Supporting Information

Highly selective electroreduction of nitrate to ammonia on Ru-doped tetragonal Co_2P monolayer with low-limiting overpotential

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Table S1. Average energy difference (eV) between ferromagnetic and antiferromagnetic states.

Materials	$E_{AFM1} - E_{FM}$	$E_{AFM2} - E_{FM}$	$E_{AFM3} - E_{FM}$	$E_{AFM4} - E_{FM}$
Co_2P	0.476	0.135	0.180	0.107
Ni_2P	0	0	0	0
Ru_2P	0	0	0	0
Pd_2P	0	0	0	0

Table S2 Optimized structures of possible products for each elementary step along the NO_3RR process on the Co_2P monolayer and their relative energies to the most stable configuration.

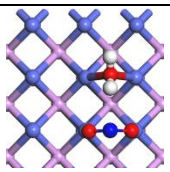
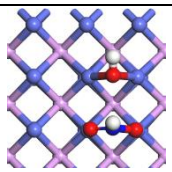
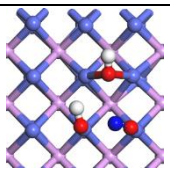
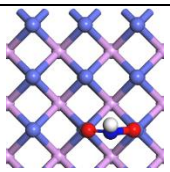
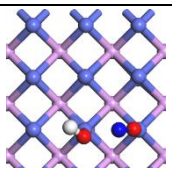
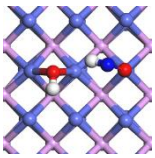
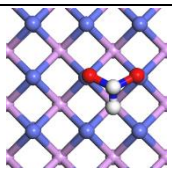
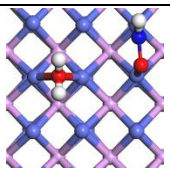
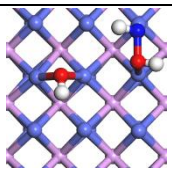
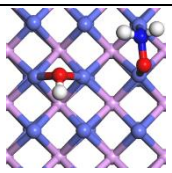
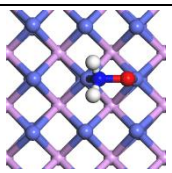
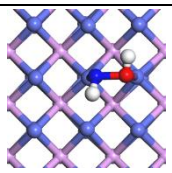
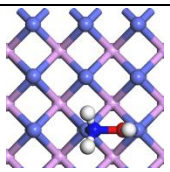
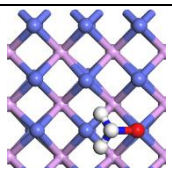
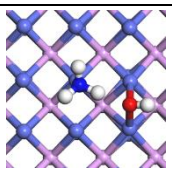
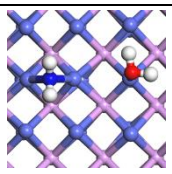
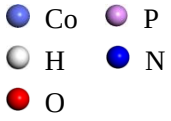
Intermediates	Structures and relative energies		
NO_3H_2			
	ΔE = 0.00 eV	ΔE = 0.17 eV	ΔE = 0.19 eV
NO_2H			
	ΔE = 0.00 eV	ΔE = 0.08 eV	
NO_2H_2			
	ΔE = 0.00 eV	ΔE = 0.67 eV	
NO_2H_3			
	ΔE = 0.00 eV	ΔE = 0.73 eV	ΔE = 0.10 eV
NOH_2			
	ΔE = 0.00 eV	ΔE = 0.70 eV	
NOH_3			
	ΔE = 0.00 eV	ΔE = 0.31 eV	
NOH_4			
	ΔE = 0.00 eV	ΔE = 0.54 eV	

Table S3 Optimized structures of various possible products for each elementary step along the NO_3RR process on the Ni_2P monolayer and their relative energies referred to the most stable configuration.

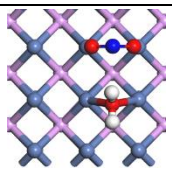
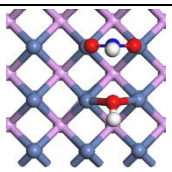
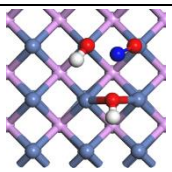
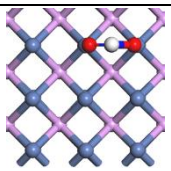
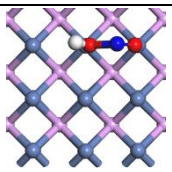
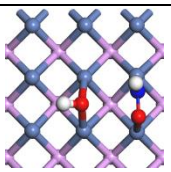
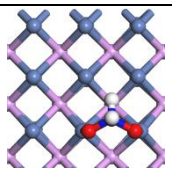
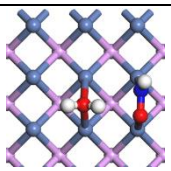
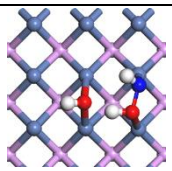
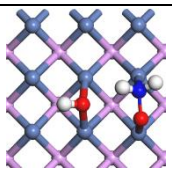
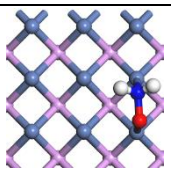
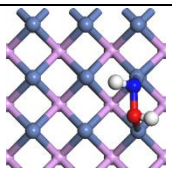
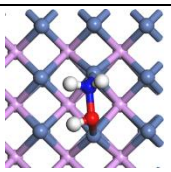
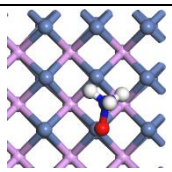
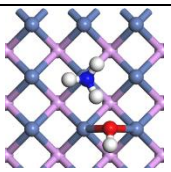
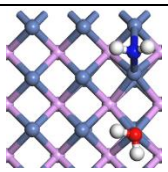
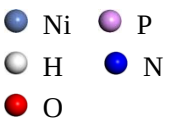
Intermediates	Structures and relative energies		
NO_3H_2	 ΔE = 0.00 eV	 ΔE = 0.42 eV	 ΔE = 0.47 eV
NO_2H	 ΔE = 0.00 eV	 ΔE = 0.08 eV	
NO_2H_2	 ΔE = 0.00 eV	 ΔE = 1.54 eV	
NO_2H_3	 ΔE = 0.00 eV	 ΔE = 0.50 eV	 ΔE = 0.18 eV
NOH_2	 ΔE = 0.00 eV	 ΔE = 0.64 eV	
NOH_3	 ΔE = 0.00 eV	 ΔE = 0.42 eV	
NOH_4	 ΔE = 0.00 eV	 ΔE = 0.63 eV	 Ni P H N O

Table S4 Optimized structures of various possible products for each elementary step along the NO_3RR process on the Ru_2P monolayer and their relative energies referred to the most stable configuration.

