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PdRuIr Ternary alloy as an Effective NO Reduction Catalyst: Insights from First Principles Calculation

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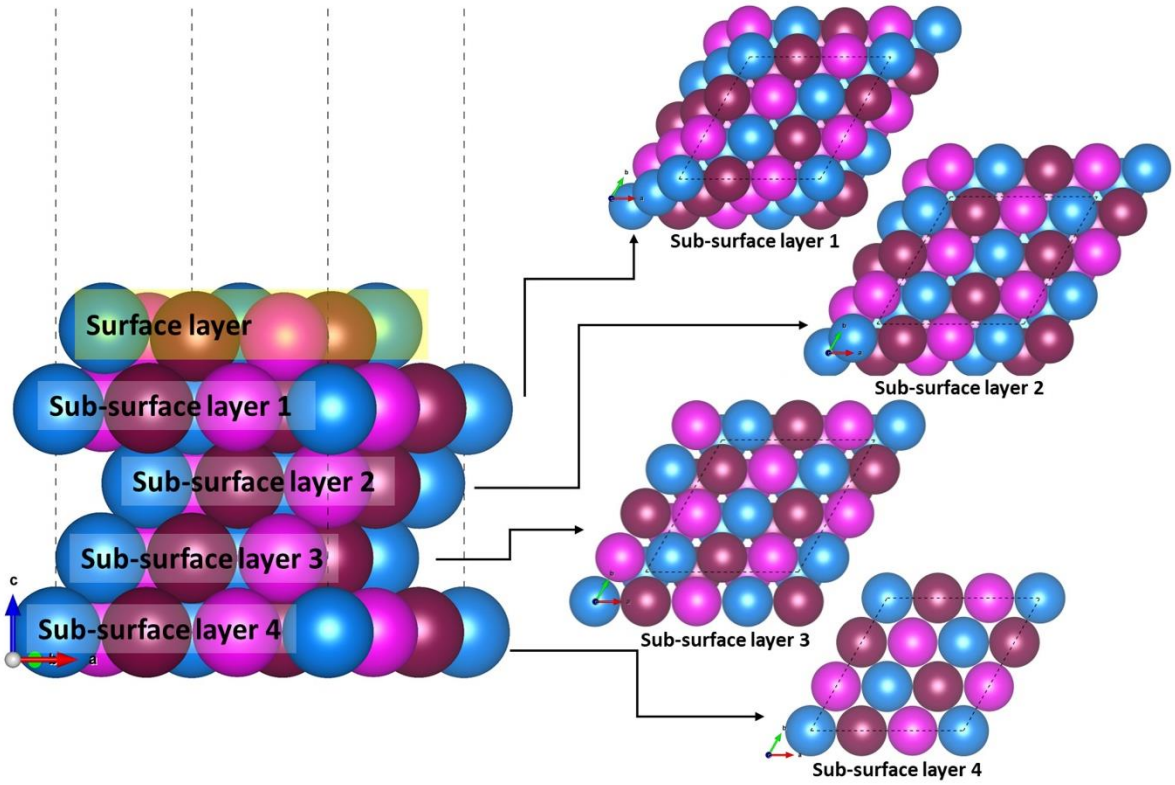
Supplementary Information

Supplementary Information 1: Sub-surface layer configuration

The configurations of the sub-surface layers are illustrated below. Reference of the configuration can be the boundary of the supercell used (dashed line). Blue, pink, maroon, grey and red spheres represent Pd, Ru, Ir, N and O atoms, respectively. The dash line shows the boundary of the supercell used. The VESTA code was used for visualization[1].

