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A comparative DFT study of the oxidation of Al crystals and nanoparticles

Supporting information

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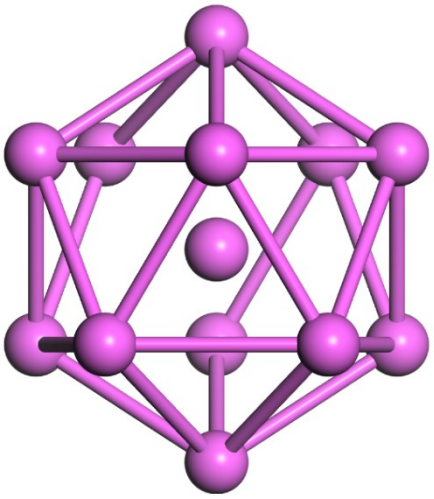
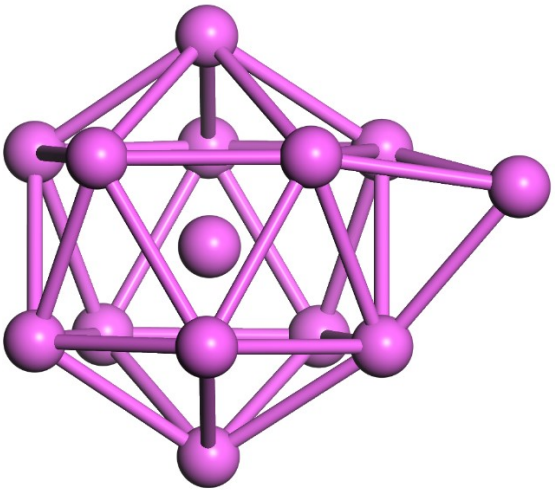
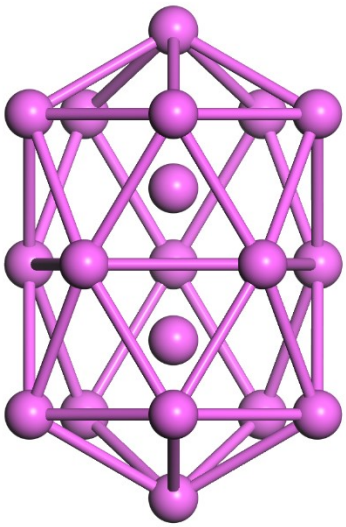


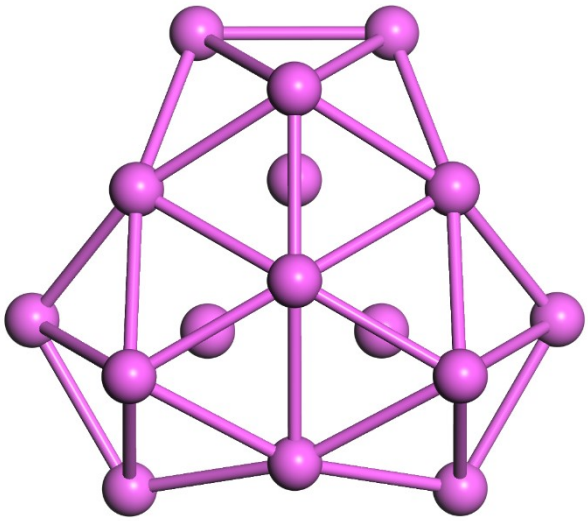
Al_{13}(5.3 Å, I_h)



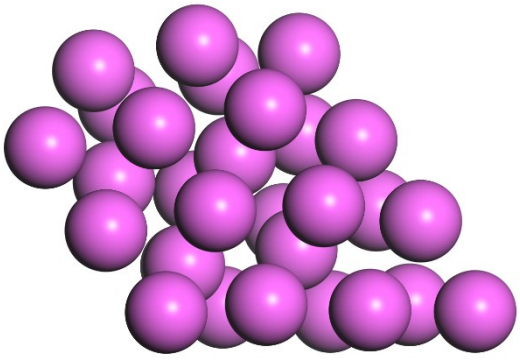
Al_{14} (6.5 Å, C_{3v})



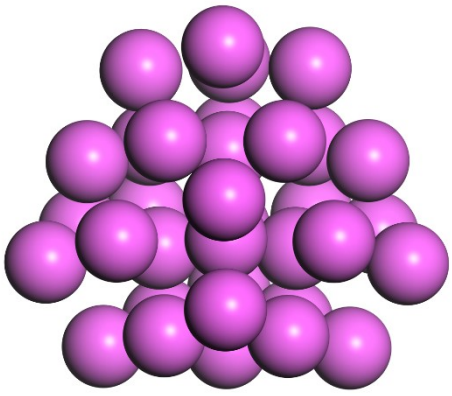
Al_{19} (7.5 Å, D_{5h})



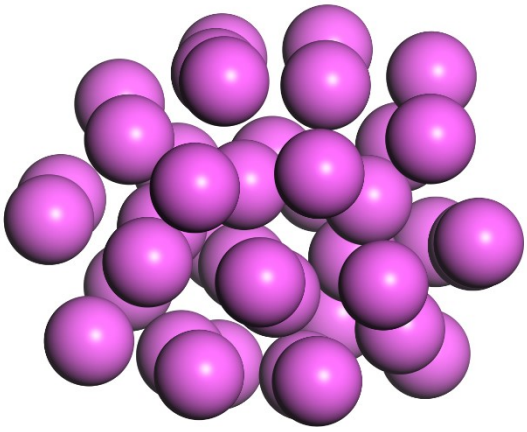
Al_{23} (7.7 Å, D_{3h})