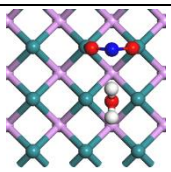
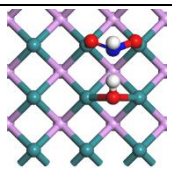
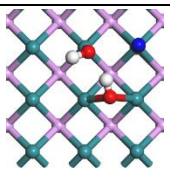
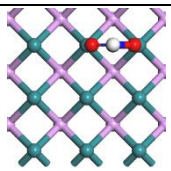
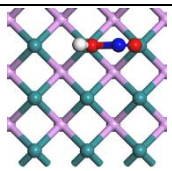
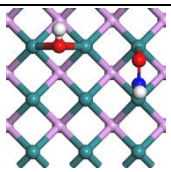
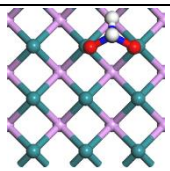
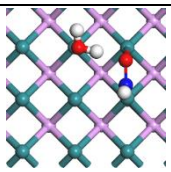
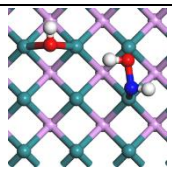
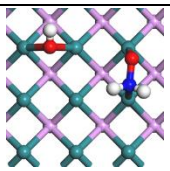
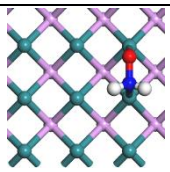
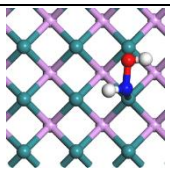
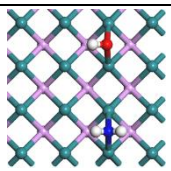
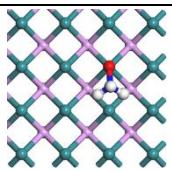
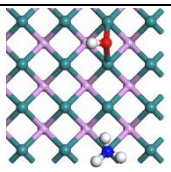
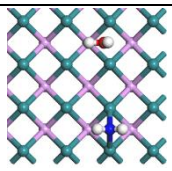
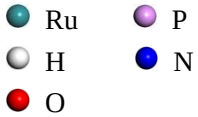
Intermediates	Structures and relative energies		
NO_3H_2	 ΔE = 0.00 eV	 ΔE = 0.20 eV	 ΔE = 0.27 eV
NO_2H	 ΔE = 0.00 eV	 ΔE = 0.14 eV	
NO_2H_2	 ΔE = 0.00 eV	 ΔE = 2.15 eV	
NO_2H_3	 ΔE = 0.00 eV	 ΔE = 0.51 eV	 ΔE = 0.07 eV
NOH_2	 ΔE = 0.00 eV	 ΔE = 0.67 eV	
NOH_3	 ΔE = 0.00 eV	 ΔE = 3.15 eV	
NOH_4	 ΔE = 0.00 eV	 ΔE = 0.54 eV	

Table S5 Optimized structures of various possible products for each elementary step along the NO_3RR process on the Pd_2P monolayer and their relative energies referred to the most stable configuration.

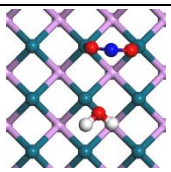
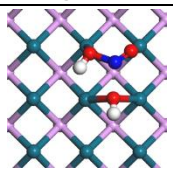
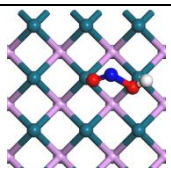
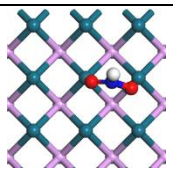
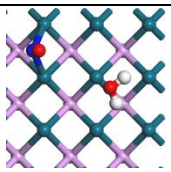
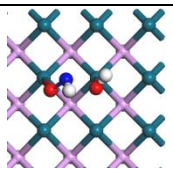
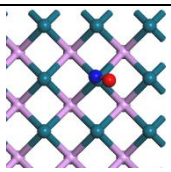
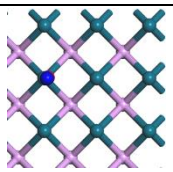
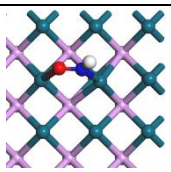
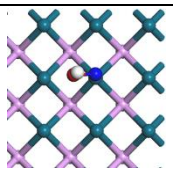
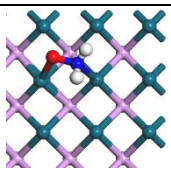
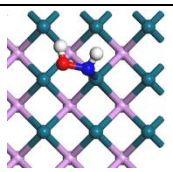
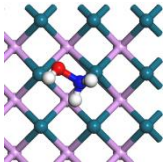
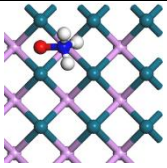
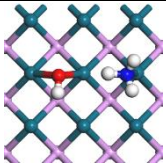
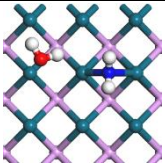
Intermediates	Structures and relative energies		
NO_3H_2			
	ΔE = 0.00 eV	ΔE = 0.78 eV	
NO_2H			
	ΔE = 0.00 eV	ΔE = 0.10 eV	
NO_2H_2			
	ΔE = 0.00 eV	ΔE = 1.70 eV	
NO			
	ΔE = 0.00 eV	ΔE = 1.21 eV	
NOH			
	ΔE = 0.00 eV	ΔE = 1.20 eV	
NOH_2			
	ΔE = 0.00 eV	ΔE = 0.64 eV	
NOH_3			
	ΔE = 0.00 eV	ΔE = 0.27 eV	
NOH_4			Pd P H N O
	ΔE = 0.00 eV	ΔE = 0.21 eV	

Table S6 Calculated zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on the Co_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*NO_3	0.4156	0.2243	0.0025
*NO_3H	0.6593	0.2179	0.0038
*NO_2-H_2O	0.9380	0.2921	0.0053
*NO_2	0.2882	0.1569	0.0018
*NHO_2	0.6032	0.1928	0.0034
*NHO_2H	0.8158	0.2507	0.0046
*NHO-H_2O	1.2182	0.1876	0.0064
*NHO	0.4931	0.1160	0.0027
*NH_2O	0.8467	0.1264	0.0044
*NH_2OH	1.1418	0.2075	0.0060
*NH_3OH	1.4310	0.1704	0.0074
*OH	0.3686	0.0691	0.0020
*H_2O	0.6679	0.1186	0.0036