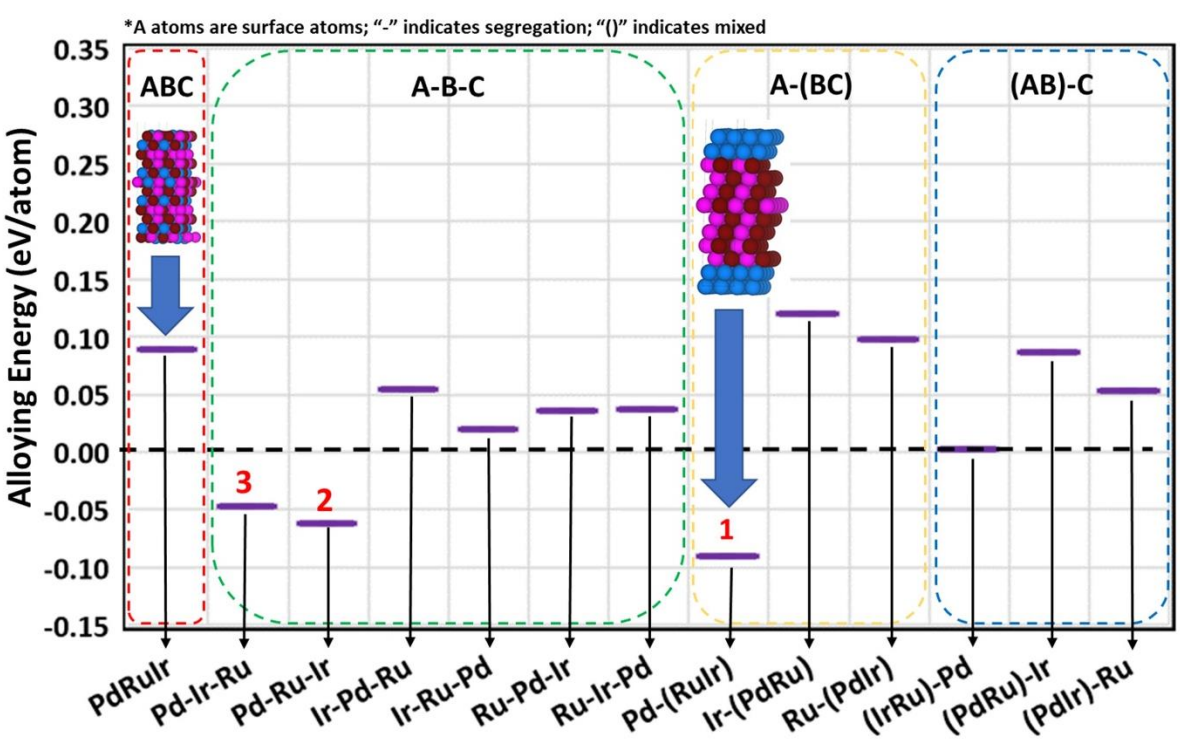


Supplementary Information 2: Stability analysis of ternary alloy configurations

A 2×2 supercell with 12 atomic layers and a vacuum distance of 7 atomic layers was used for each of the surface models of the ternary alloy systems. Four models were used to represent the tendency for possible phase formation arrangements: (1) mixed, (2) segregating, (3) segregating surface and mixed core, and (4) mixed surface and segregating core. For each of the slab models, the same kind and number of atoms was ensured to both surfaces terminations of the slab. The 2 middle layers of the slab were fixed while the other layers were relaxed upon slab optimization. For each arrangement, the alloying energy per atom were compared using:

$$E_{alloying_surf} = [(\sum n_j)E_{cohesive_{surf}} - \left(\sum n_j E_{cohesive_{surf(i)}}\right)]$$