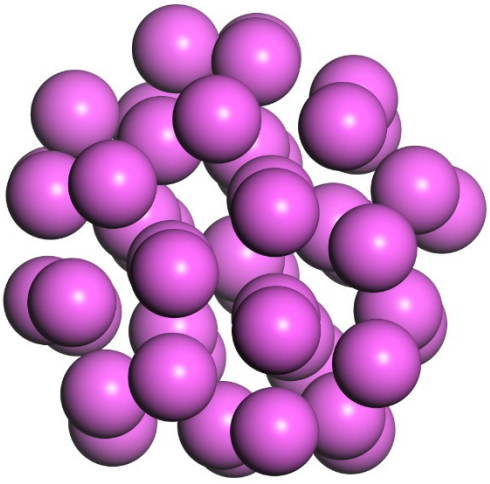
Al_{29}(11.1 Å, C_1)



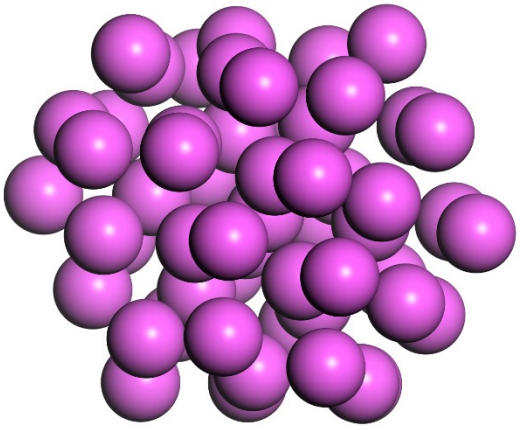
Al_{34}(8.9 Å, C_1)



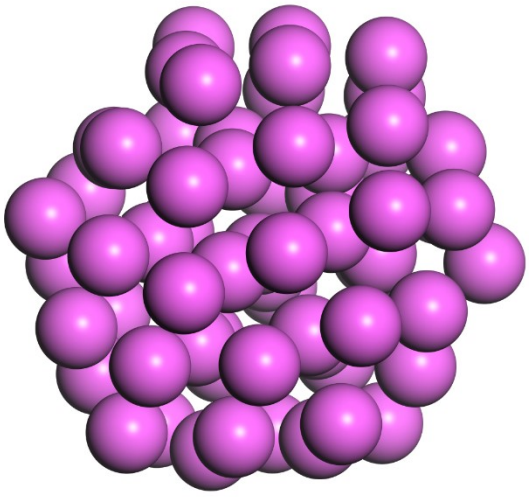
Al_{40} (10.1 Å, C_1)



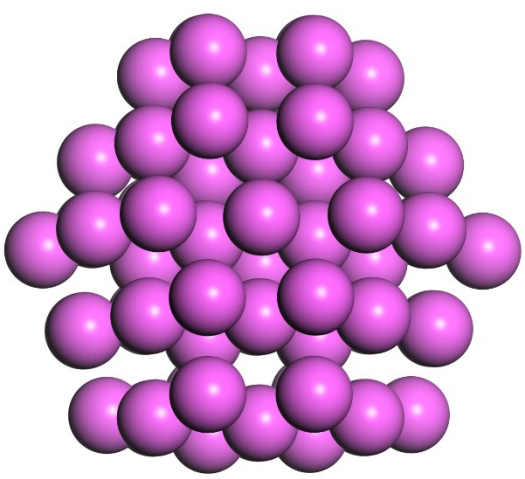
Al_{48} (10.5 Å, C_1)



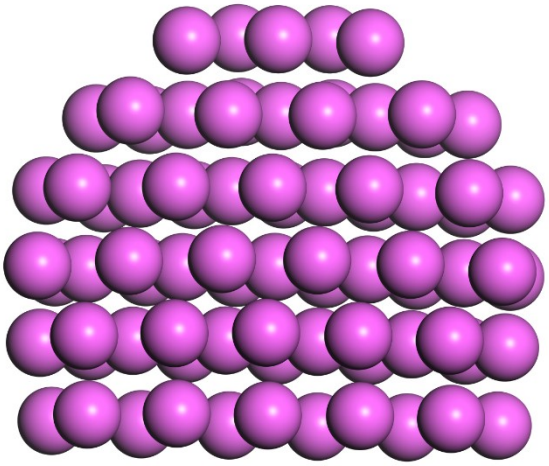
Al_{55} (11.6 Å, C_1)



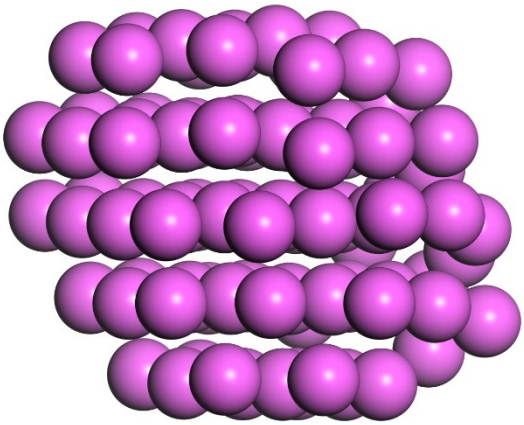
Al_{64}(11.2 Å, C_1)