Table S7 Calculated zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on the Ni_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*NO_3	0.4098	0.2518	0.0025
*NO_3H	0.6471	0.2410	0.0038
*NO_2-H_2O	0.9227	0.3318	0.0053
*NO_2	0.2790	0.1836	0.0018
*NHO_2	0.5991	0.2127	0.0034
*NHO_2H	0.8422	0.1972	0.0046
*NHO-H_2O	1.1343	0.2672	0.0062
*NHO	0.4836	0.1237	0.0027
*NH_2O	0.8370	0.1436	0.0044
*NH_2OH	1.0734	0.1349	0.0056
*NH_3OH	1.4064	0.1961	0.0073
*OH	0.3583	0.0761	0.0019
*H_2O	0.6407	0.1573	0.0035

Table S8 Calculated zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on the Ru_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*NO_3	0.4384	0.1884	0.0026
*NO_3H	0.6518	0.2137	0.0037
*NO_2-H_2O	0.9605	0.2673	0.0054
*NO_2	0.2771	0.1783	0.0018
*NHO_2	0.5856	0.2266	0.0034
*NHO_2H	0.8594	0.1725	0.0046
*NHO-H_2O	1.2028	0.1896	0.0063
*NHO	0.5005	0.1024	0.0027
*NH_2O	0.8473	0.1310	0.0044
*NH_2OH	1.1080	0.1235	0.0057
*NH_3OH	1.4575	0.1628	0.0075
*OH	0.3839	0.0534	0.0020
*H_2O	0.6635	0.1438	0.0036

Table S9 Calculated zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on the Pd_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*NO_3	0.4074	0.2824	0.0026
*NO_3H	0.6989	0.2793	0.0040
*NO_2-H_2O	0.9388	0.3408	0.0054
*NO_2	0.2722	0.1961	0.0018
*NO_2H	0.5480	0.2620	0.0033
*NO-H_2O	0.8936	0.2331	0.0049
*NO	0.1927	0.1432	0.0013
*NHO	0.4879	0.1138	0.0027
*NH_2O	0.8373	0.1360	0.0044
*NH_2OH	1.1791	0.1550	0.0061
*NH_3OH	1.4681	0.1544	0.0075
*OH	0.3514	0.0891	0.0019
*H_2O	0.6569	0.1456	0.0035

Table S10 Optimized structures of various possible products for each elementary step along the NO_3RR process on the Ru-doped Co_2P monolayer and their relative energies referred to the most stable configuration.

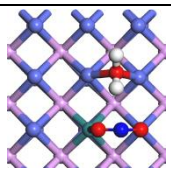
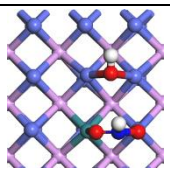
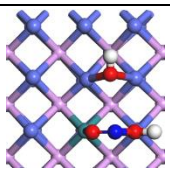
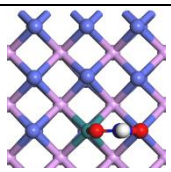
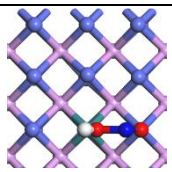
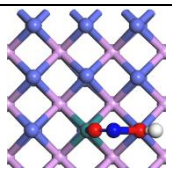
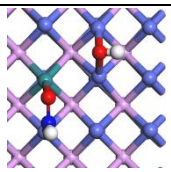
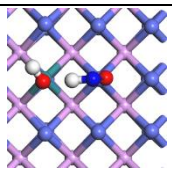
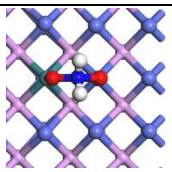
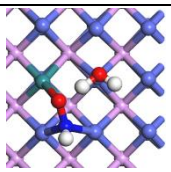
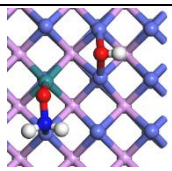
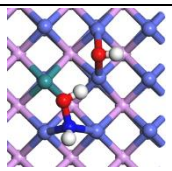
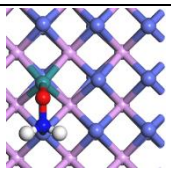
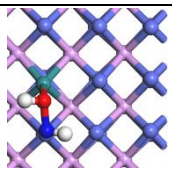
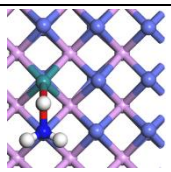
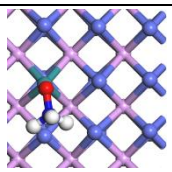
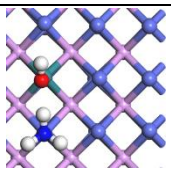
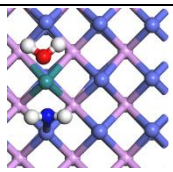
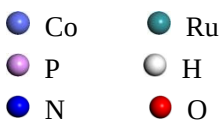
Intermediates	Structures and relative energies		
NO_3H_2			
	ΔE = 0.00 eV	ΔE = 0.20 eV	ΔE = 0.19 eV
NO_2H			
	ΔE = 0.00 eV	ΔE = 0.20 eV	ΔE = 0.14 eV
NO_2H_2			
	ΔE = 0.00 eV	ΔE = 1.97 eV	ΔE = 2.51 eV
NO_2H_3			
	ΔE = 0.00 eV	ΔE = 0.86 eV	ΔE = 0.87 eV
NOH_2			
	ΔE = 0.00 eV	ΔE = 0.59 eV	
NOH_3			
	ΔE = 0.00 eV	ΔE = 0.37 eV	
NOH_4			
	ΔE = 0.00 eV	ΔE = 0.49 eV	

Table S11 Calculated zero point energy (ZPE), entropy (TS) and enthalpy (ΔH) of different adsorption species on the Ru-doped Co_2P monolayer, where T is set to be 298.15 K and the * denotes the adsorption site.