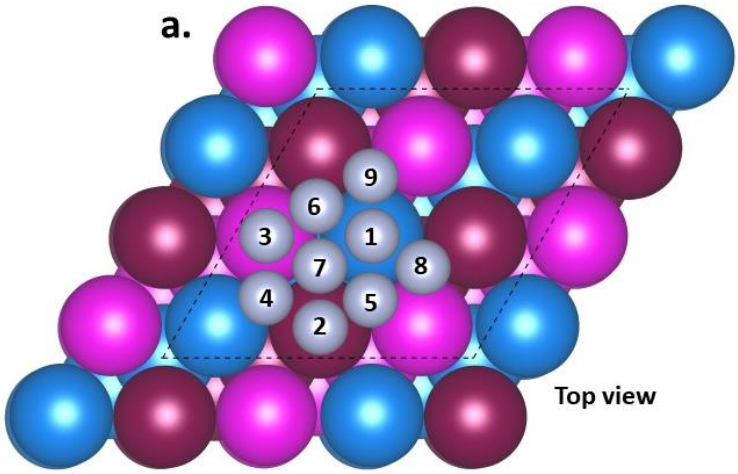
where $E_{alloying_surf}$ is the alloying energy per layer of the metal alloy slab, $E_{cohesive_surf}$ is the cohesive energy of the metal alloy slab, n_j is the number of each kind of atoms in the ternary bulk model with the total $\mathrm{M} = \sum n_j$. $E_{cohesive_{surf(i)}}$ is the cohesive energy per atom of the pure slab of the constituent atoms calculated with the same slab size as the bulk alloy and same condition for optimization, i.e., the 2 middle layers were fixed while the other layers were allowed to relax upon optimization. As a reference, the average alloying energy for randomly generated structure of the binary alloy PdRu is ~0.103 eV/atom and for the ternary alloy PdRuIr is ~0.059 eV/atom.



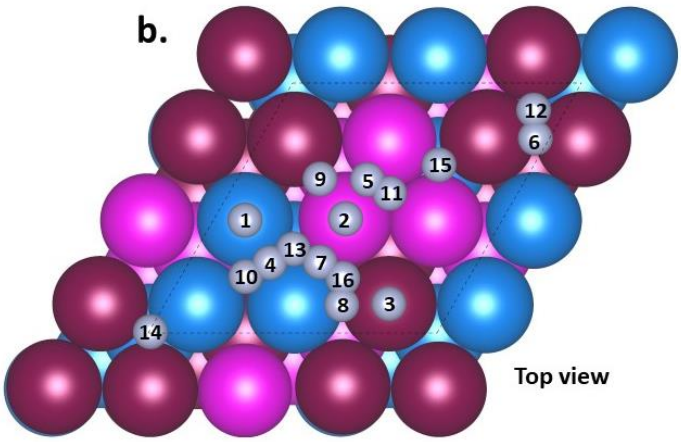
Supplementary Information 3: Definition of initial adsorption sites

The initial adsorption position considers the symmetry of the adsorption sites, i.e. top site, bridge site, fcc hollow site and hcp hollow site; and the type of atoms at its direct coordination, i.e., Pd, Ru or Ir.

The following are the definition for the initial adsorption sites for the mixed and clustered surfaces, respectively.



1 - Pd_top
2 - Ni_top
3 - Ru_top
4 - Pd_fcc
5 - Ni_fcc
6 - Ru_fcc
7 - Pd_hcp
8 - Ir_hcp
9 - Ru_hcp