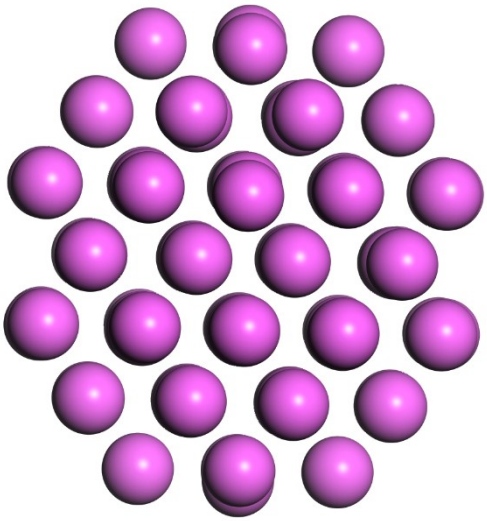
Al_{72}(11.5 Å, C_{2v})



Al_{78}(13.2 Å, C_1)



Al_{85}(12.8Å, C_1)



Al_{92}(13.1Å, C_{3v})

Figure S1. Structures of ANPs (Al_n). Their longest diameter and point group are labeled.

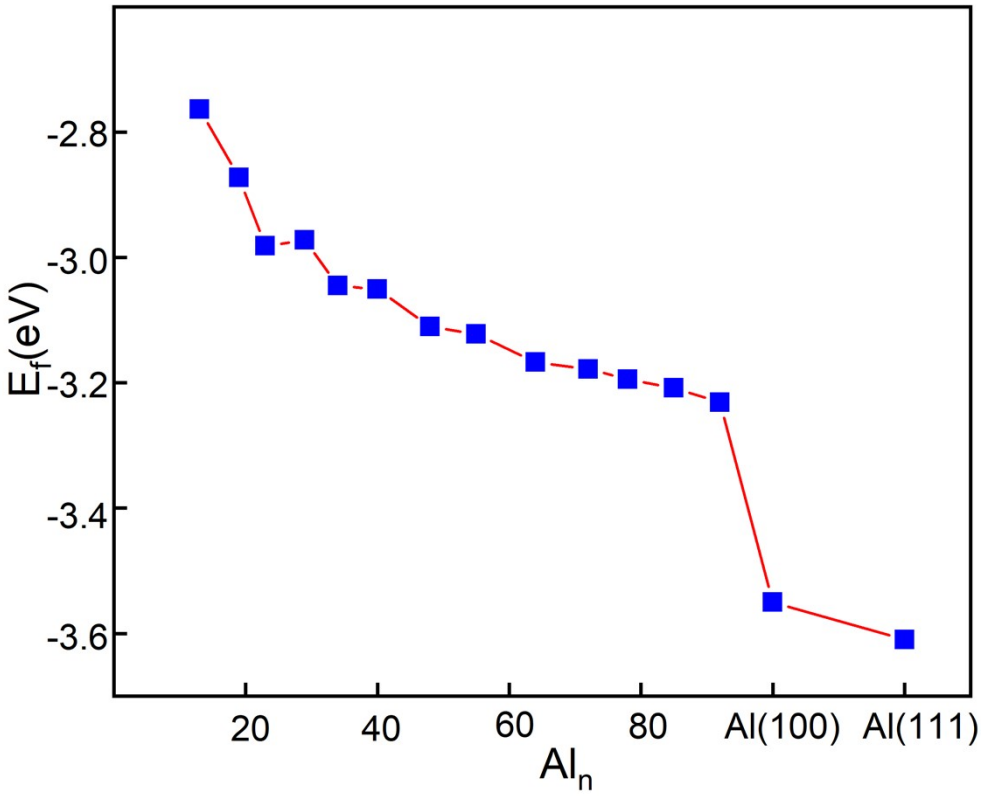
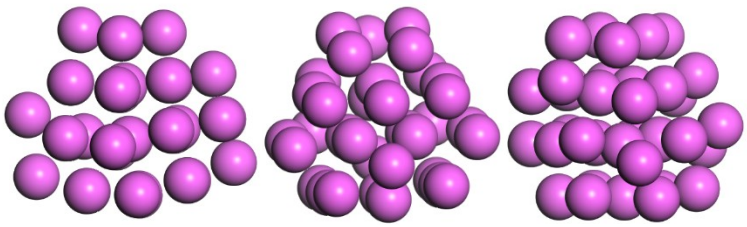
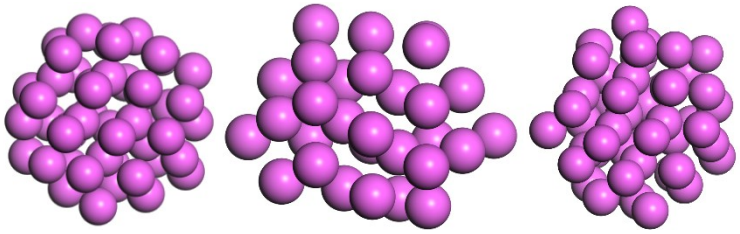


Figure S2. Formation energy of Al_n. E_f (eV) = ($E_{cluster}$ - nE_{Al}) / n. E_{Al} is the energy of an isolated Al atom.