Adsorption Species	E_{ZPE} (eV)	TS (eV)	ΔH (eV)
*NO_3	0.4291	0.2035	0.0026
*NO_3H	0.6604	0.2227	0.0038
*NO_2-H_2O	0.9494	0.2892	0.0053
*NO_2	0.2990	0.1428	0.0018
*NHO_2	0.6077	0.1868	0.0034
*NHO_2H	0.8514	0.2005	0.0047
*NHO-H_2O	1.1315	0.1816	0.0060
*NHO	0.4967	0.1118	0.0027
*NH_2O	0.8501	0.1246	0.0044
*NH_2OH	1.1471	0.1535	0.0060
*NH_3OH	1.3964	0.2366	0.0073
*OH	0.3623	0.0679	0.0020
*H_2O	0.6628	0.1531	0.0036

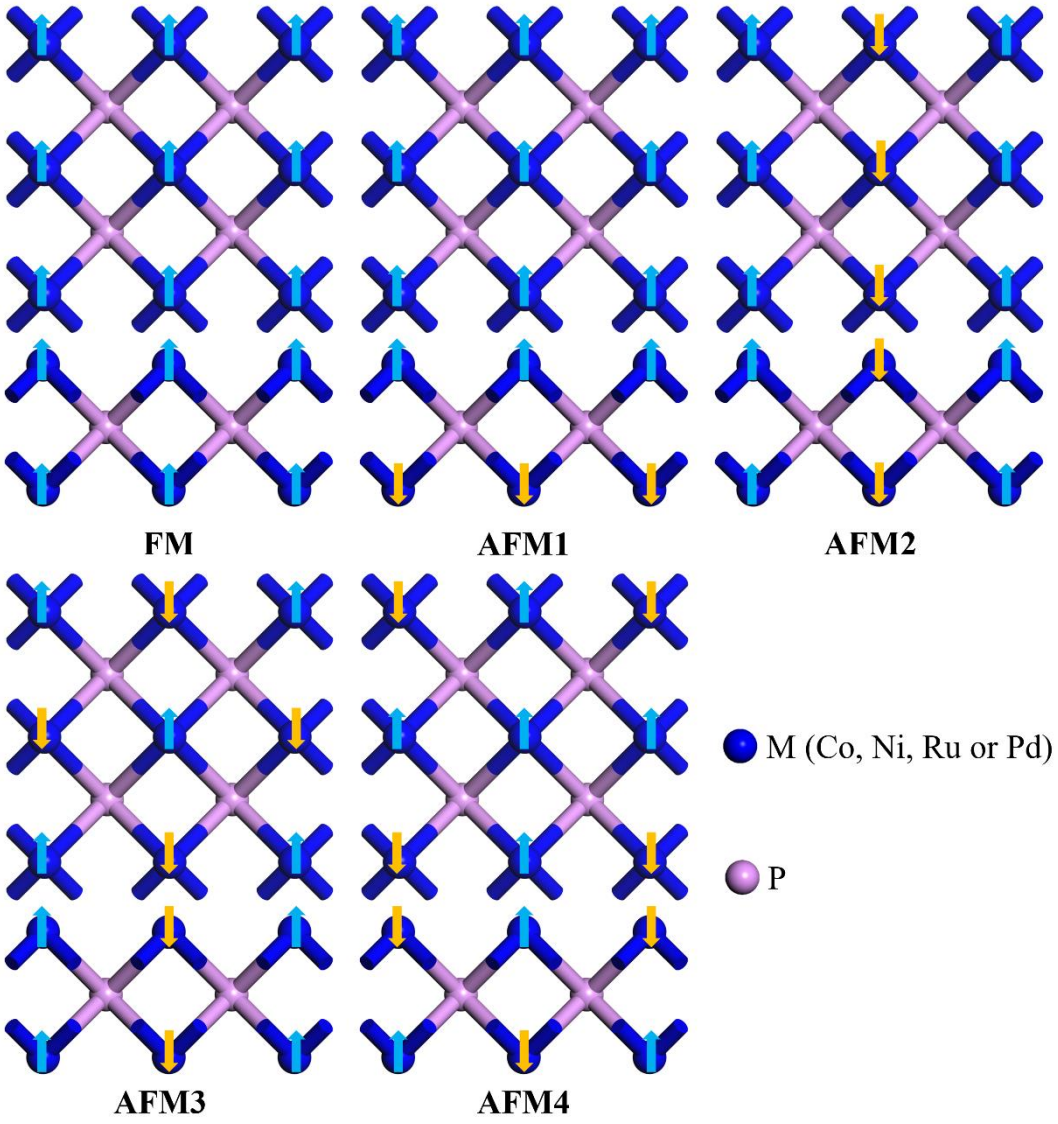


Fig. S1 Top and side views of five considered magnetic configurations of the tetragonal M_2P monolayer: (a) ferromagnetic (FM), (b) antiferromagnetic 1 (AFM1), (c) AFM2, (d) AFM3 and (e) AFM4.

