Electronic Supplementary Information

A first-principles understanding of the CO-assisted NO reduction on the $IrRu/Al_2O_3$ catalyst in O_2-rich condition

Malik Waqar Arshad[1,2], Dong Hun Kim[3], Young-Woo You[3,4], Soo Min Kim[2,3,4], Il Jeong Heo[3,4]* Seok Ki Kim[1,2]*

[1]C1 Gas & Carbon Convergent Research Center, Korea Research institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea.

[2]University of Science & Technology, Advanced Materials and Chemical Engineering Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea.

[3]Environment & Sustainable Resources Research Center, Korea Research institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea.

[4]Convergent Chemistry of Air Pollution Center, Korea Research institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea.

*Corresponding authors: skkim726@krict.re.kr, zaiseok@krict.re.kr

List of Figures

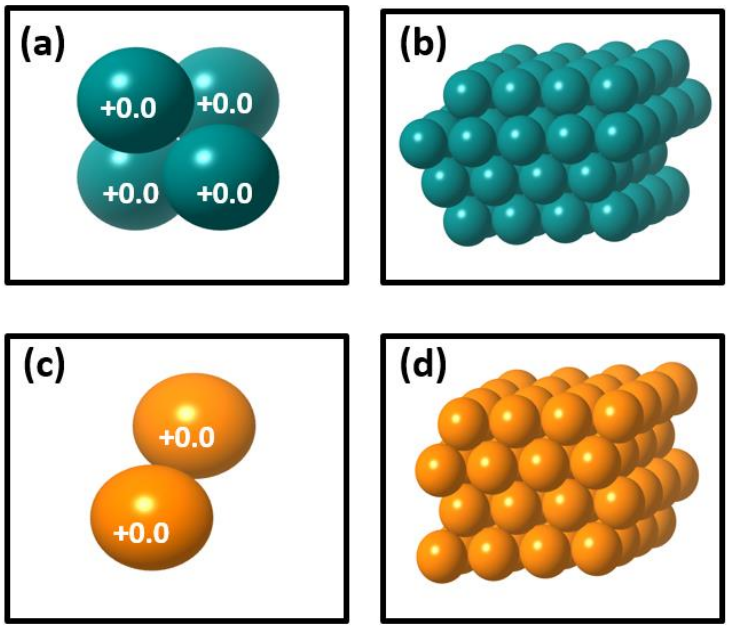

Fig. S1. Optimized geometry (a) Ir (111) primitive cell with bader charges (b) Ir_{64} (111) supercell (c) Ru (001) primitive cell with bader charges and (d) Ru_{64} (001) supercell. Green and orange balls represent the Ir and Ru, respectively.

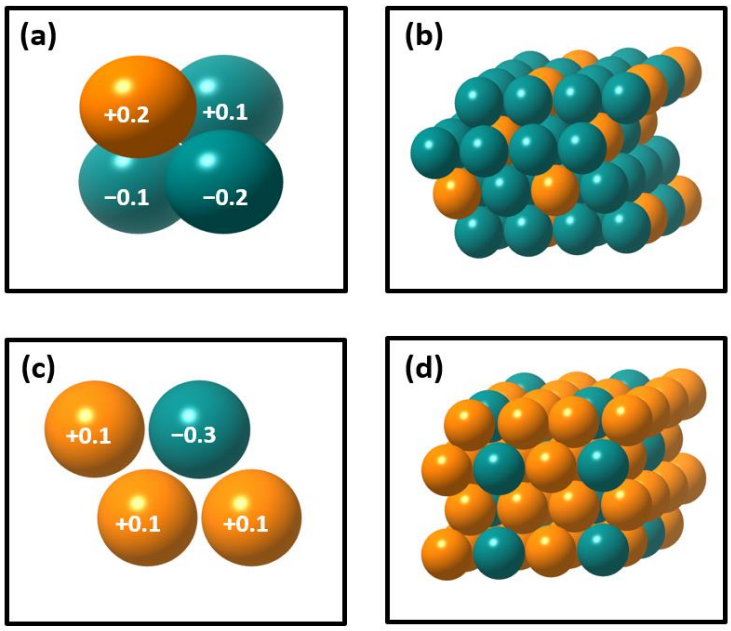

Fig. S2. Optimized bulk alloy models used for lattice parameter analysis (a) Ir_3Ru_1 primitive cell with bader charges (b) $Ir_{48}Ru_{16}$ supercell (c) Ru_3Ir_1 primitive cell with bader charges (d) $Ru_{48}Ir_{16}$ supercell. Green and orange balls represent the Ir and Ru, respectively.

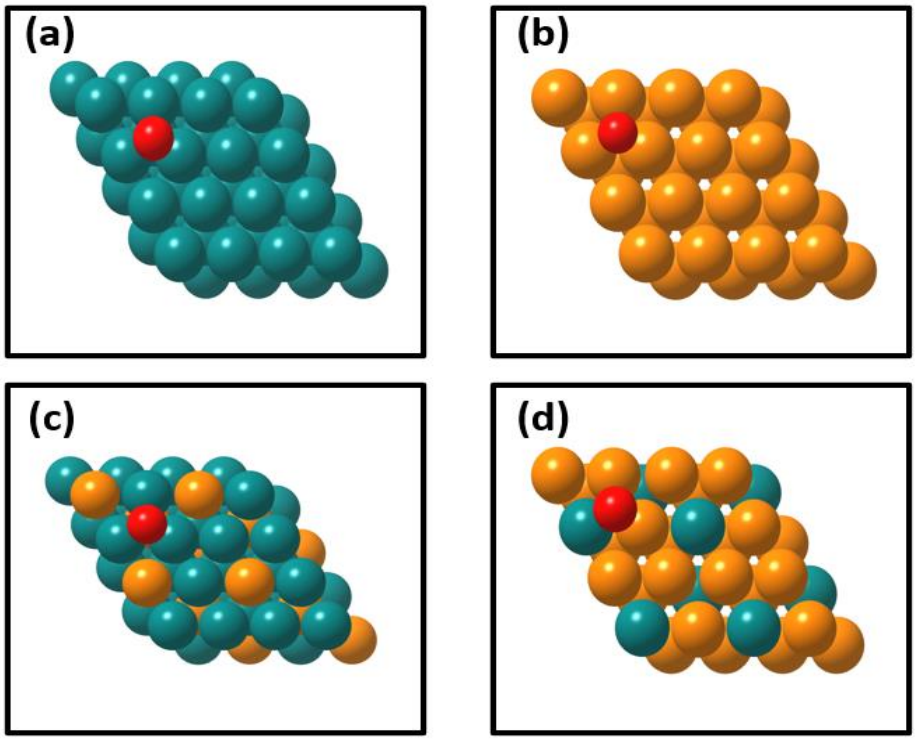

Fig. S3. Optimized bulk alloy slab models used for surface oxygen analysis. O* was adsorbed on three fold hollow hcp site.(a) $Ir_{64}O_1(111)$ super cell (b) $Ru_{64}O_1$ (001) supercell (c) $Ir_{48}Ru_{16}O_1(111)$ super cell (d) $Ru_{48}Ir_{16}O_1$ supercell. Green, orange, and red balls represent the Ir, Ru, and oxygen, respectively.