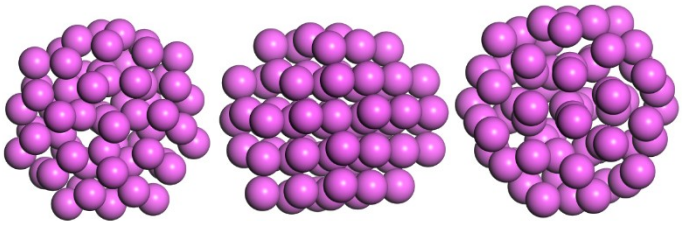
0.00 0.13 eV 0.28 eV

Al_{34}



0.00 0.21 eV 0.33 eV

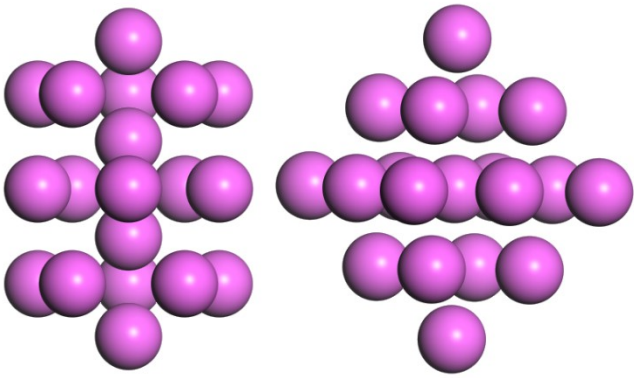
Al_{48}



0.00 0.23 eV 0.32 eV

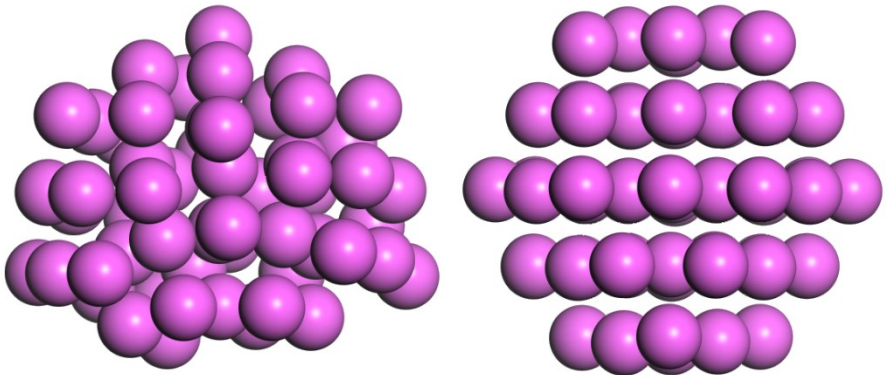
Al_{64}

Figure S3. Low energy isomers of Al_{34}, Al_{48}, and Al_{64}. Relative energy is labeled for each structure.



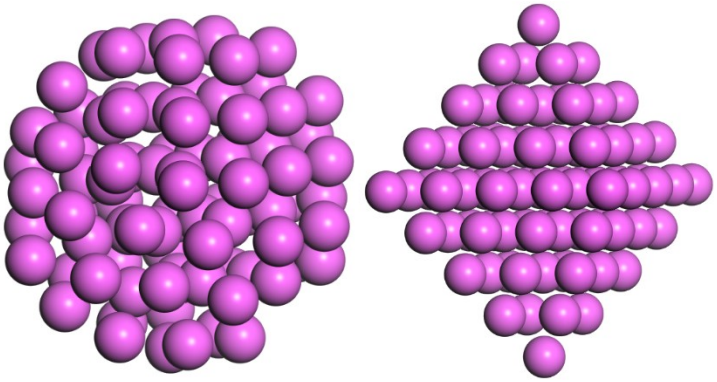
0.00 0.50 eV

Al_{19}



0.00 0.86 eV

Al_{55}



0.00 0.89 eV

Al_{85}

Figure S4. Energy difference between clusters with the Wulff structure and ball-like structure.

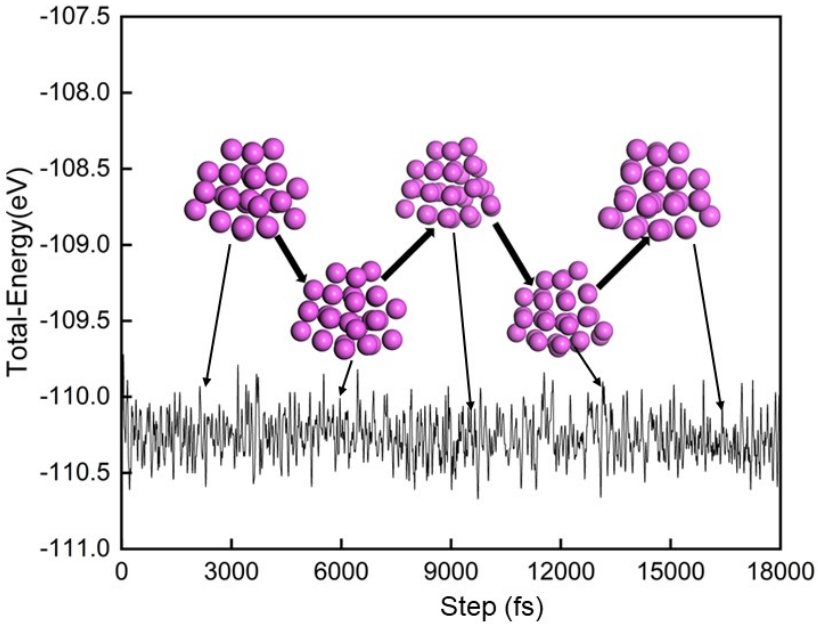


Figure S5. The stability of Al_{34} tested by AIMD at 300 K.