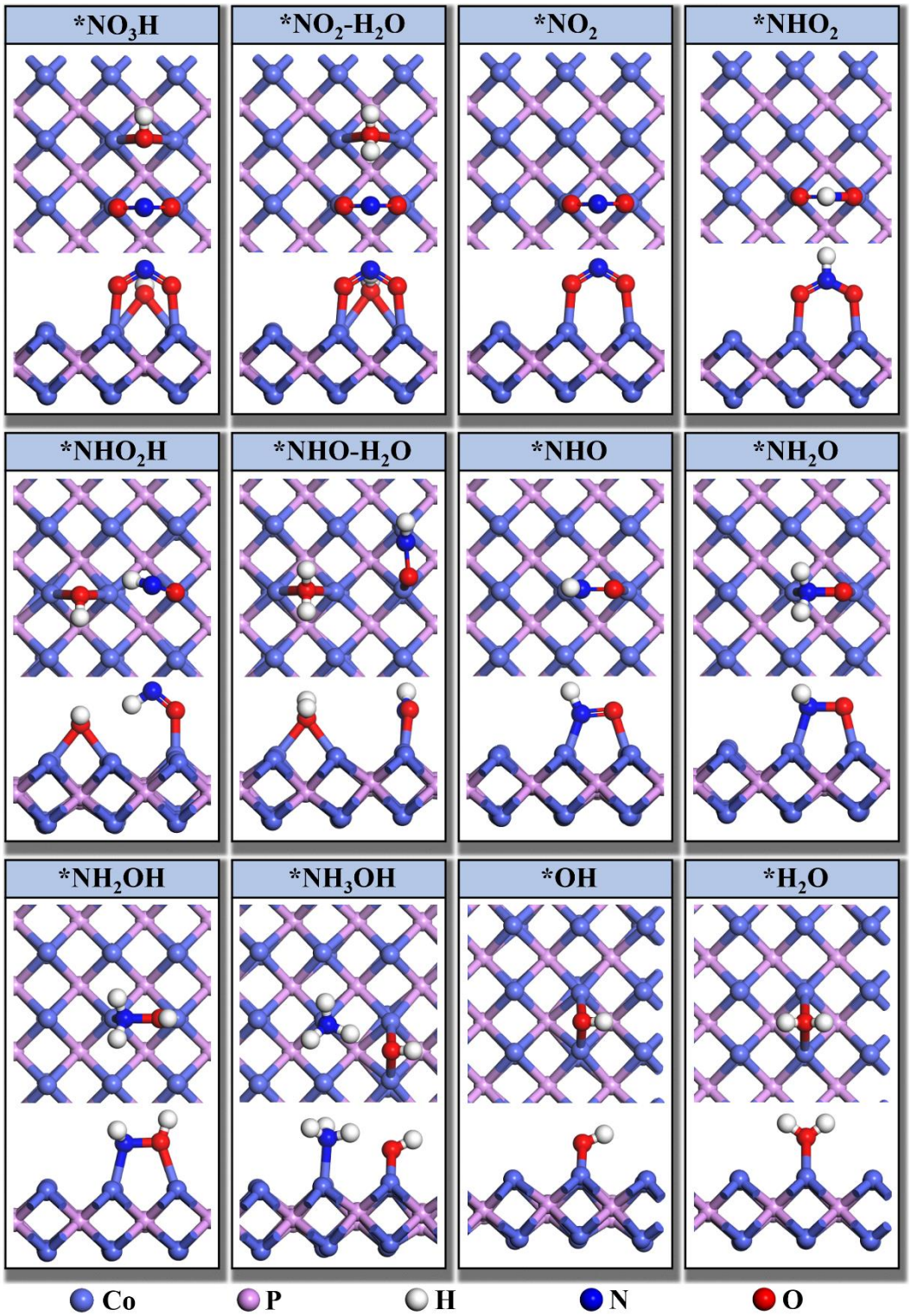


Fig. S2 Optimized structures of various reaction intermediates along the thermodynamically favorable NO_3RR pathway on the Co_2P monolayer.

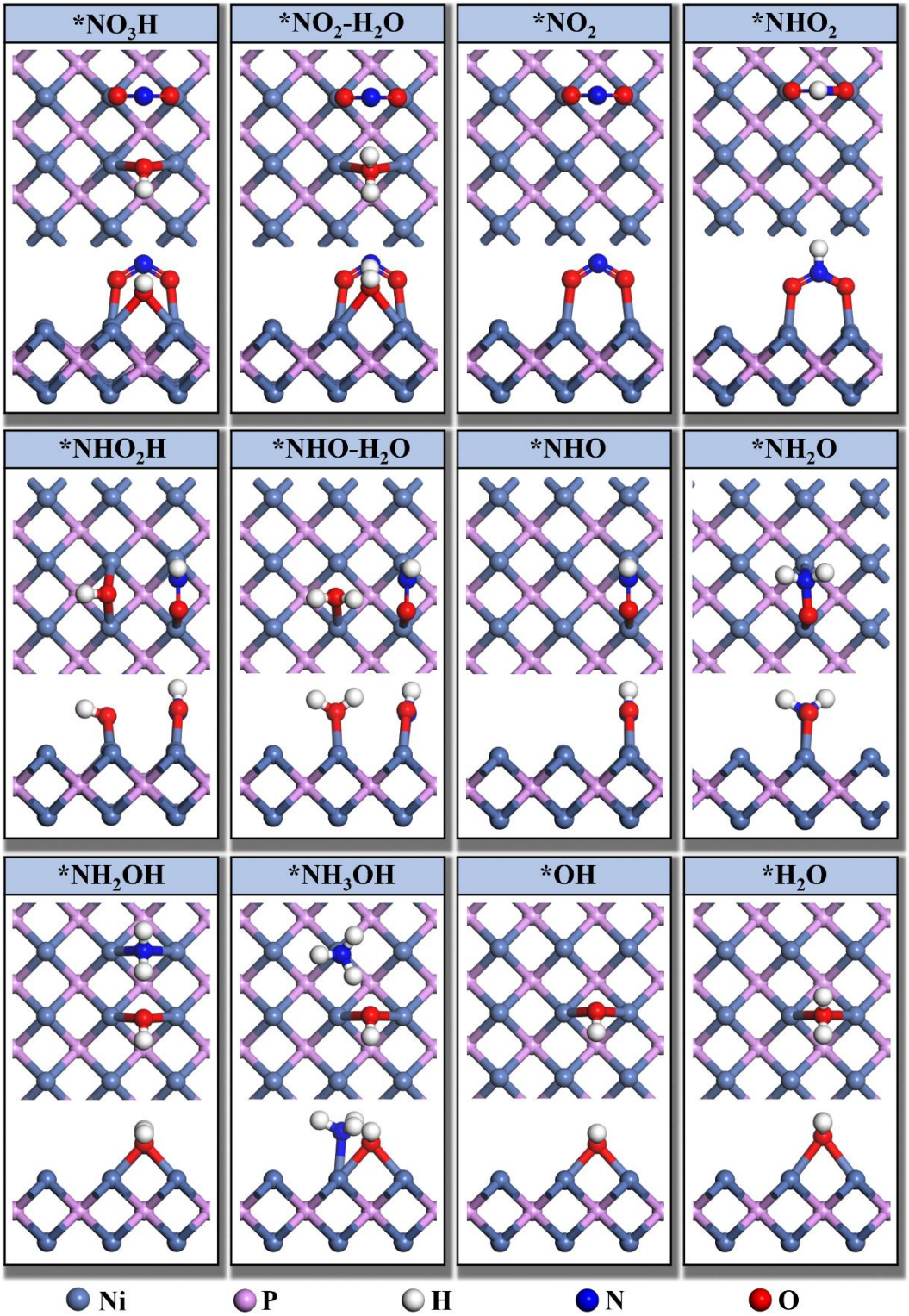


Fig. S3 Optimized structures of various reaction intermediates along the thermodynamically favorable NO_3RR pathway on the Ni_2P monolayer.

