Supporting Information: Modified Activation-Relaxation Technique (ARTn) Method Tuned For Efficient Identification of Transition States in Surface Reactions

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1 Details of the training set for NNP

The dataset consists of 7149 configurations with 402 515 training points. The detailed number of atoms, structures, and training points are summarized in Table S1.

Table S1: The detailed information of reference structures

Structure type	Methods	# of atoms		# of structures	# of training points
		Pt	O		
Pt ($Fm\bar{3}m$)	Distortion	4		147	588
	NVT MD	32		150	4800
PtO ($P4_2/mmc$)	Distortion	2	2	147	588
	NVT MD	16	16	150	4800
Pt_3O_4 ($Pm\bar{3}m$)	Distortion	6	8	147	2058
	NVT MD	6	8	150	2100
α-PtO_2 ($P6_3mc$)	Distortion	2	4	147	882
	NVT MD	18	36	150	8100
β-PtO_2 ($Pnnm$)	Distortion	2	4	147	882
	NVT MD	16	32	150	7200
O_2 molecule	EOS		2	98	196
Pt–O mixture	NVT MD	40	20	500	30 000
Pt (111) + random O	Relaxation	80	7–20	3254	297 588
Pt (111)	RDA [a]	20		151	3020
Pt (111) @ 0.25 ML	RDA	20	1	151	3171
Pt (111) @ 0.5 ML	RDA	20	2	151	3322
Pt (111) @ 0.75 ML	RDA	20	3	151	3473
Pt (111) @ 1 ML	RDA	20	4	151	3624
Pt (111) + HCP	RDA	20	1	151	3171
Pt (111) + TOP	RDA	20	1	151	3171
Pt (111) + TET1[b]	RDA	20	1	151	3171
Pt (111) + TET2[c]	RDA	20	1	151	3171
Pt (111) + OCT[d]	RDA	20	1	151	3171
Pt (111) + α-PtO_2	RDA	24	8	151	4832
Pt (111) + β-PtO_2	RDA	24	12	151	5436
Total				7149	402 515

[a] Random displacement of atom
[b] Subsurface sites below HCP sites
[c] Subsurface sites below TOP sites
[d] Subsurface sites below FCC sites

2 Snapshots of MD simulations

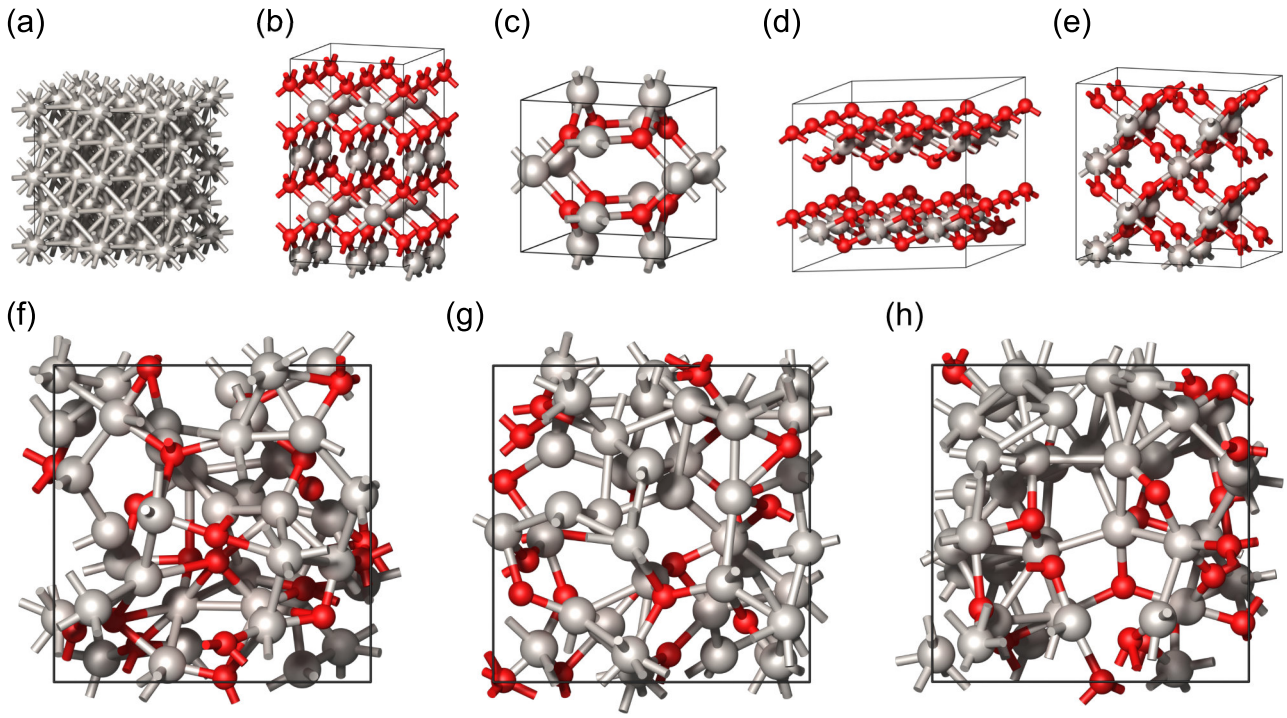

Figure S1: Snapshots of MD simulations. (a–e) The initial structure of Pt ($Fm\bar{3}m$), PtO ($P4_2/mmc$), Pt_3O_4 ($Pm\bar{3}m$), α-PtO_2 ($P6_3mc$), and β-PtO_2 ($Pnnm$), respectively. (f) The initial structure of melt simulation. (g) The final (initial) structure of melt (quench) simulation. (h) The final structure of quench simulation.