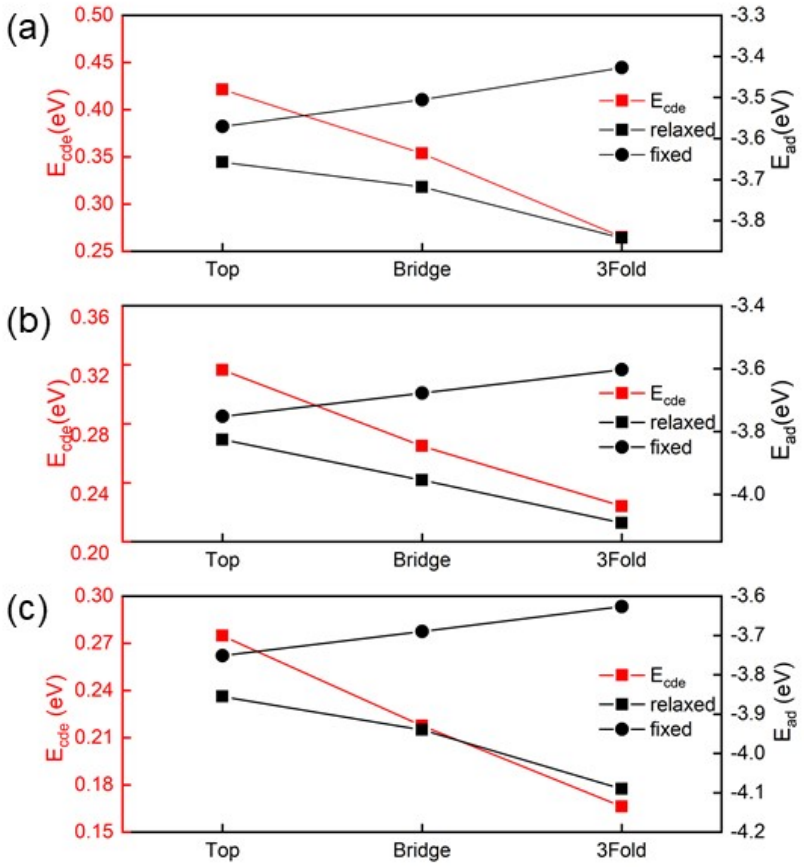


Figure S6. The adsorption energy and cluster deformation energy of O* adatoms at different sites of different ANPs. (a) Al_{34}, (b) Al_{48}, and (c) Al_{64}.

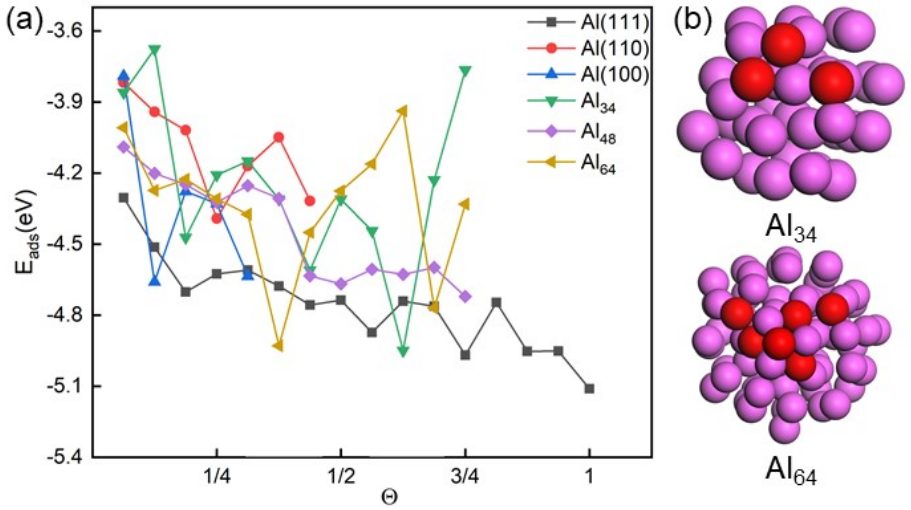


Figure S7. (a) Stepwise O adsorption energy as a function of the O coverage for Al surfaces and clusters. (b) Structure of Al_{64} at 0.38 ML and Al_{34} at 0.25 ML of O coverage. The stepwise O adsorption energy is defined as: $E_{ads} = E_{(N+1)O/substrate} - E_{NO/substrate} - \frac{1}{2}E_{O_2}$. The two most stable configurations at their own coverages are used for the calculation.