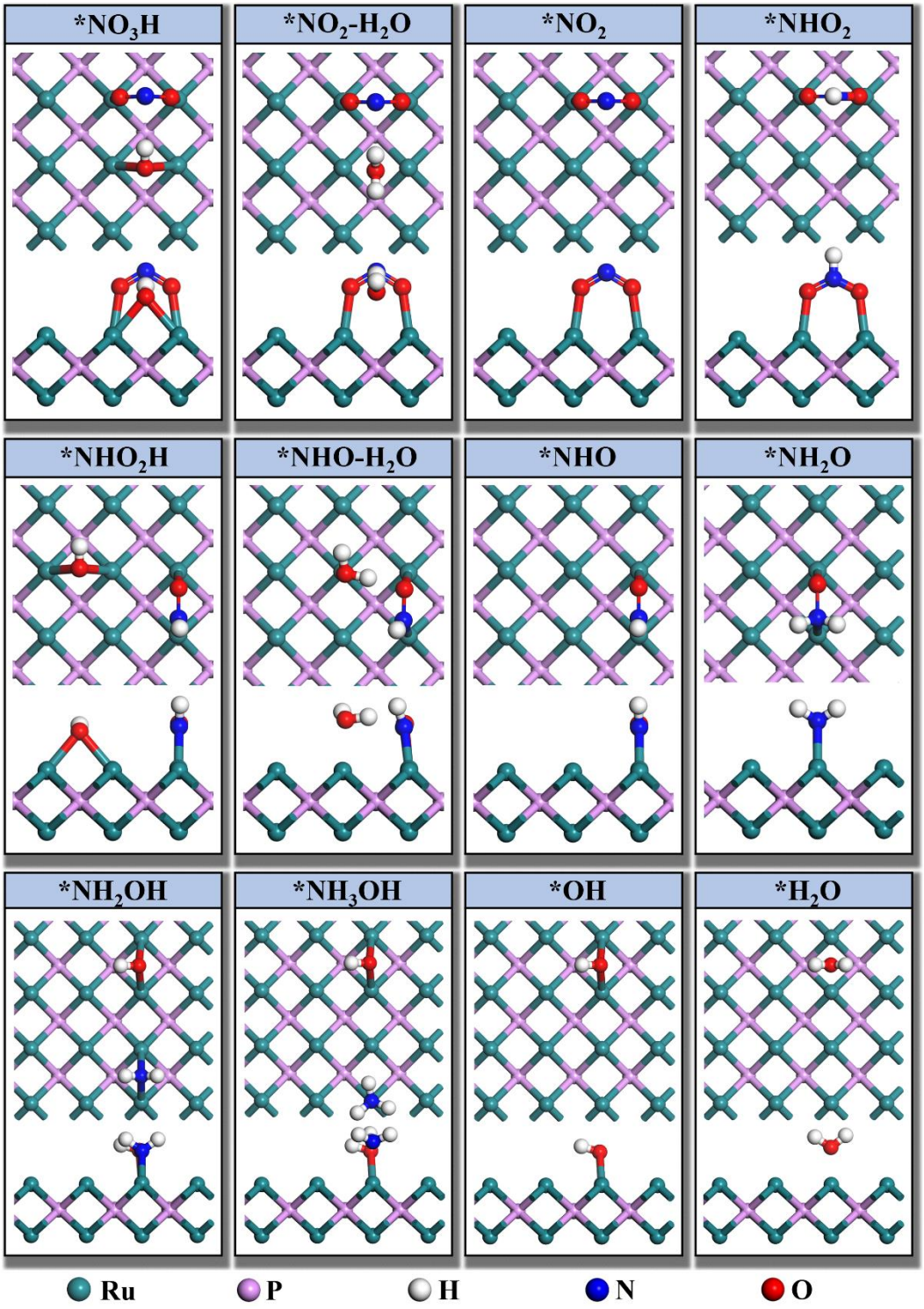


Fig. S4 Optimized structures of various reaction intermediates along the thermodynamically favorable NO_3RR pathway on the Ru_2P monolayer.

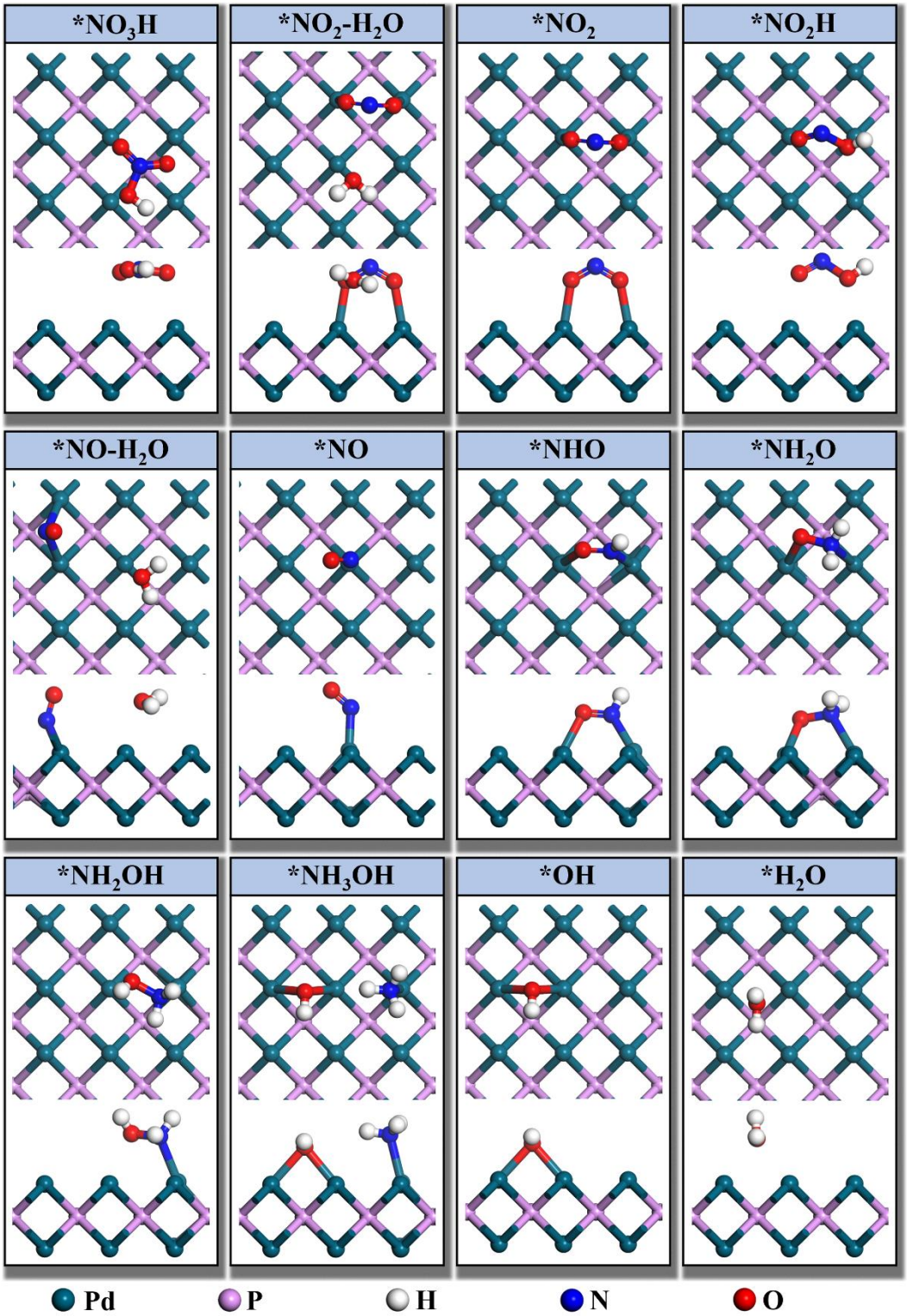


Fig. S5 Optimized structures of various reaction intermediates along the thermodynamically favorable NO_3RR pathway on the Pd_2P monolayer.

