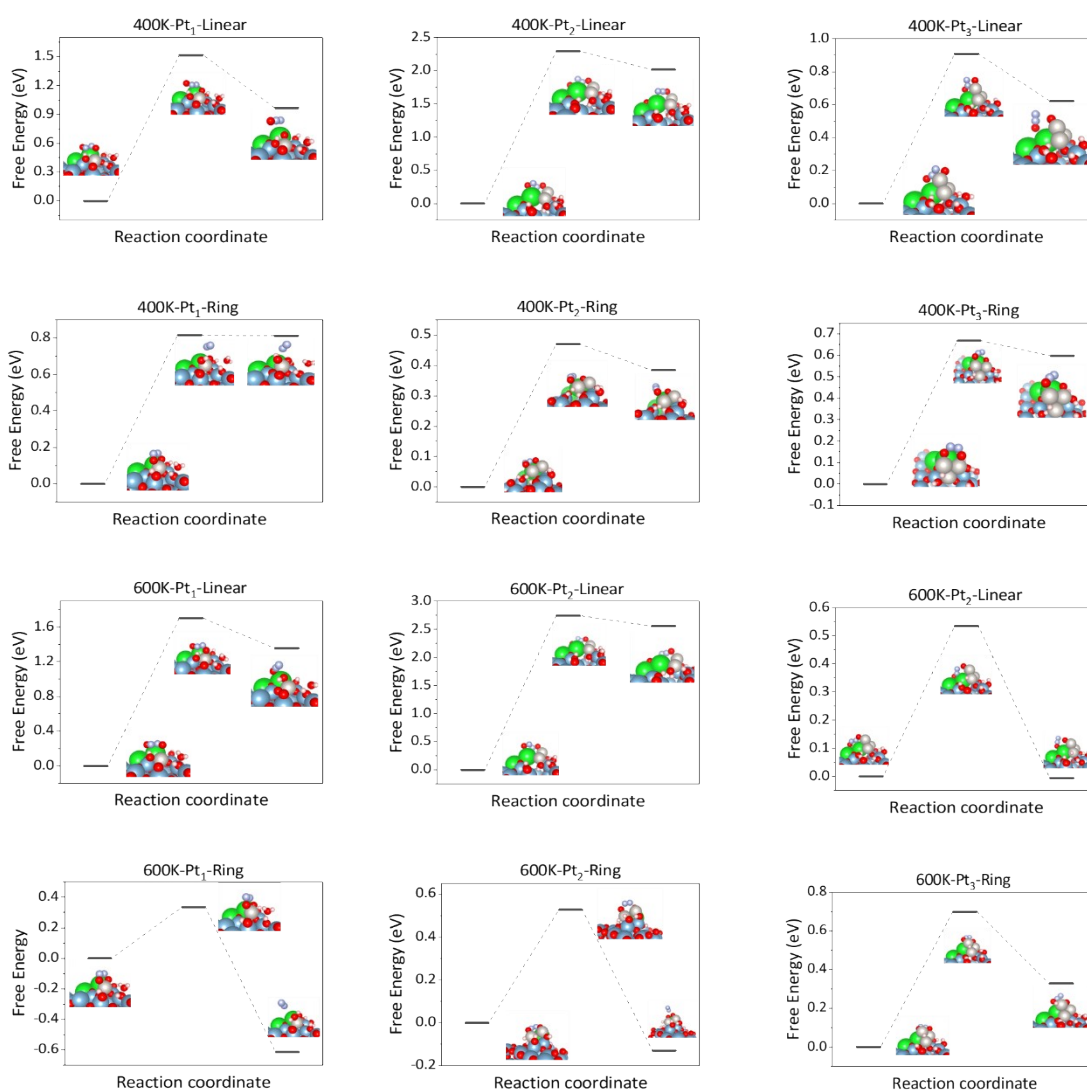

Figure S3. Reaction paths and free energy barriers of NO dimer to N$_2$O on Pt$_n$ clusters with different atomic numbers

(The FPMD simulation trajectory animations for the 12 reaction paths are shown in the attachment "PCCP_FPMD-movie.rar")

References

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