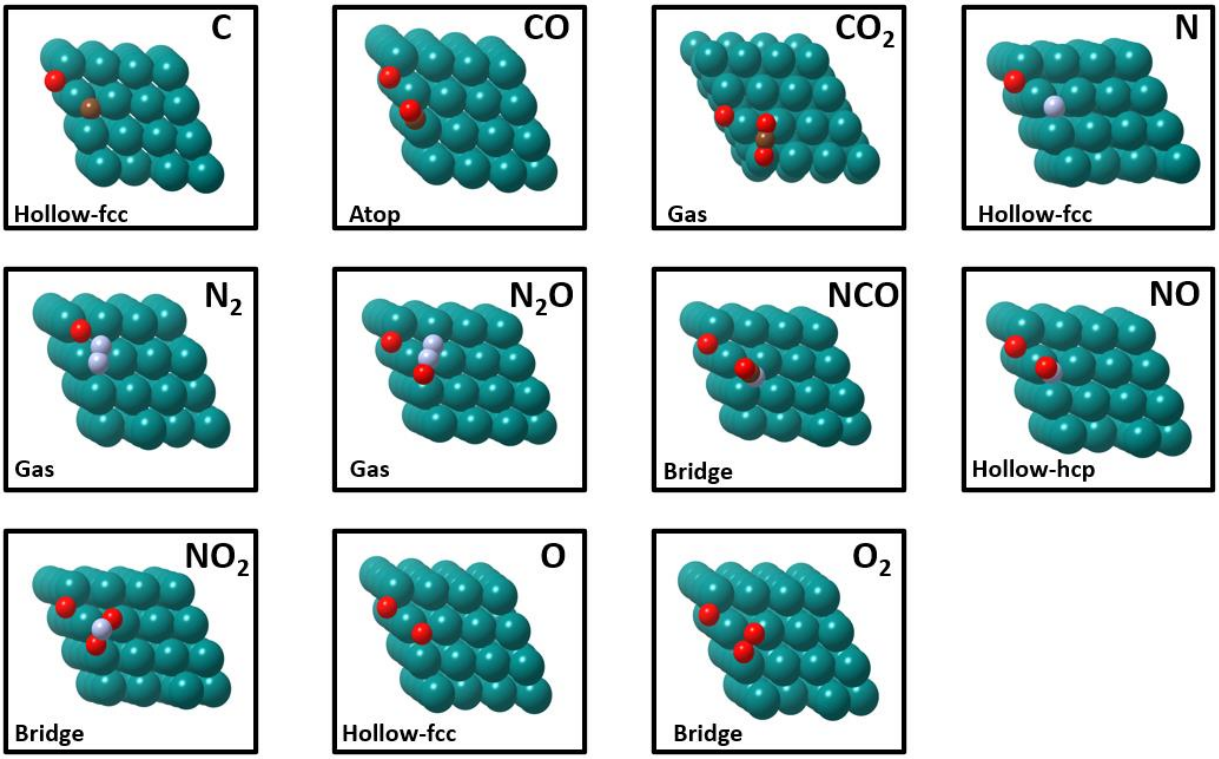

Fig. S4. Optimized surface oxygen Ir-slab model with different adsorbates at their stable sites. O* was adsorbed on hcp hollow site and most stable site of each adsorbate is mention under each figure. Green, red, brown, and violet balls represent the Ir, O, C, and N, respectively.

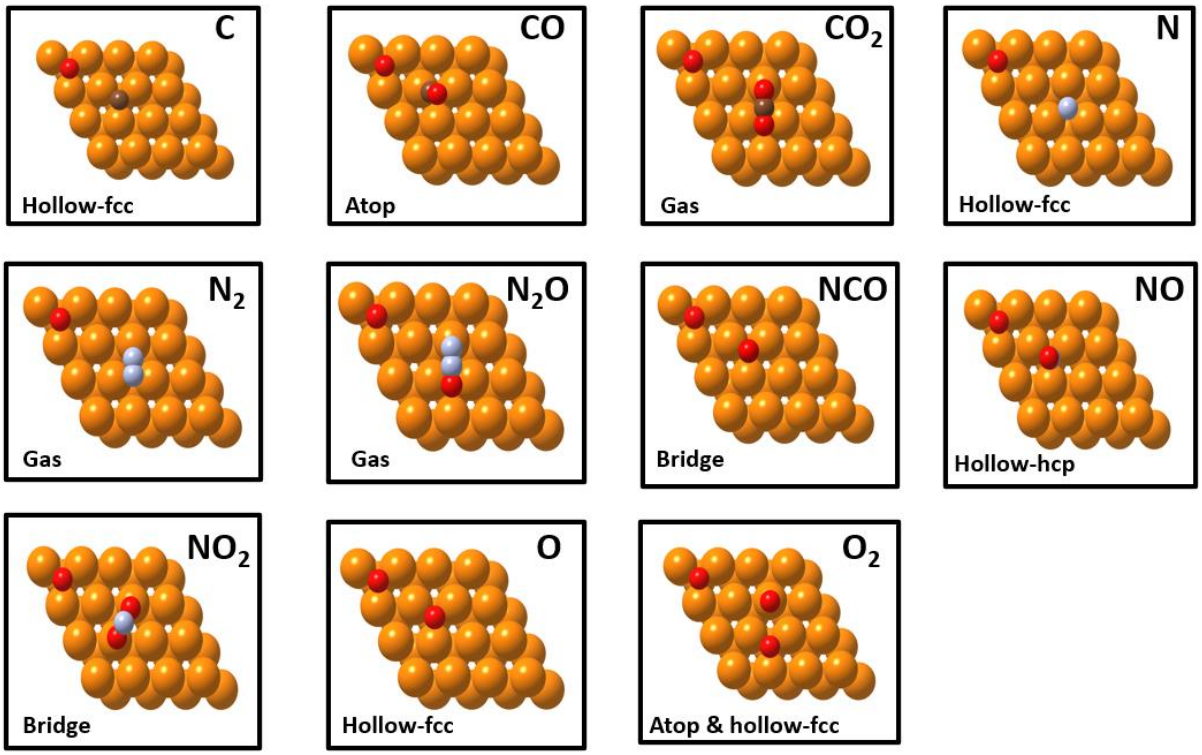

Fig. S5. Optimized surface oxygen Ru-slab model with different adsorbates at their stable sites. O* was adsorbed on hcp hollow site and most stable site of each adsorbate is mention under each figure. Orange, red, brown, and violet balls represent the Ru, O, C, and N, respectively.

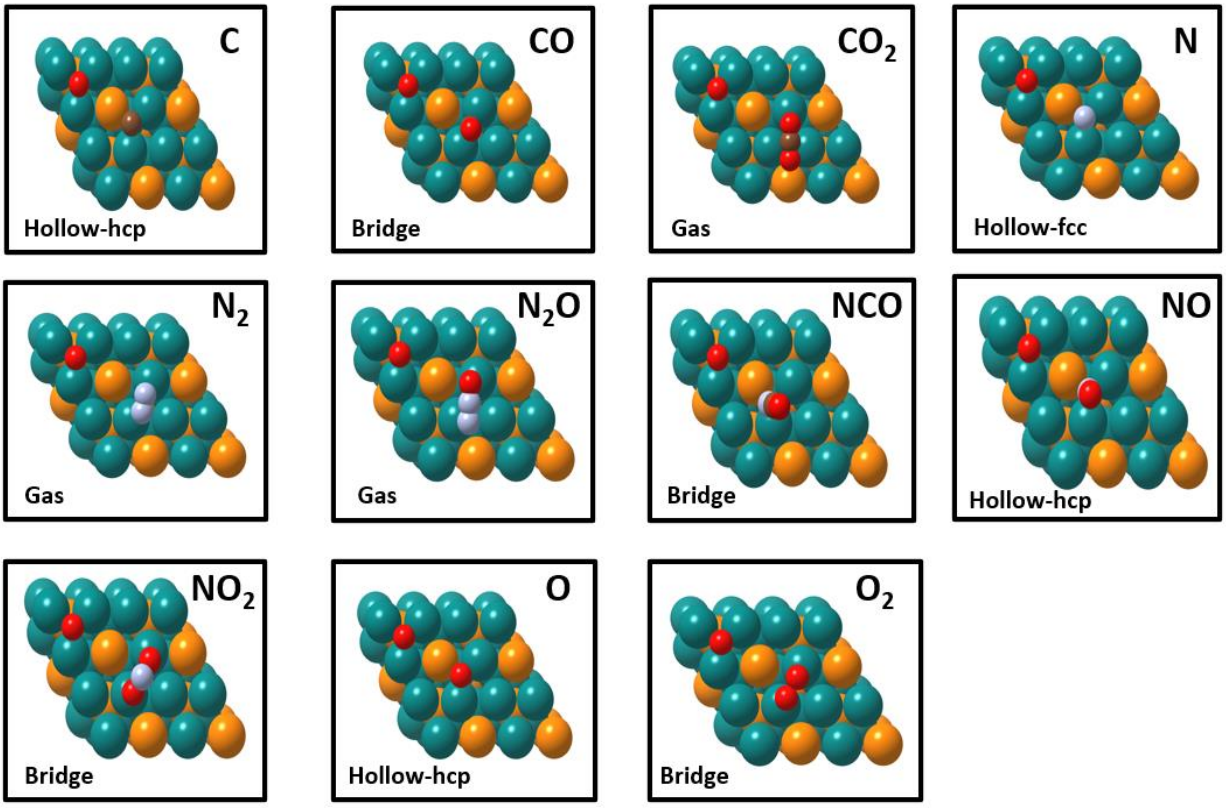

Fig. S6. Optimized surface oxygen Ir_3Ru_1-slab model with different adsorbates at their stable sites. O* was adsorbed on hcp hollow site and most stable site of each adsorbate is mention under each figure. Green, orange, red, brown, and violet balls represent the Ir, Ru, O, C, and N, respectively.