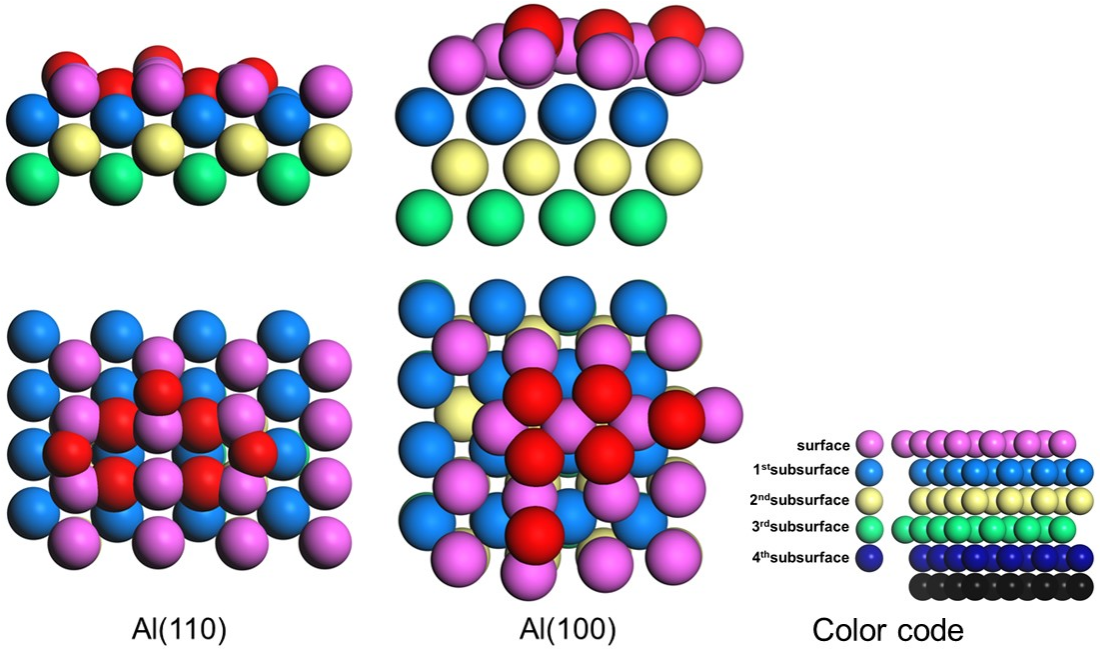


Figure S8. Surface restructure of Al(110) and Al(100).

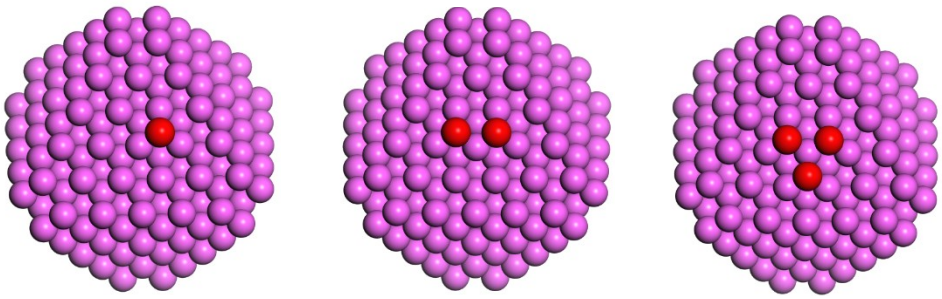
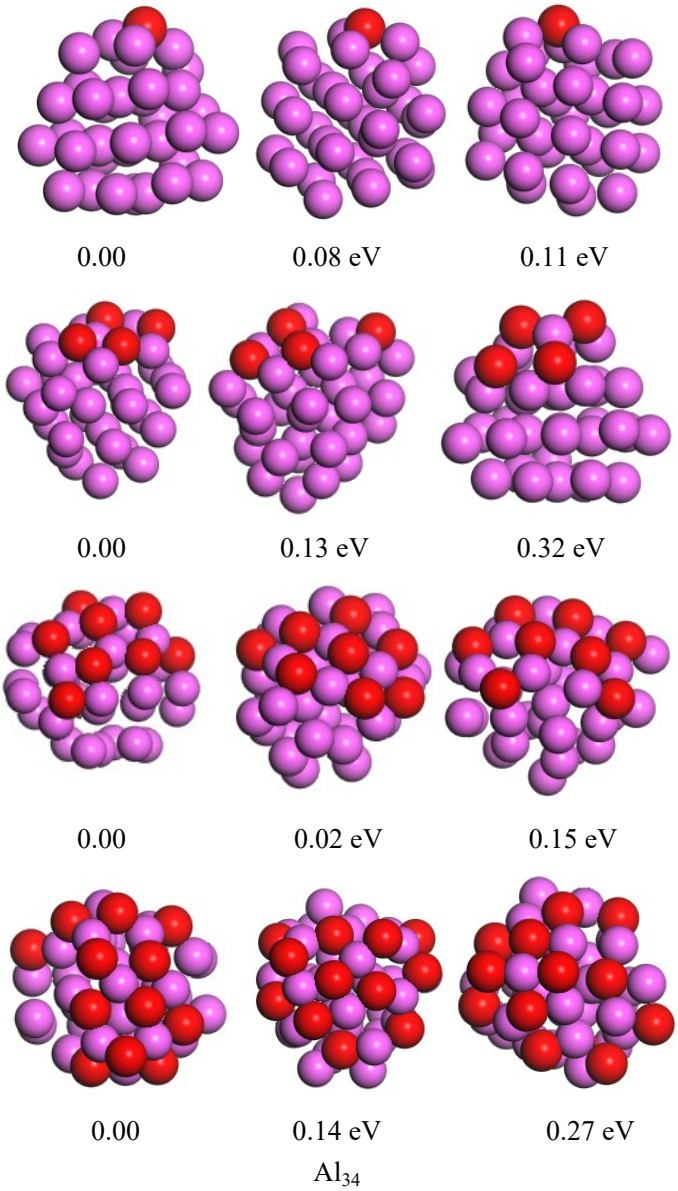
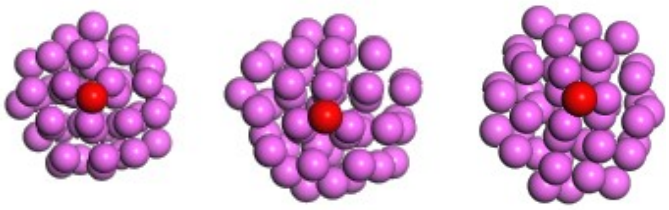


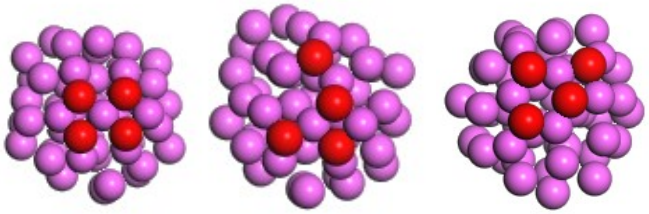
Figure S9. Optimized structures of O* adsorbed on Al_{225}.