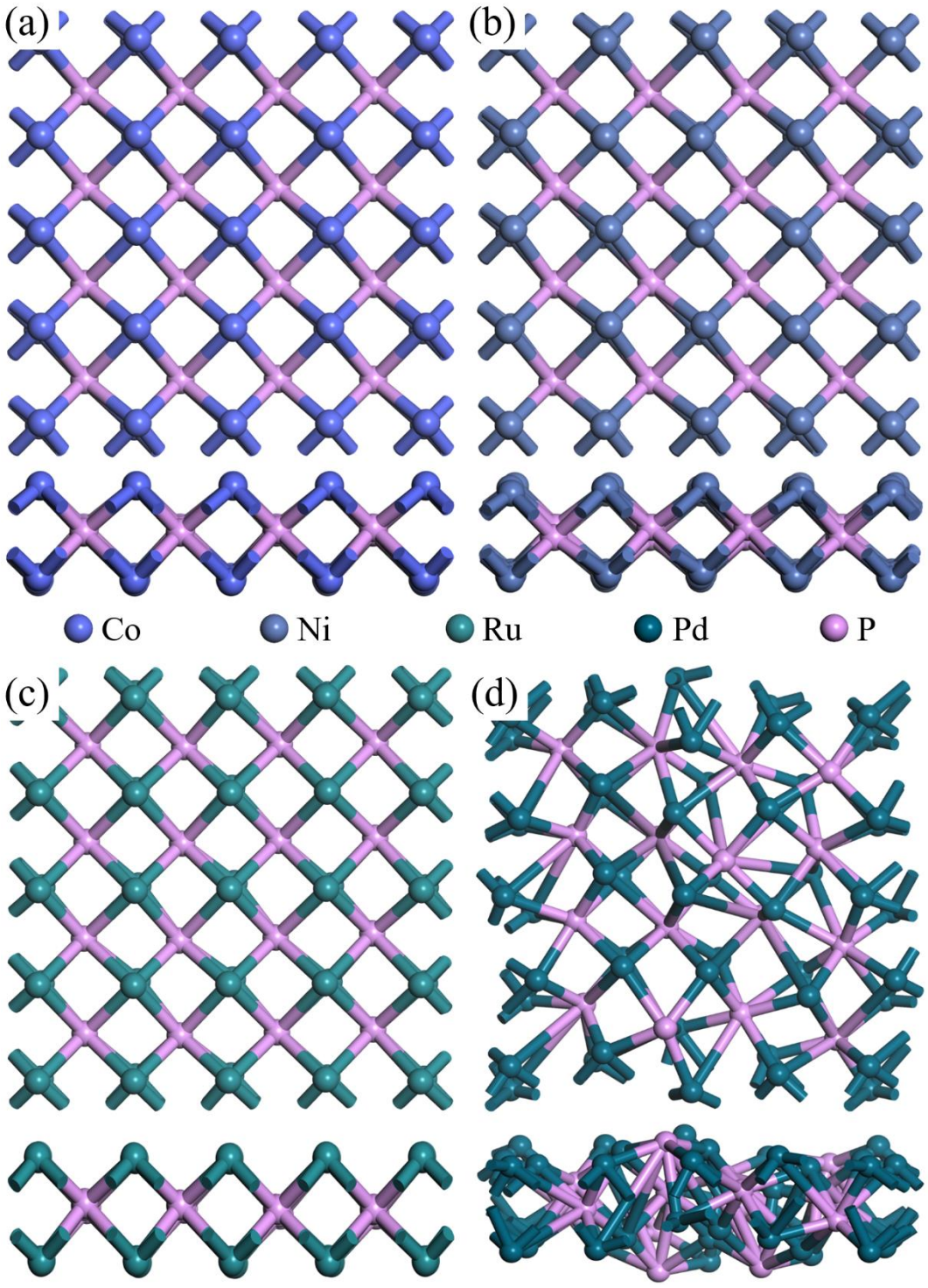


Fig. S6 Structures of the (a) Co_2P, (b) Ni_2P, (c) Ru_2P and (d) Pd_2P monolayers after AIMD simulations at 300 K for 2 ps with a time step of 1 fs.