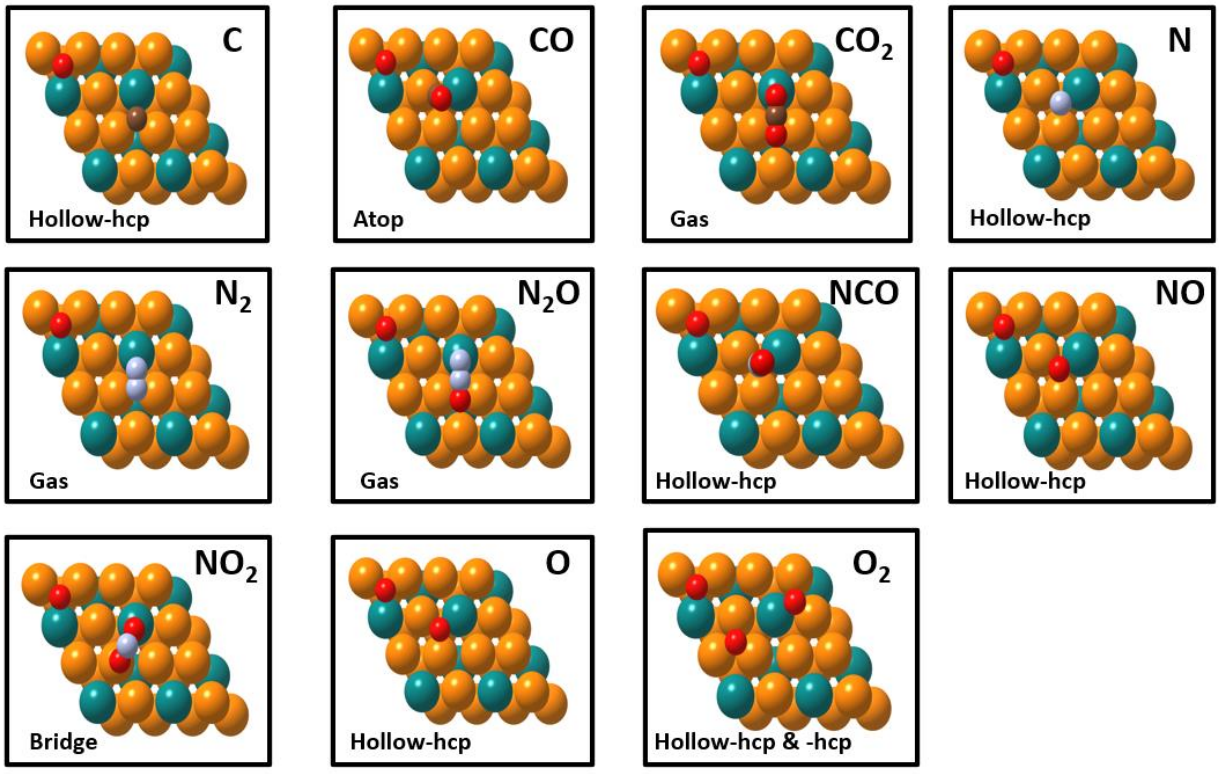

Fig. S7. Optimized surface oxygen Ru_3Ir_1-slab model with different adsorbates at their stable sites. O* was adsorbed on hcp hollow site and most stable site of each adsorbate is mention under each figure. Green, orange, red, brown, and violet balls represent the Ir, Ru, O, C, and N, respectively.

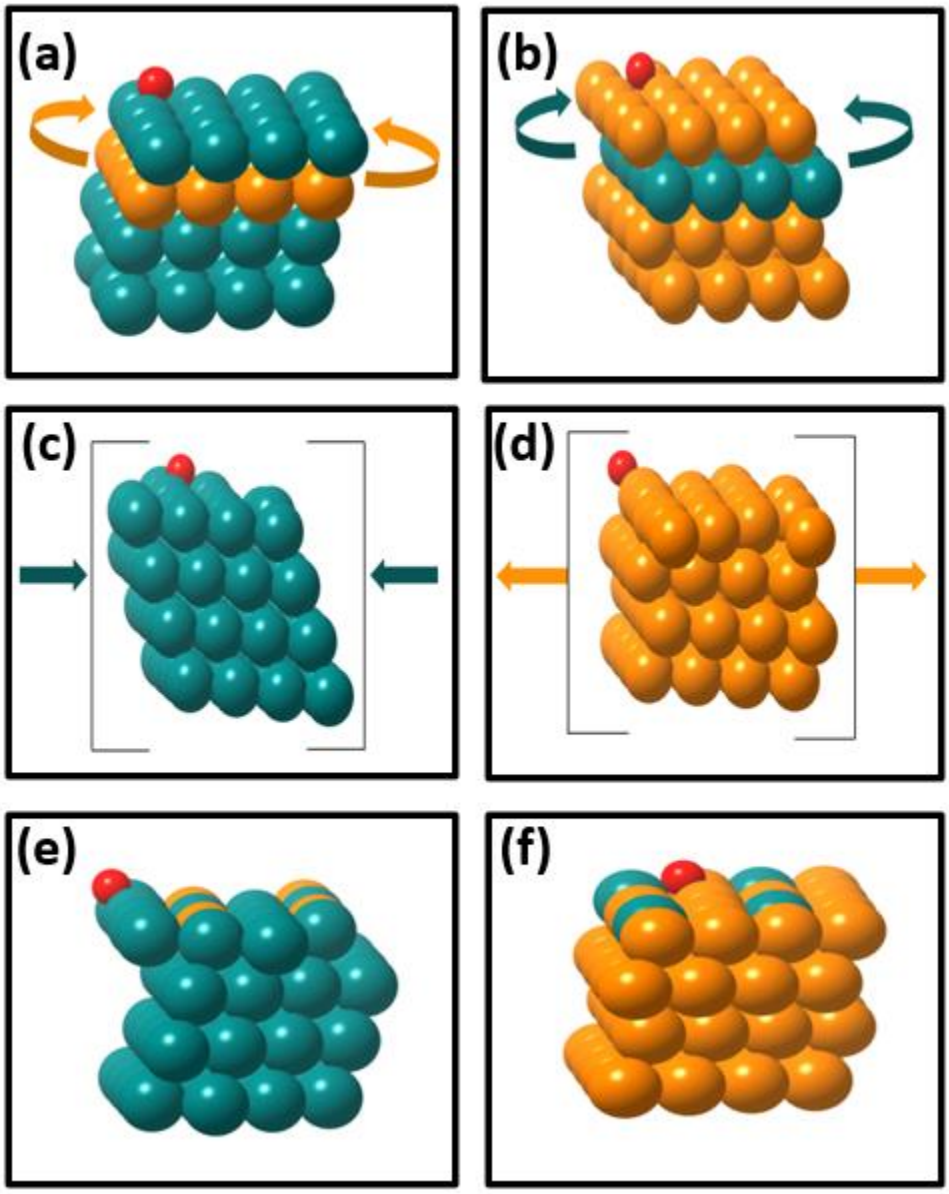

Fig. S8. Optimized surface oxygen slab models used for dominant effect study (a) Ir-Ru_{ligand} (b) Ru-Ir_{ligand} (c) Ir compressive strain (d) Ru tensile strain (e) Ir-$Ru_{ensemble}$ (f) Ru-$Ir_{ensemble}$ models. Green, orange, and red balls represent the Ir, Ru, and O, respectively.