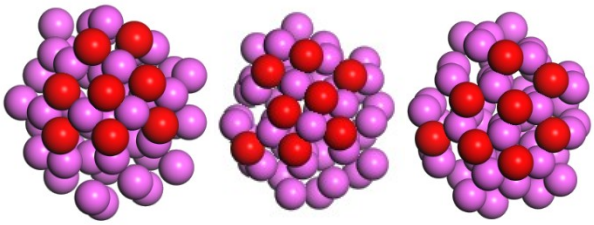
Al_{34}



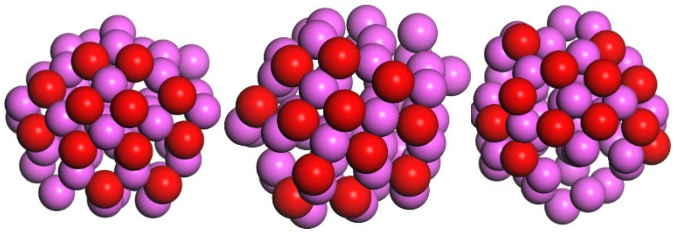
0.00 0.23 eV 0.38 eV



0.00 0.35 eV 0.45 eV

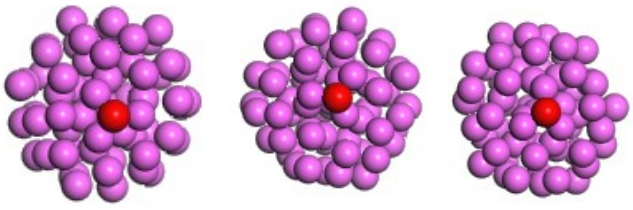


0.00 0.26 eV 0.41 eV

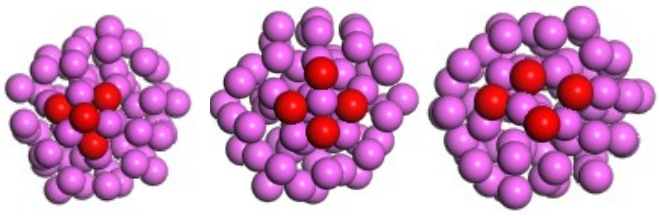


0.00 0.16 eV 0.28Ev

Al_{48}



0.00 0.19 eV 0.22 eV



0.00 0.36 eV 0.49 eV

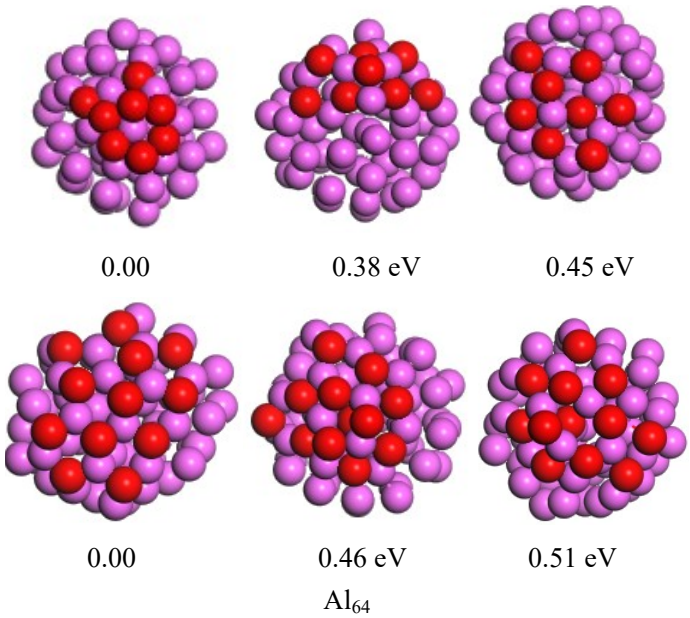


Figure S10. Selected low energy configurations of O adsorbed on ANPs. Configurations in the same row have the same O coverage and their relative energies are labeled.