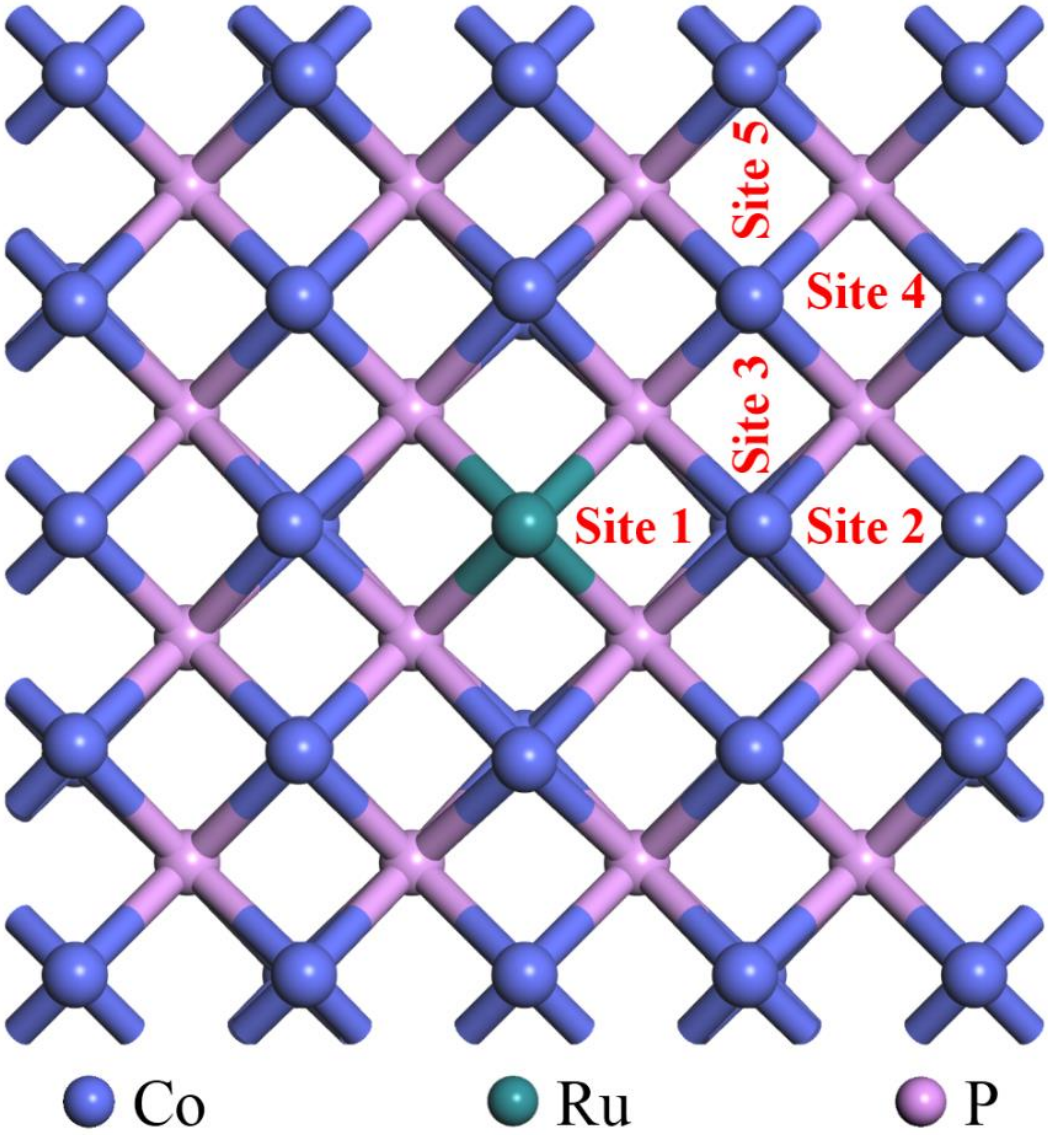


Fig. S7 Five possible adsorption sites (Site 1, Site 2, Site 3, Site 4 and Site 5) for NO_3^- on the Ru-doped Co_2P monolayer.

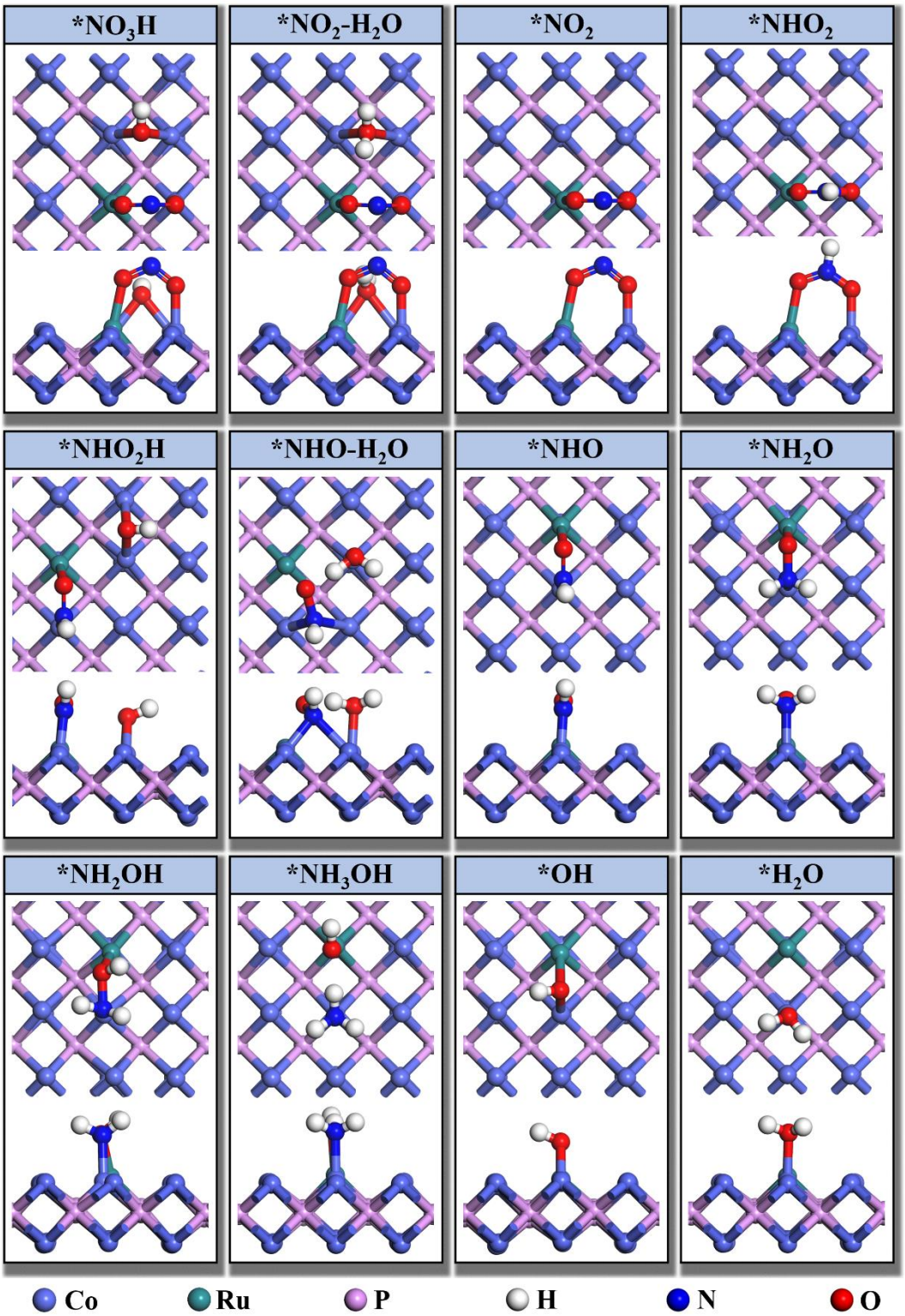


Fig. S8 Optimized structures of various reaction intermediates along the thermodynamically favorable NO_3RR pathway on the Ru-doped Co_2P monolayer.