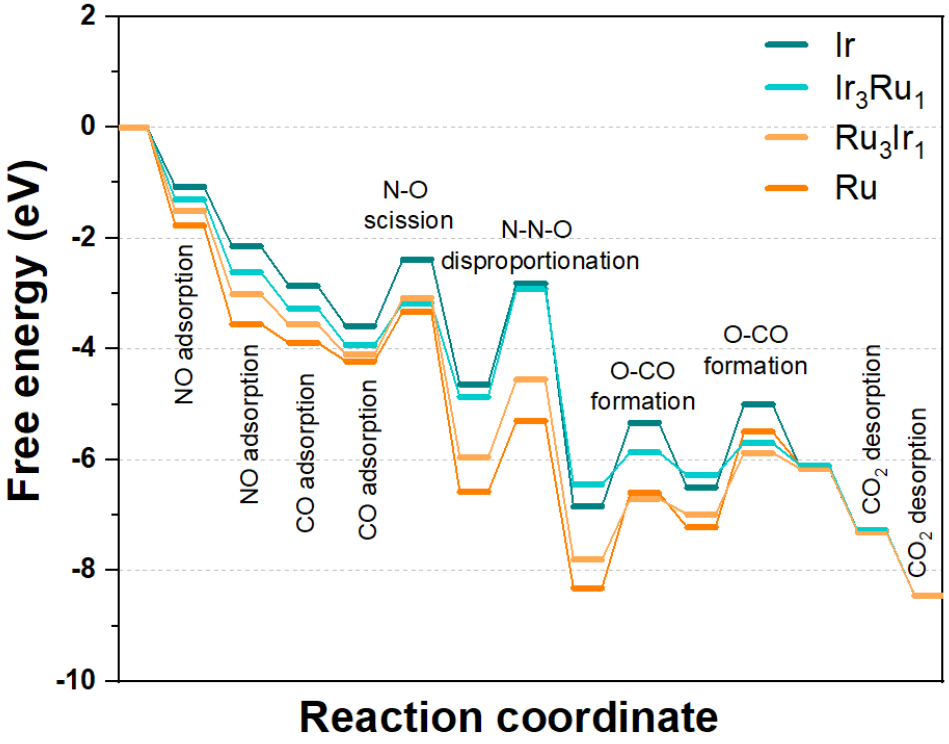

Fig. S9. Reaction energy profile, NO+CO reactions. T = 150 °C and P = 0.1 MPa

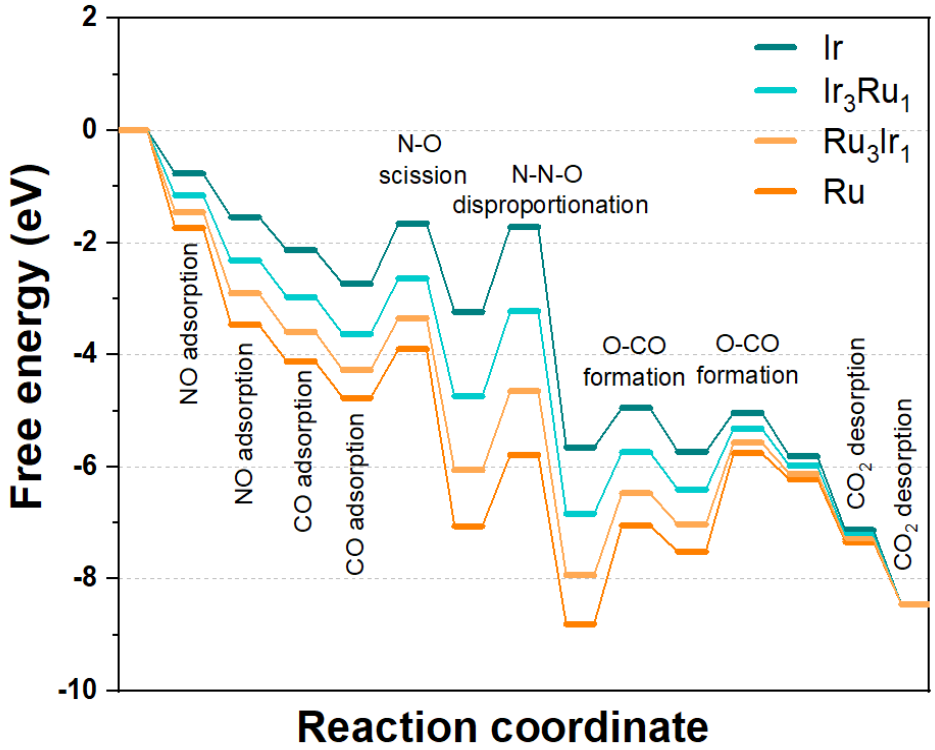

Fig. S10. Reaction energy profile, NO+CO+O_2 reactions. T = 150 °C and P = 0.1 MPa

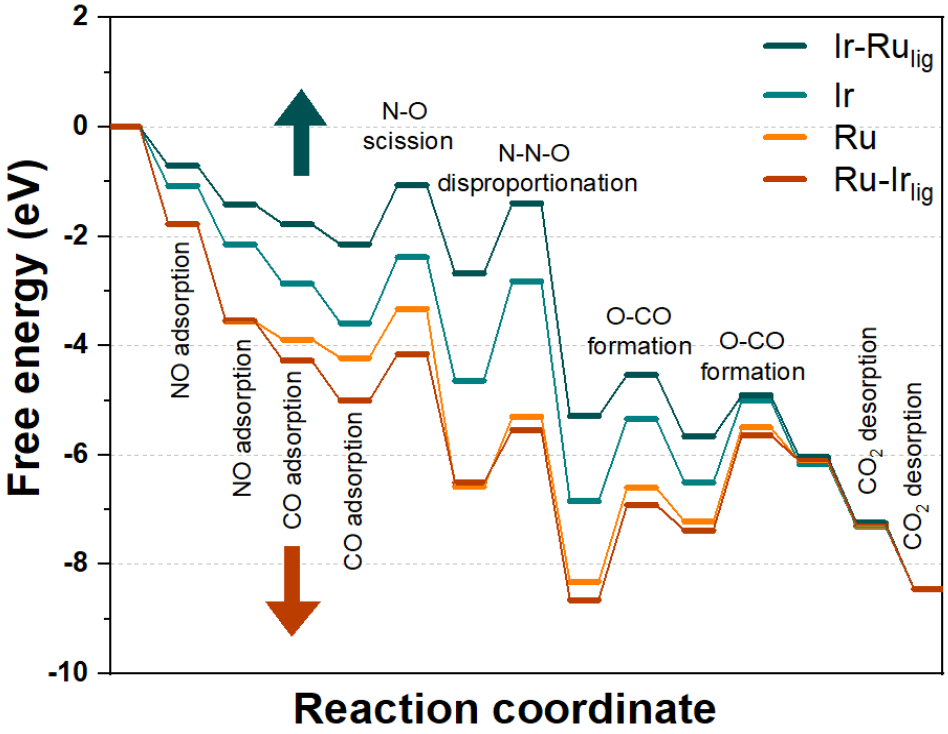

Fig. S11. Reaction energy profile of ligand effect without surface oxygen. T = 150 °C and P = 0.1 MPa

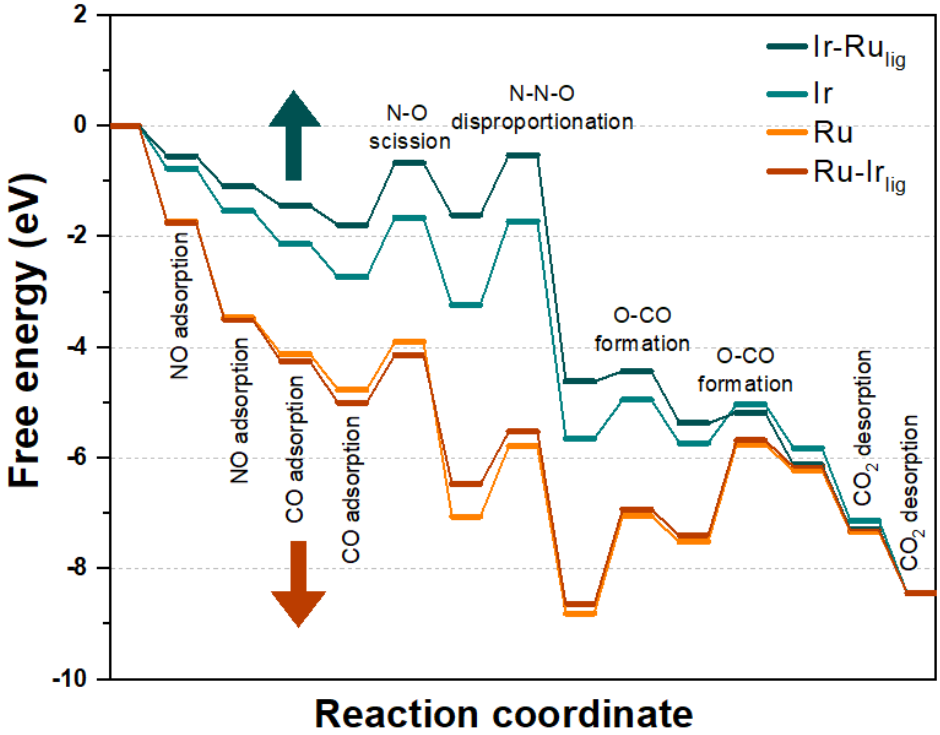

Fig. S12. Reaction energy profile of ligand effect with surface oxygen. T = 150 °C and P = 0.1 MPa