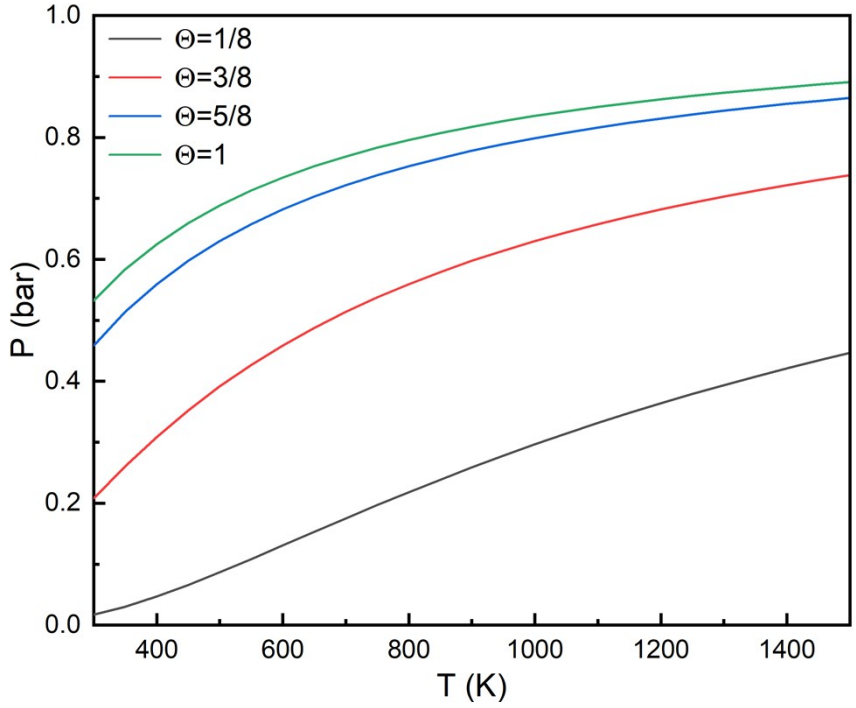


Figure S11. Phase diagram O chemisorbed on Al(111).

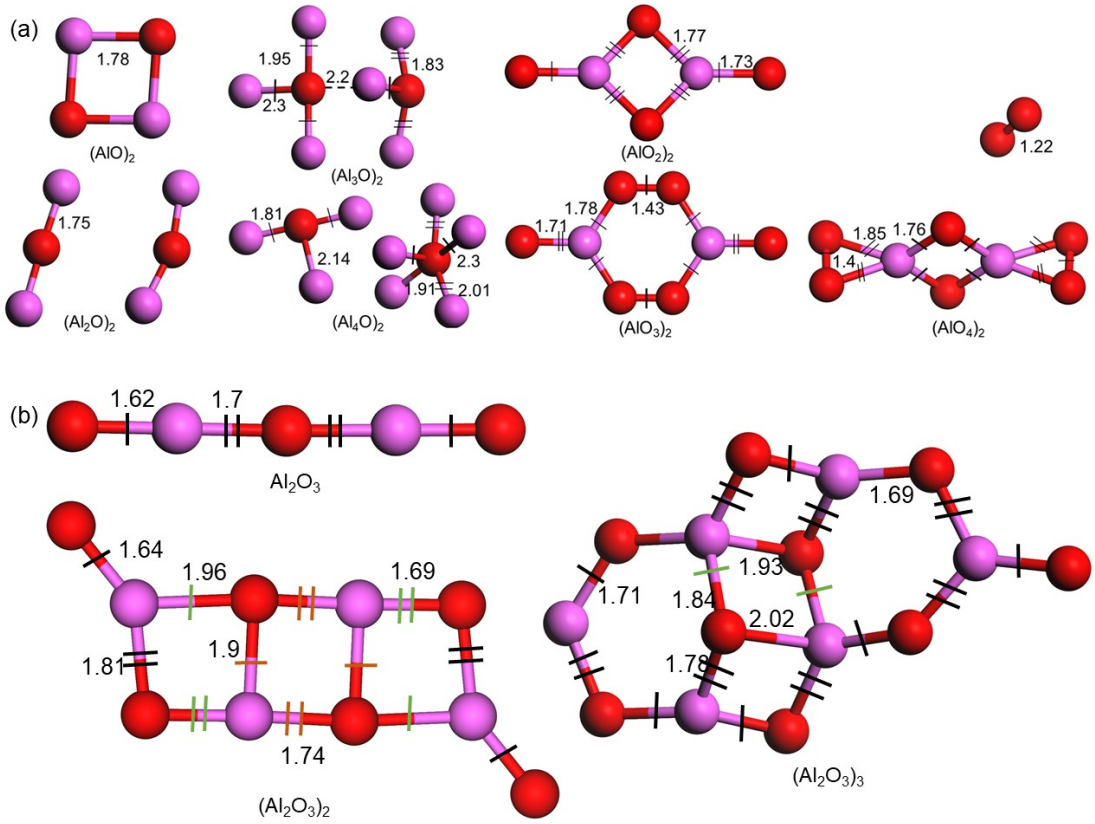


Figure S12. Al_xO_y clusters. (a) Dimers of Al_xO_y. (b) Al_2O_3 monomer, dimer and trimer.

Table S1. The O adsorption energy over Al_{225} and Al(111).

	Al_{225}			Al(111)		
Number of O	1	2	3	1	2	3
E_{ad} (eV)	-4.27	-4.42	-4.53	-4.29	-4.40	-4.50
Lateral O-O interaction (eV)		0.15			0.11	

Table S2. Energy difference of optimized clusters before adsorbing O atoms and after removing the adsorbed O atoms.

	Al_{34}	Al_{48}	Al_{64}
Θ		ΔE (eV)	
1/16	0.000	0.027	0.000
1/4	0.005	0.043	0.064
1/2	0.004	0.055	0.021

Table S3. Imaginary frequencies of transition states.

Diffusion	In-surface	Surface to 1st sub	In-1st sub
Imaginary frequency (cm^{-1})	fcc to hcp	fcc to tet1	tet1 to oct
Isolated O	-199	-167	-94
(Sub)surface 1 ML O	-259	-276	-200

Table S4. The symmetry of Al_xO_y monomers.

monomers	AlO	Al_2O	Al_3O	Al_4O	Al_5O	Al_6O	AlO_2	AlO_3	AlO_4	AlO_5	AlO_6
symmetry	C_{nv}	D_{nh}	C_{2v}	D_{4h}	C_1	C_s	D_{nh}	C_{2v}	D_{4d}	C_1	C_1