3 Energy and force correlations of the NNP and DFT

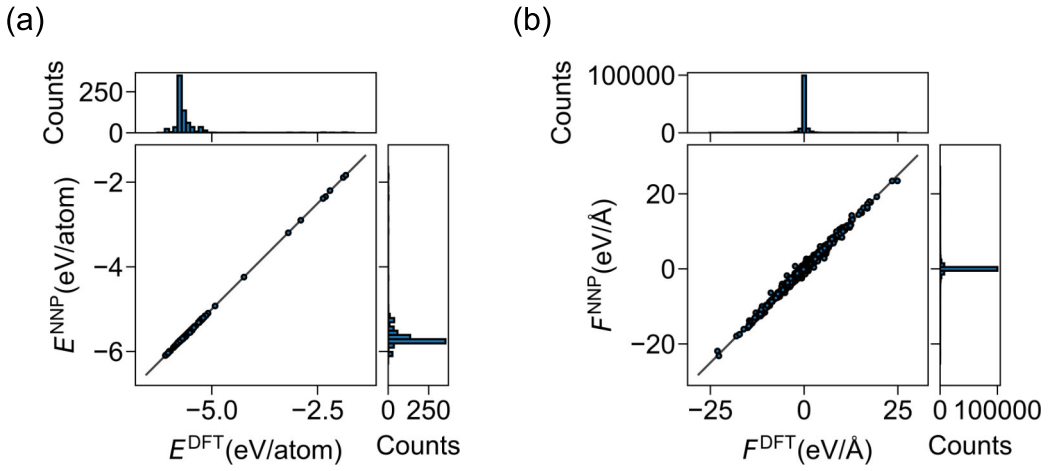

Figure S2: Parity plots between DFT and NNP. (a) Energy and (b) forces for the validation set

Trained NNP achieved root-mean-squared errors (RMSEs) for energy and forces of 7 meV/atom and 0.22 eV/Å on the validation set, respectively. Their correlations are depicted in Figure S2.

4 Details for counting possible reactions

We enumerate all possible reactions to demonstrate the completeness of iso-ARTn. In the case of O in-plane diffusion, the free O atoms on the FCC and HCP sites have three directions to hop in-plane. Therefore, we generate the candidates for the final states of 57 O in-plane diffusions (19 O atoms $\times$ 3 directions = 57 reactions) by locating an O atom on adjacent hollow sites. Then, we optimize their geometry to check whether they have a local minimum on those sites. Among 57 candidates, the O atom in only two configurations diffuses to other sites spontaneously, resulting in 55 possible reactions. Similarly, we create 19 O atom out-of-plane diffusions by dragging an O atom downward (19 O atoms $\times$ 1 directions = 19 reactions). Six candidates have a local minimum at the subsurface sites. Lastly, for Pt buckling, we rely on the patterns of already sampled reactions. We observe that Pt atoms

with two O atoms in opposite directions or three O atoms nearby can be buckled. While five Pt atoms satisfy the first condition, only one Pt atom meets the second condition in our test configuration. Additionally, the buckling of the Pt atoms with three O atoms has two types: single oxygen-involved buckling and multi-oxygen-involved buckling (see Figure S3). A single oxygen-involved buckling has two directions (clockwise and counterclockwise) for each oxygen atom. Likewise, a multi-oxygen-involved buckling also has two ways for the Pt atom (left- and right-curved uplift). Thereby, in total, 17 (5 Pt atoms with two oxygen + 3 O atoms $\times$ 2 directions + 3 Pt directions $\times$ 2 ways) configurations are tested as the final states of Pt buckling. Among them, 16 states are connected to the initial states through first-order saddle points. In summary, the numbers of possible reactions are 55, 6, and 16 for O in-plane, O out-of-plane, and Pt buckling.

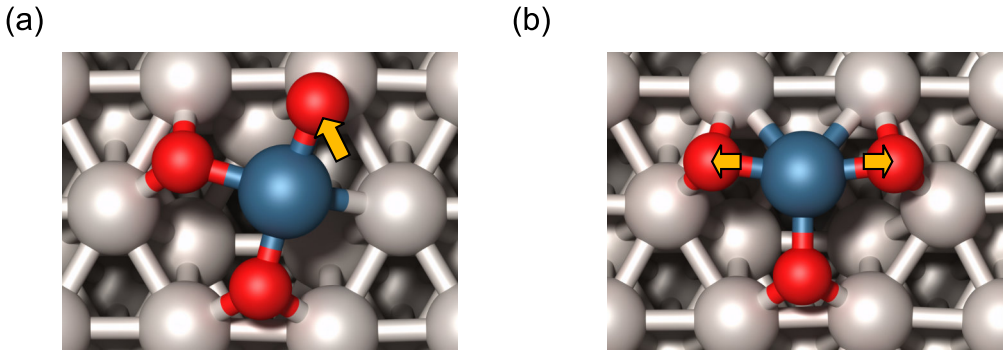

Figure S3: Two types of Pt buckling. (a) Single oxygen-involved and (b) multi-oxygen-involved buckling. Blue atoms stand for buckled Pt atoms. Yellow arrows indicate the oxygen displacement direction.