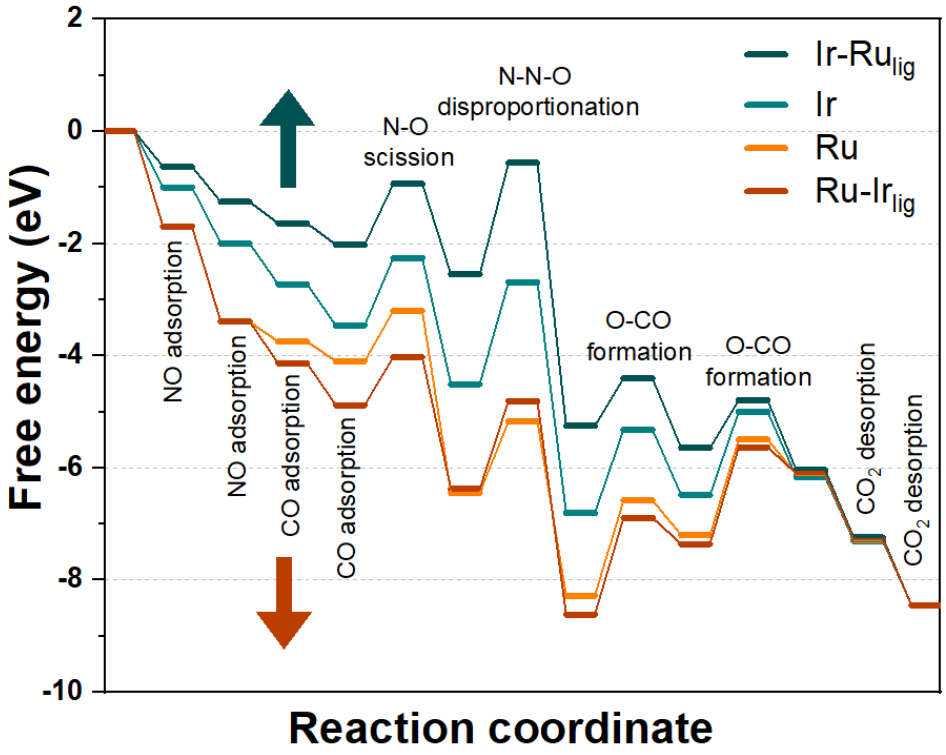

Fig. S13. Reaction energy profile of ligand effect without surface oxygen. T = 200 °C and P = 0.1 MPa

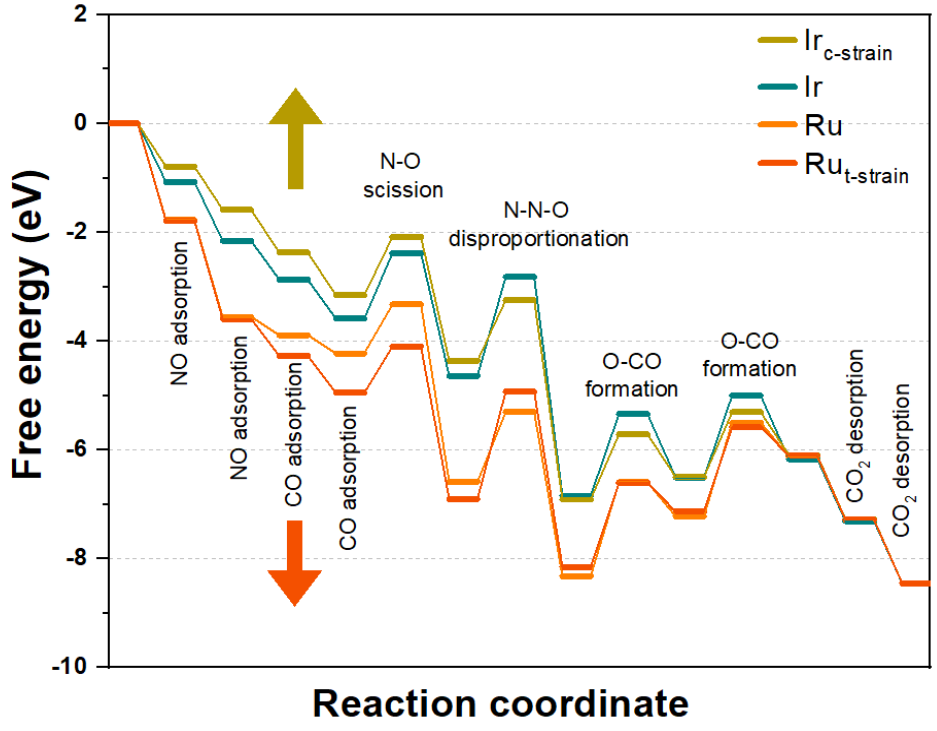

Fig. S14. Reaction energy profile of strain effect without surface oxygen. T = 150 °C and P = 0.1 MPa

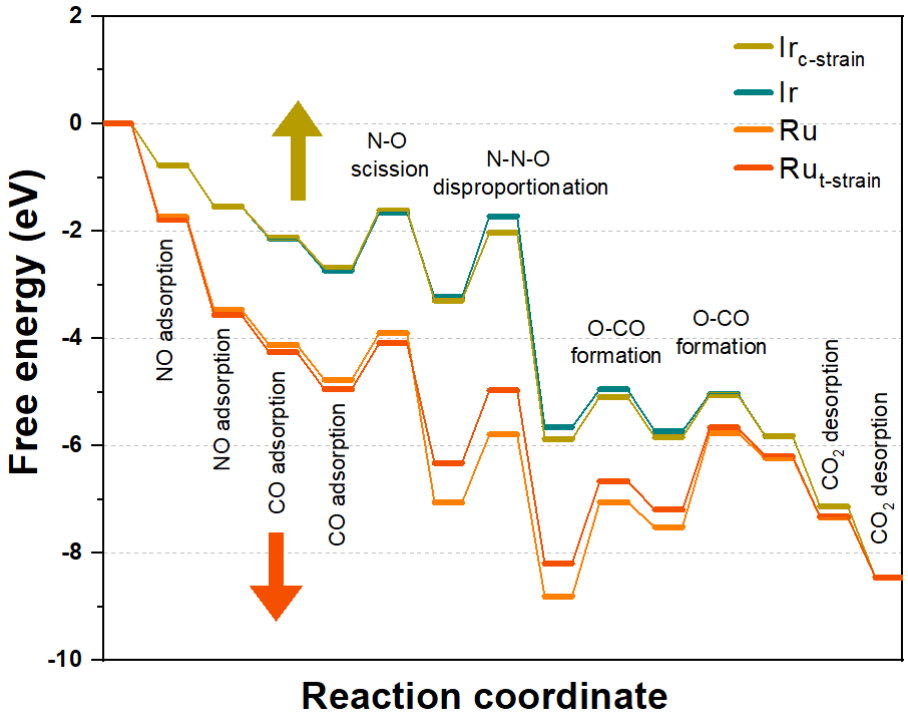

Fig. S15. Reaction energy profile of strain effect with surface oxygen. T = 150 °C and P = 0.1 MPa