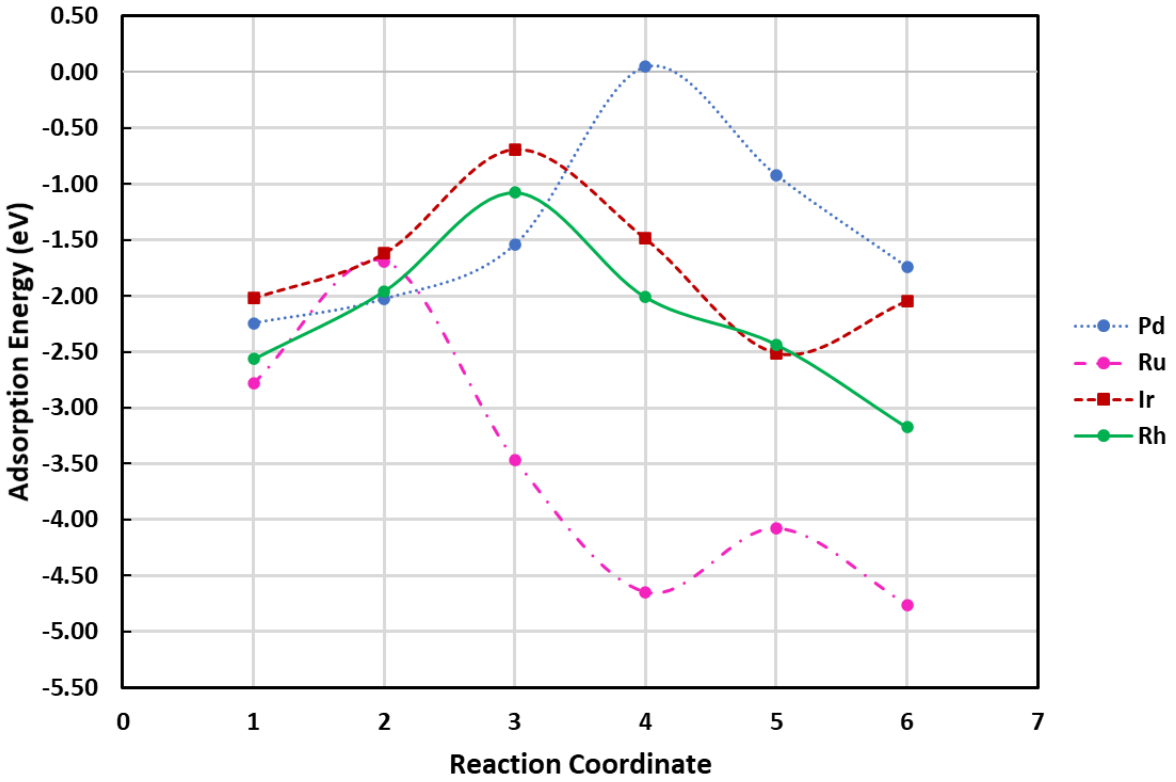
top sites
1-top_Pd
2-top_Ru
3-top_Ir

bridge sites
4-bridge_Pd-Pd
5-bridge_Ru-Ru
6-bridge_Ir-Ir
7-bridge_Pd-Ru
8-bridge_Pd-Ir
9-bridge_Ru-Ir

hollow sites
10-hollow_Pd-Pd-Pd
11-hollow_Ru-Ru-Ru
12-hollow_Ir-Ir-Ir
13-hollow_Pd-Pd-Ru
14-hollow_Pd-Ir-Ir
15-hollow_Ru-Ru-Ir
16-hollow_Pd-Ru-Ir

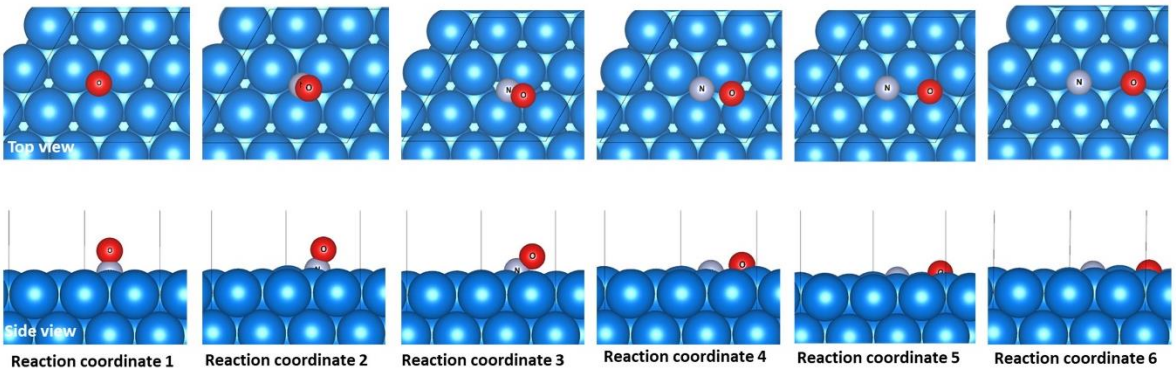
Supplementary Information 4: NO dissociation reaction path on pure surfaces

NO dissociation on the pure Pd, Ru, Ir and Rh surfaces through CiNEB method [2]. NO dissociation determined from the molecular adsorption state (reaction coordinate 1) initial state to the final co-adsorbed N and O (reaction coordinate 6). The values given are relative to the isolated NO molecule at the gaseous state and the clean surface.