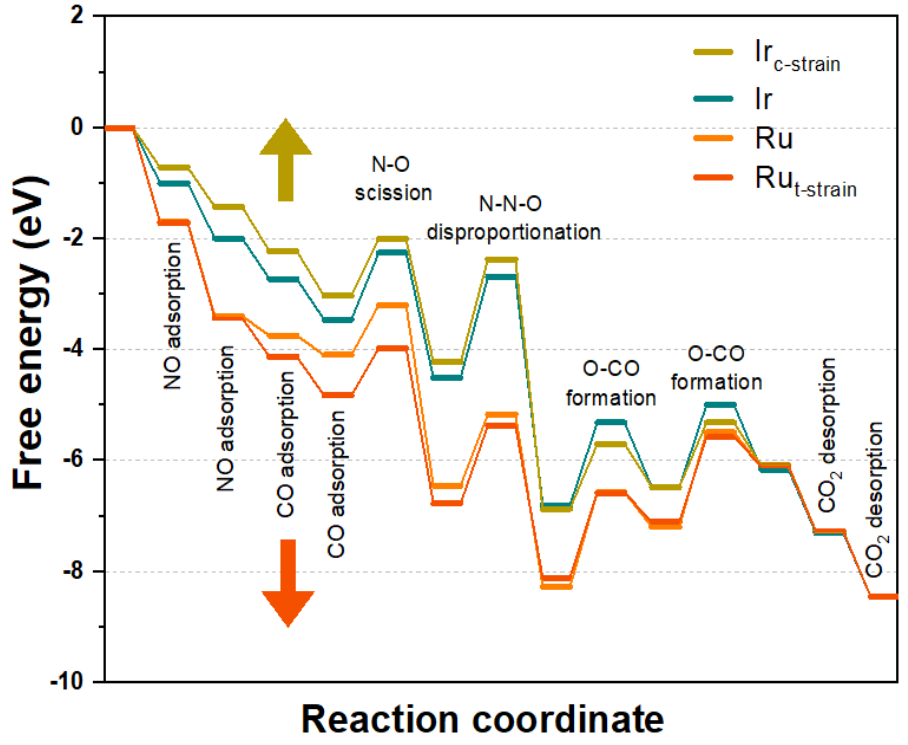

Fig. S16. Reaction energy profile of strain effect without surface oxygen. T = 200 °C and P = 0.1 MPa

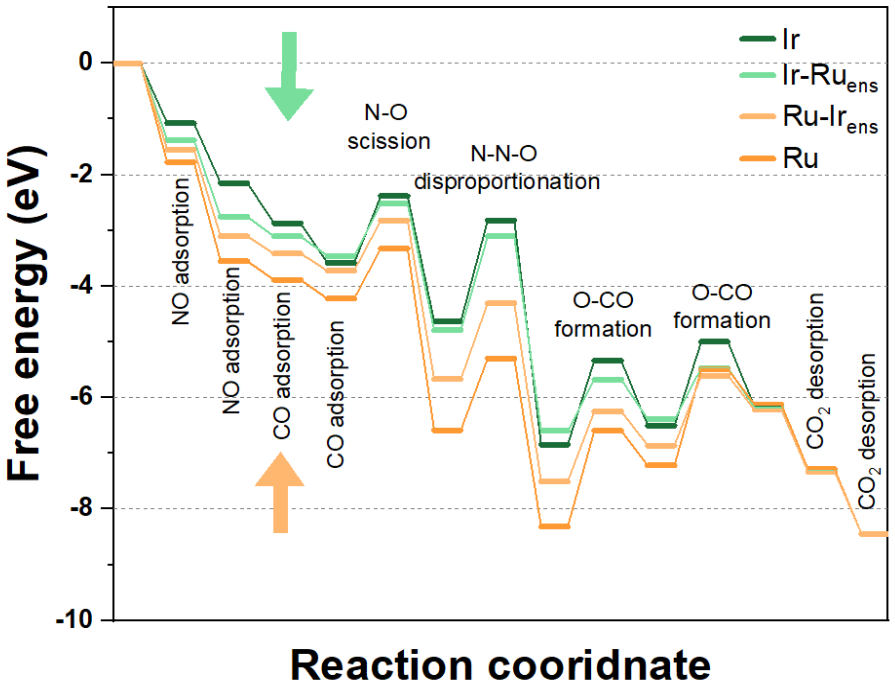

Fig. S17. Reaction energy profile of dominant effect in an IrRu alloy formation without surface oxygen. T = 150 °C and P = 0.1 MPa

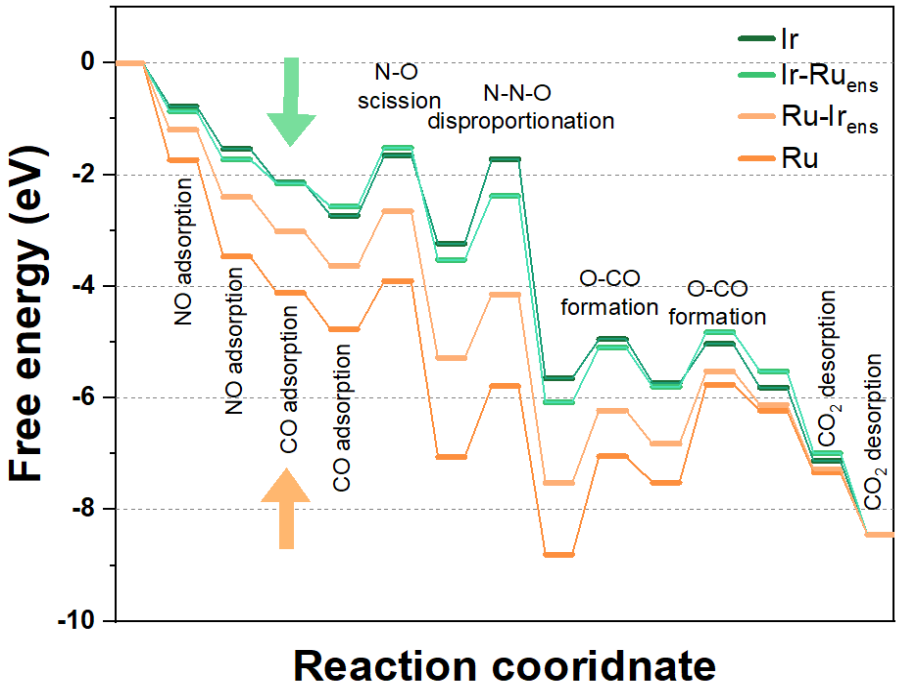

Fig. S18. Reaction energy profile of dominant effect in an IrRu alloy formation with surface oxygen. T = 150 °C and P = 0.1 MPa

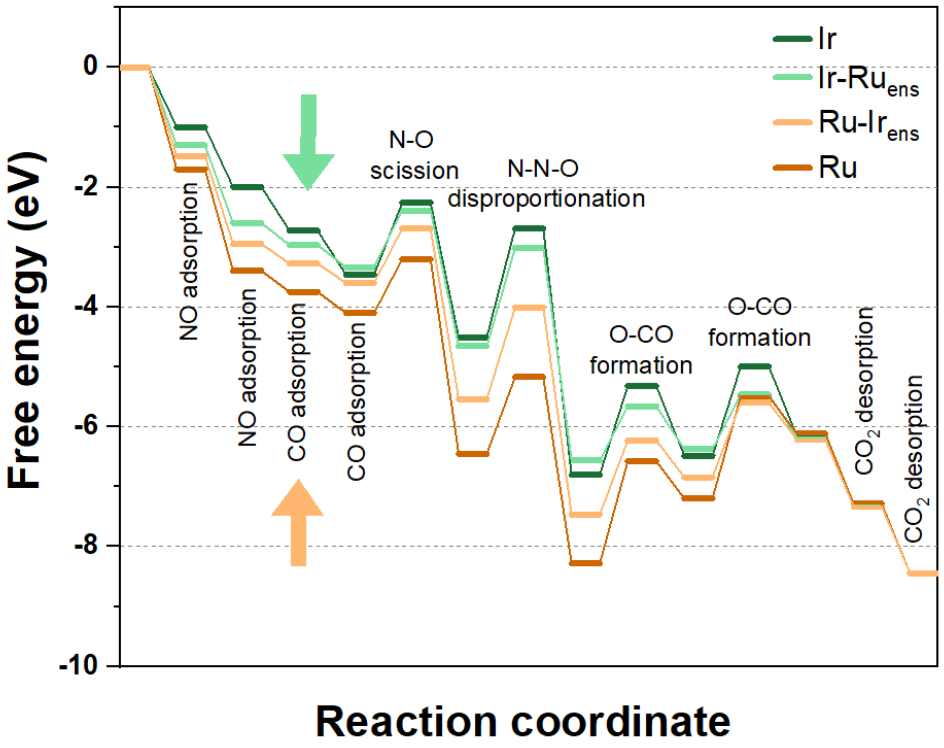

Fig. S19. Reaction energy profile of dominant effect in an IrRu alloy formation without surface oxygen. T = 200 °C and P = 0.1 MPa

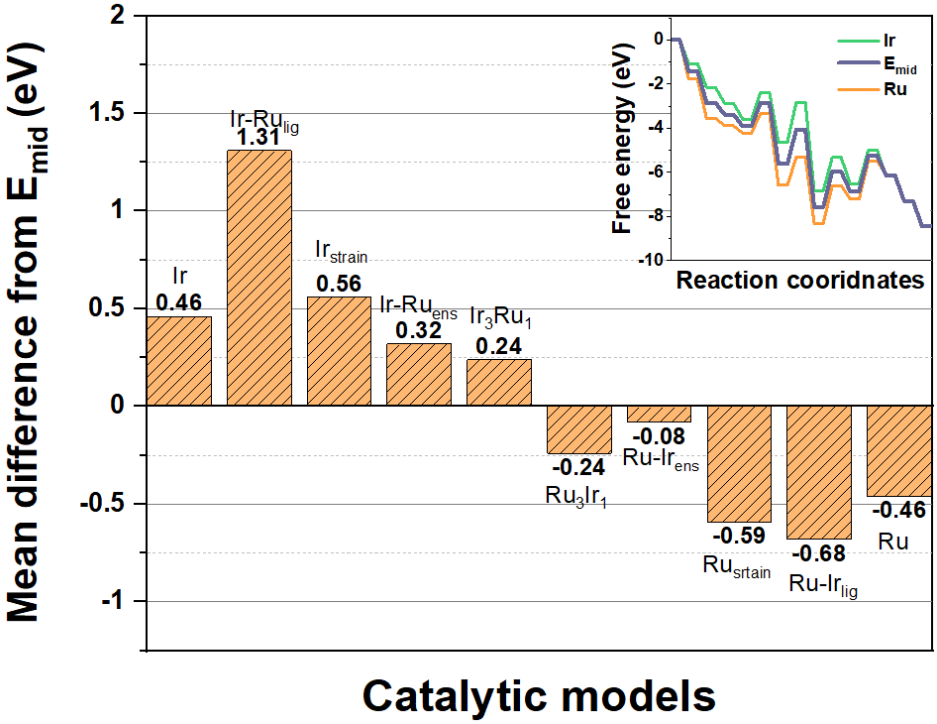

Fig. S20. Mean difference between the median values (Emid) of the pure Ir and Ru catalysts and the energy values of the different alloy surfaces without surface oxygen. T = 150 °C and P = 0.1 MPa

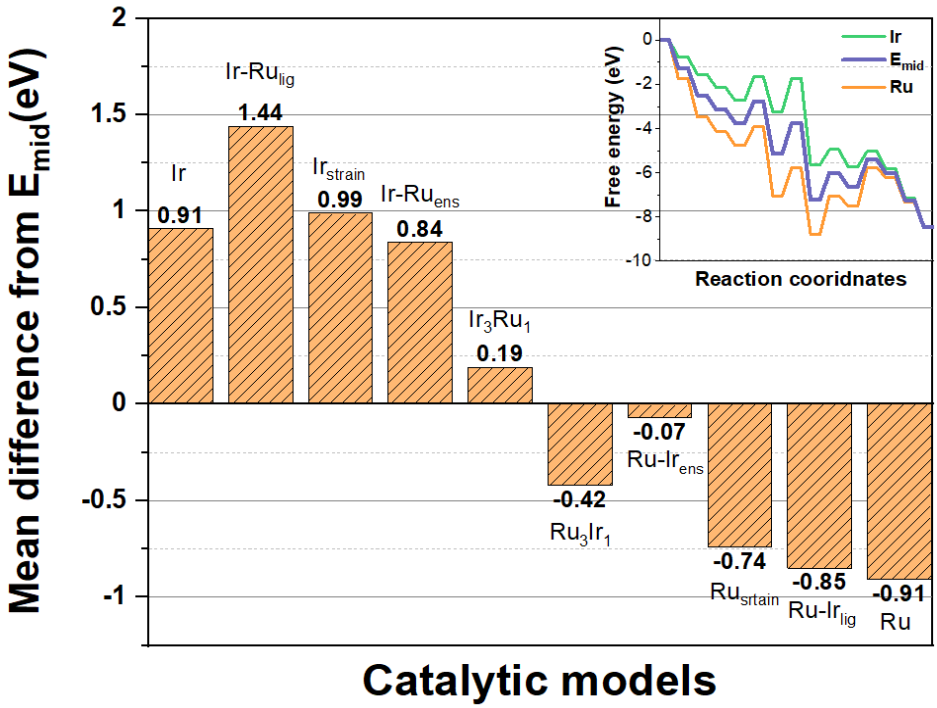

Fig. S21. Mean difference between the median values (E_{mid}) of the pure Ir and Ru catalysts and the energy values of the different alloy surfaces with surface oxygen. T = 150 °C and P = 0.1 MPa

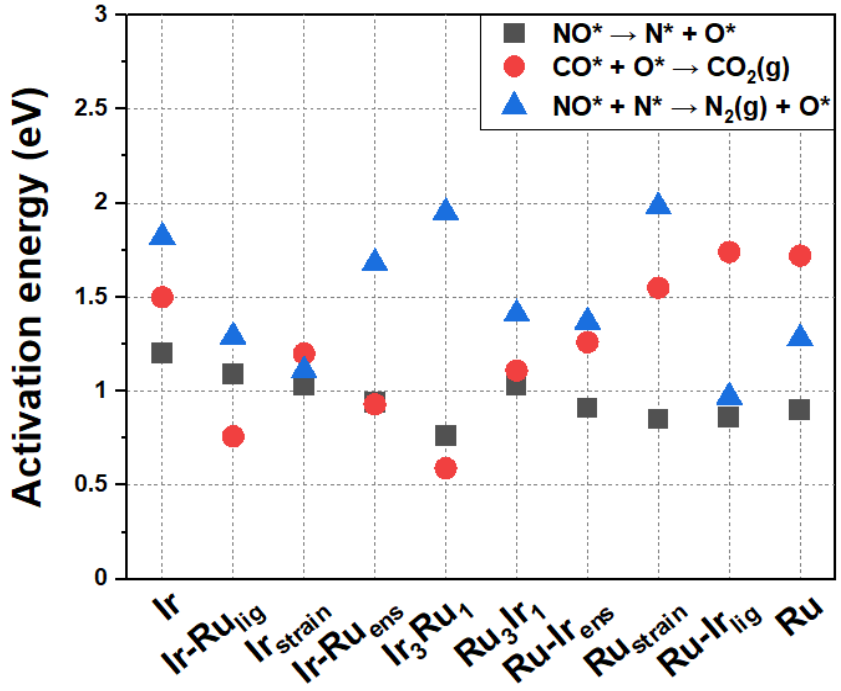

Fig. S22. Activation energy (*Ea*) trends for three important reactions among the different catalytic models without surface oxygen for different catalytic models. T = 150 °C and P = 0.1 MPa

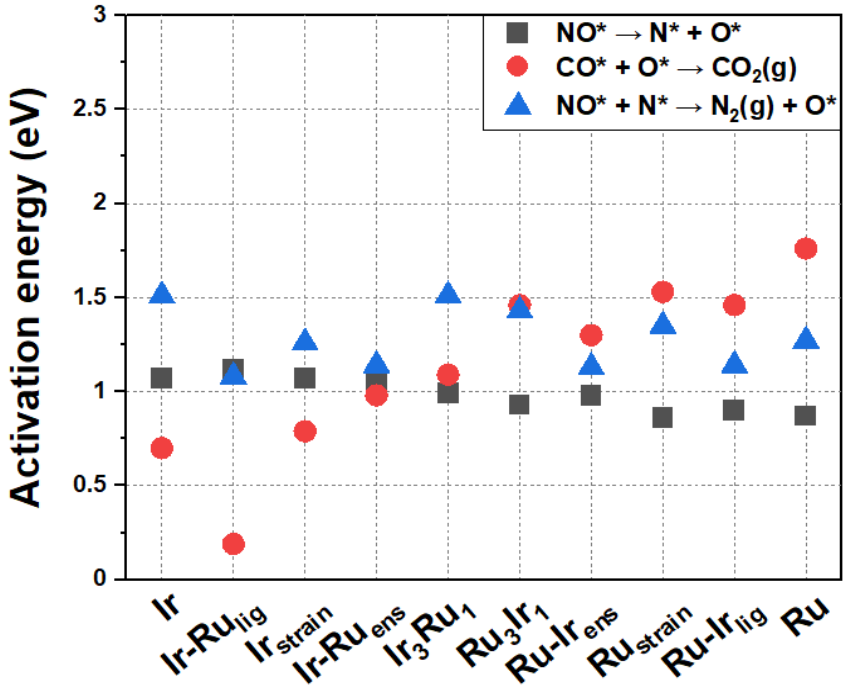

Fig. S23. Activation energy (*Ea*) trends for three important reactions among the different catalytic models with surface oxygen for different catalytic models. T = 150 °C and P = 0.1 MPa