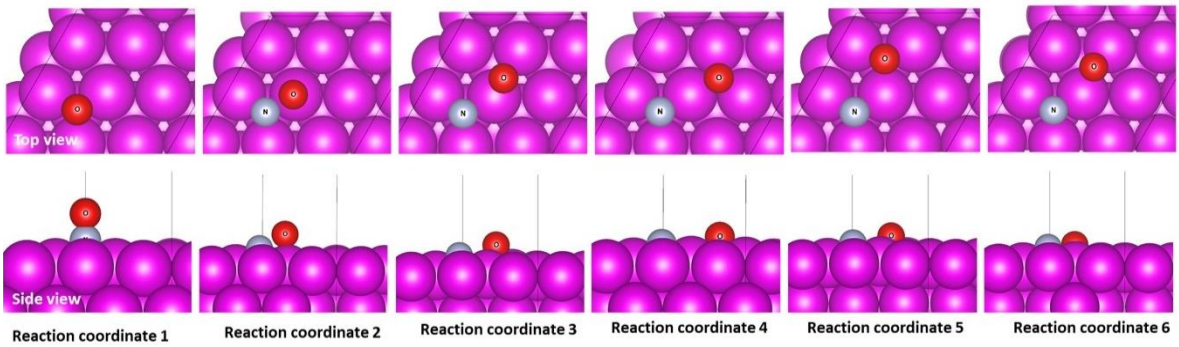


Reaction pathway for NO dissociation on:

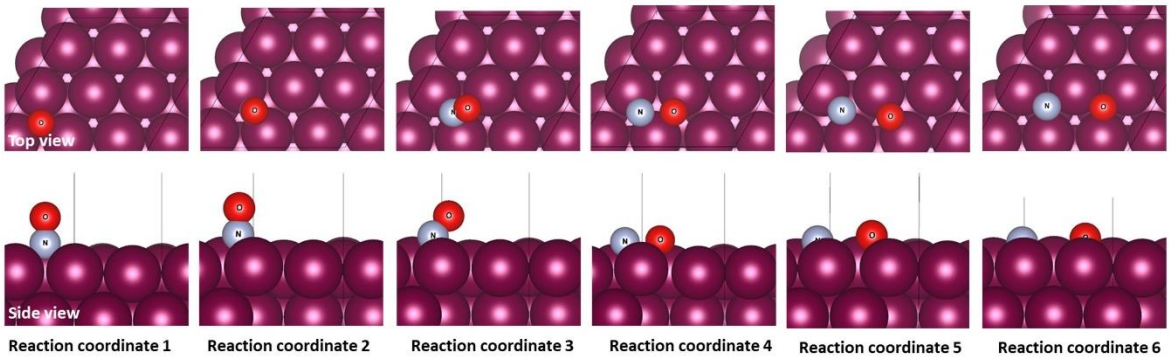
FCC Pd (111) surface



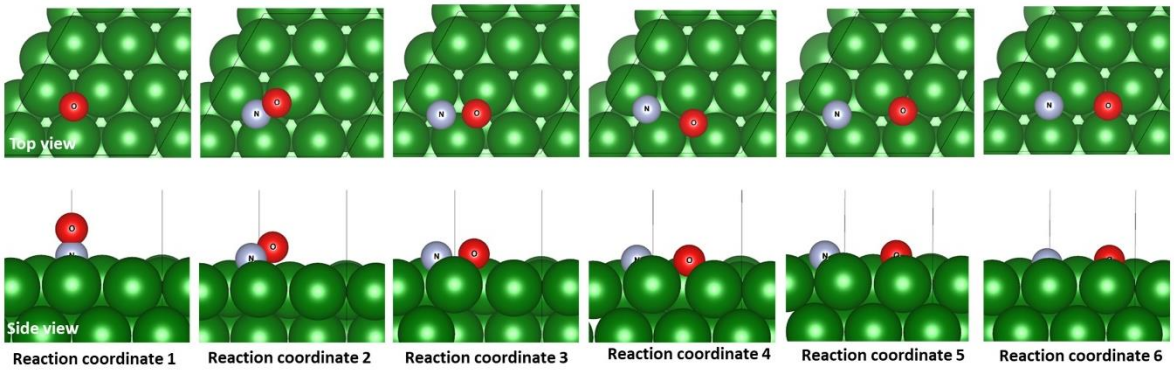
HCP Ru (0001) surface



FCC Ir (111) surface



FCC Rh (111) surface



Supplementary Information 5: NO and O adsorption on the PdRuIr ternary alloy

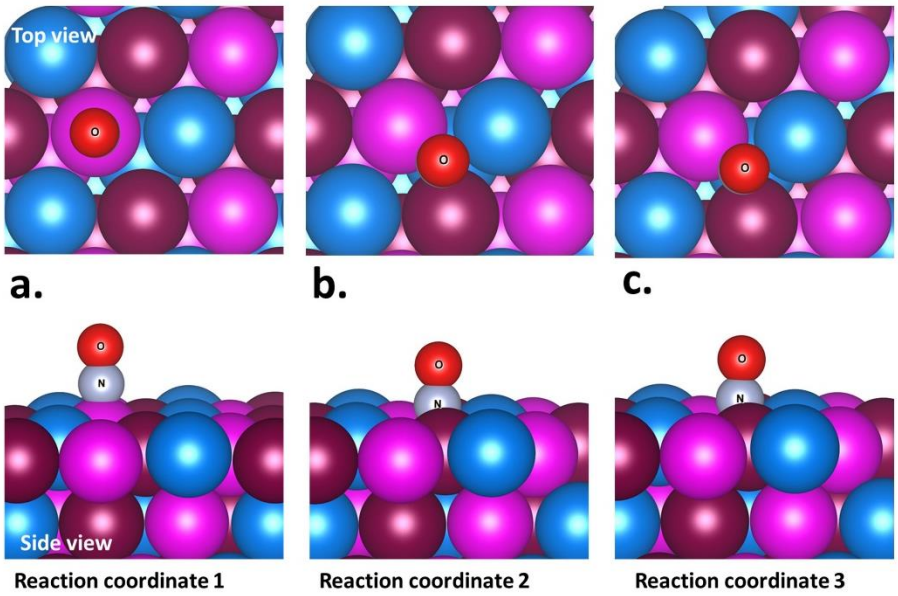
The adsorption energy, adsorption site, N-O bond elongation, NO additional charge upon adsorption at different initial adsorption sites for the different surface models of the PdRuIr ternary alloy. The adsorption energy of O, adsorption site and additional charge obtained by O upon adsorption are also depicted. NO bond length in the gaseous state is 1.17 Å.

Initial Adsorption Site	NO adsorption			O adsorption	
	Adsorption Energy (eV)	N-O bond length (Å)	NO additional charge (e)	Adsorption Energy (eV)	NO additional charge (e)
Mixed Surface					
Pd top	-1.330	1.18	-0.130	-2.166	-0.835
Ir top	-2.513	1.18	-0.431	-2.263	-0.828
Ru top	-2.915	1.18	-0.287	-2.092	-0.811
Pd fcc hollow	-2.537	1.21	-0.532	-2.353	-0.845
Ir fcc hollow	-2.445	1.21	-0.523	-2.146	-0.817
Ru fcc hollow	-2.555	1.21	-0.507	-2.087	-0.824
Pd hcp hollow	-2.529	1.22	-0.584	-2.166	-0.836
Ir hcp hollow	-2.556	1.21	-0.505	-2.092	-0.811
Ru hcp hollow	-2.688	1.21	-0.519	-2.264	-0.829
Clustered Surface					
Pd top	-1.138	1.18	-0.148	-1.160	-0.806
Ru top	-2.530	1.18	-0.257	-1.853	-0.805
Ir top	-2.162	1.18	-0.413	-1.946	-0.823
Pd-Pd bridge	-1.812	1.21	-0.457	-1.160	-0.807
Ru-Ru bridge	0.994	1.21	-0.475	-2.428	-0.817
Ir-Ir bridge	-2.136	1.21	-0.547	-2.221	-0.899
Pd-Ru bridge	-2.014	1.20	-0.415	-1.946	-0.827
Pd-Ir bridge	-2.295	1.21	-0.517	-1.946	-0.823
Ru-Ir bridge	-2.398	1.21	-0.515	-2.007	-0.810
Pd-Pd-Pd hollow	-1.854	1.21	-0.428	-1.160	-0.808
Ru-Ru-Ru hollow	-2.411	1.23	-0.589	-2.428	-0.818
Ir-Ir-Ir hollow	-2.195	1.23	-0.695	-2.221	-0.898
Pd-Pd-Ru hollow	-2.118	1.21	-0.498	-1.853	-0.804
Pd-Ir-Ir_hollow	-1.963	1.22	-0.570	-1.655	-0.855
Ru-Ru-Ir_hollow	-2.523	1.24	-0.674	-2.560	-0.871
Pd-Ru-Ir hollow	-2.324	1.21	-0.513	-1.946	-0.824

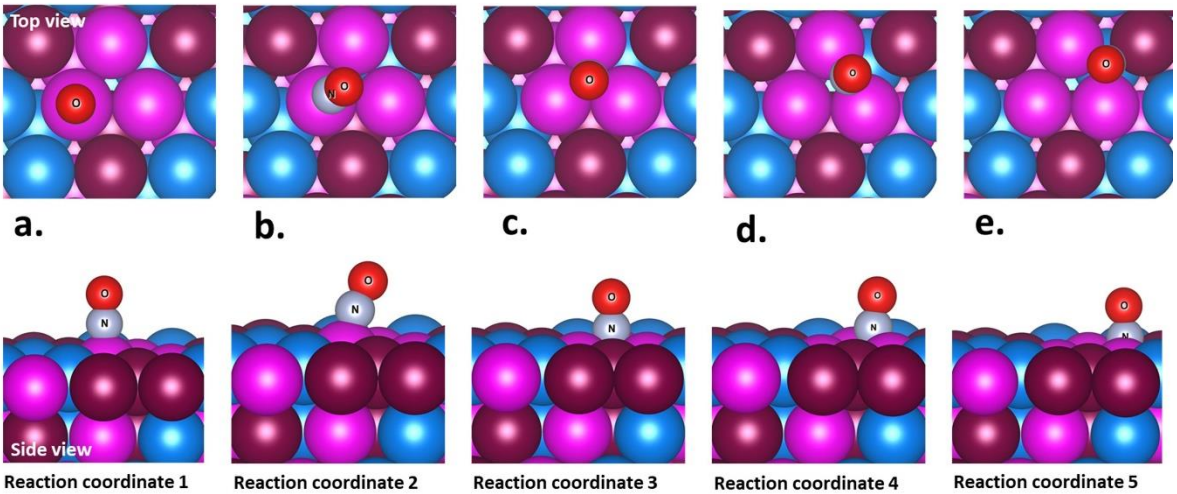
Supplementary Information 6: NO diffusion pathway

NO diffusion pathway from the most stable adsorption configuration (reaction coordinate 1) to the adsorption with the highest charge transfer to NO (reaction coordinate 3 for mixed surface and 5 for clustered surface) for both mixed and clustered configurations, respectively. The images of the pathway for diffusion were obtained through the CiNEB method . Blue, pink, maroon, grey and red spheres represent Pd, Ru, Ir, N and O atoms, respectively. The dash line shows the boundary of the supercell used. The VESTA code was used for visualization[1].

a. Mixed surface



b. Clustered surface



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1. K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2011, 44, 1272-1276.
2. G. Henkelman, B. P. Uberuaga and H. Jónsson, *The Journal of Chemical Physics*, 2000, 113, 9901-9904.