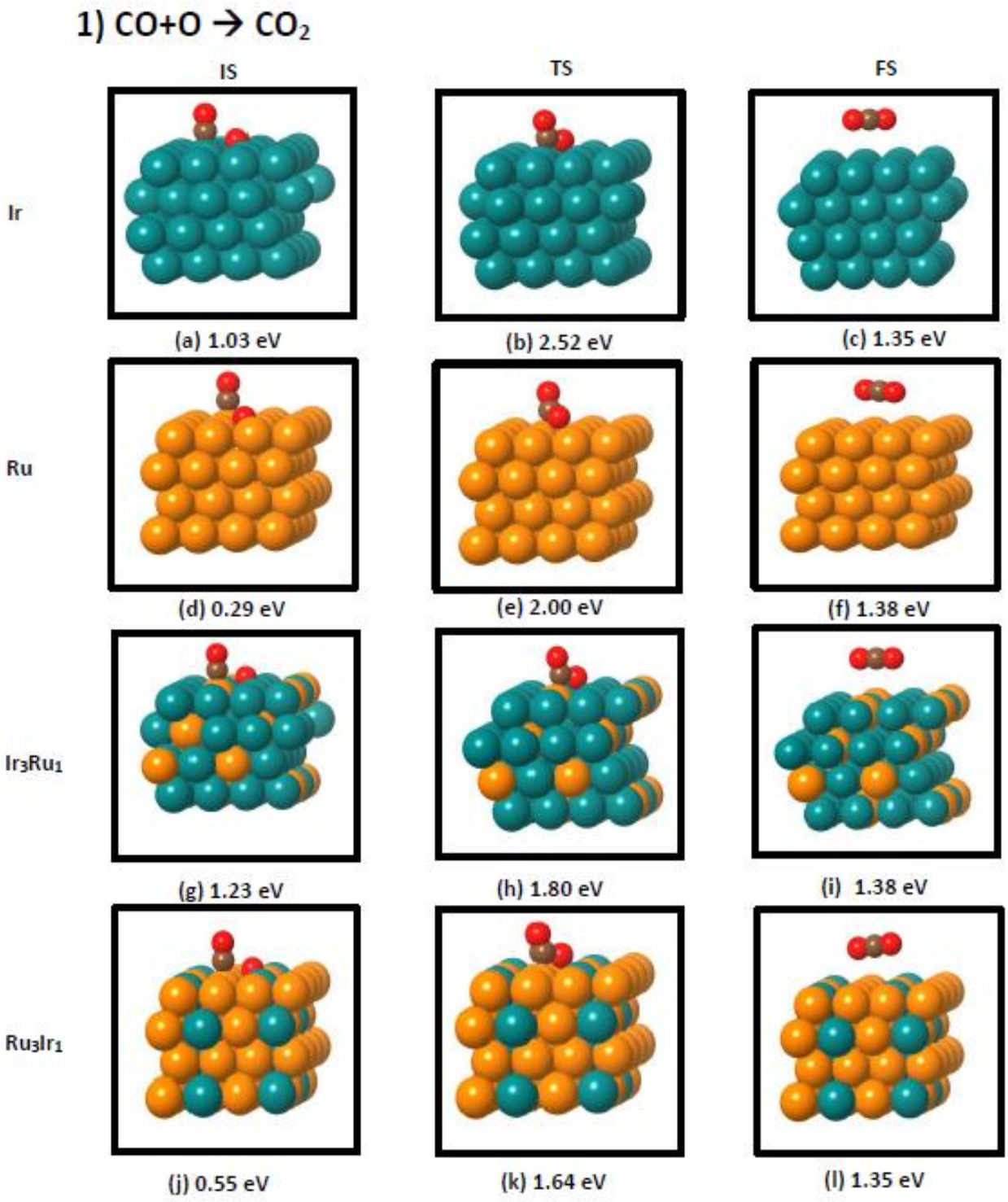

Fig. S24. Optimized geometry and gibbs free formation energy of CO oxidation reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa. To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and brown balls represent the Ir, Ru, O, and C, respectively.

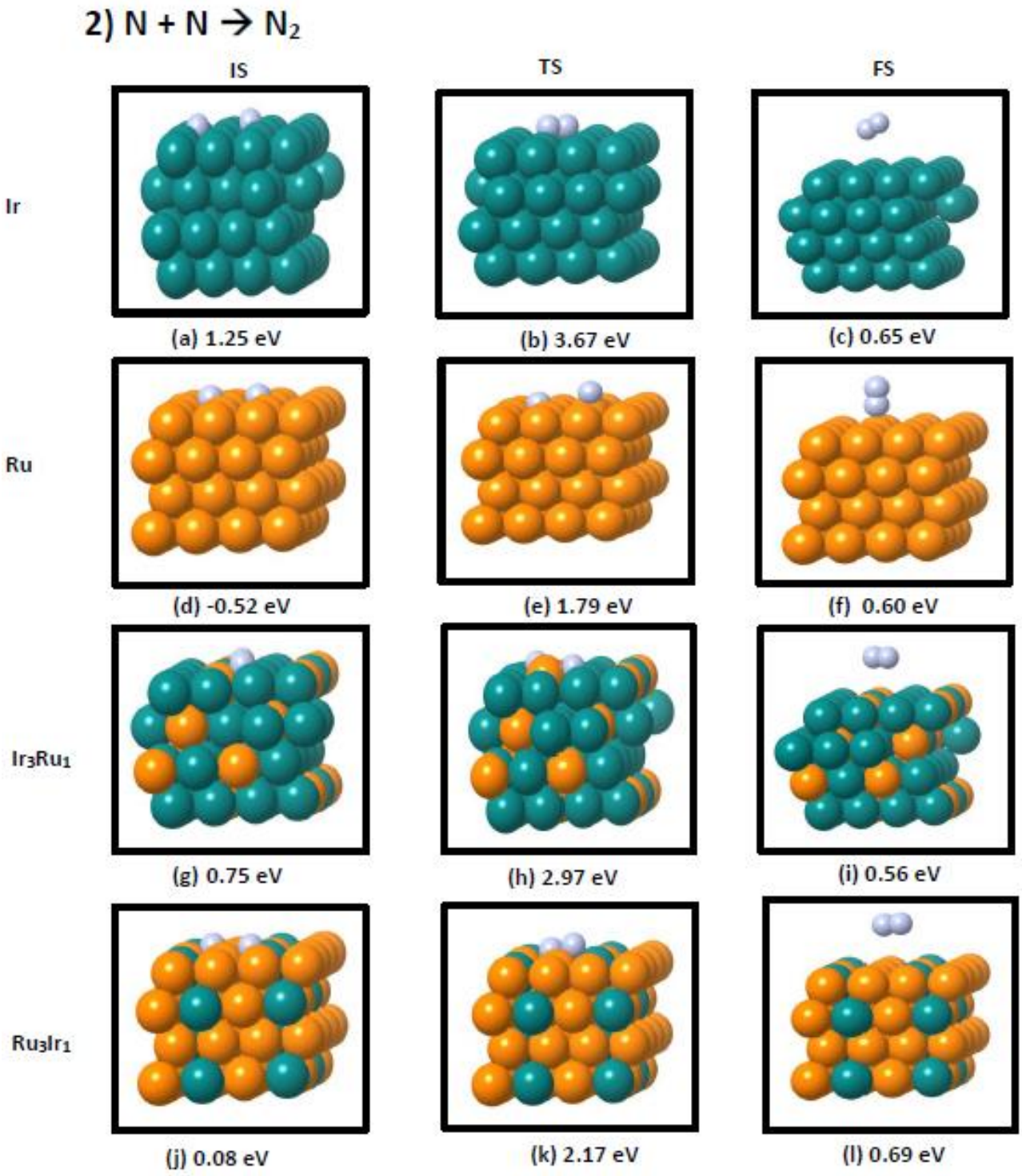

Fig. S25. Optimized geometry and gibbs free formation energy of N_2 formation via N−N recombination reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, and violet balls represent the Ir, Ru, and N, respectively.

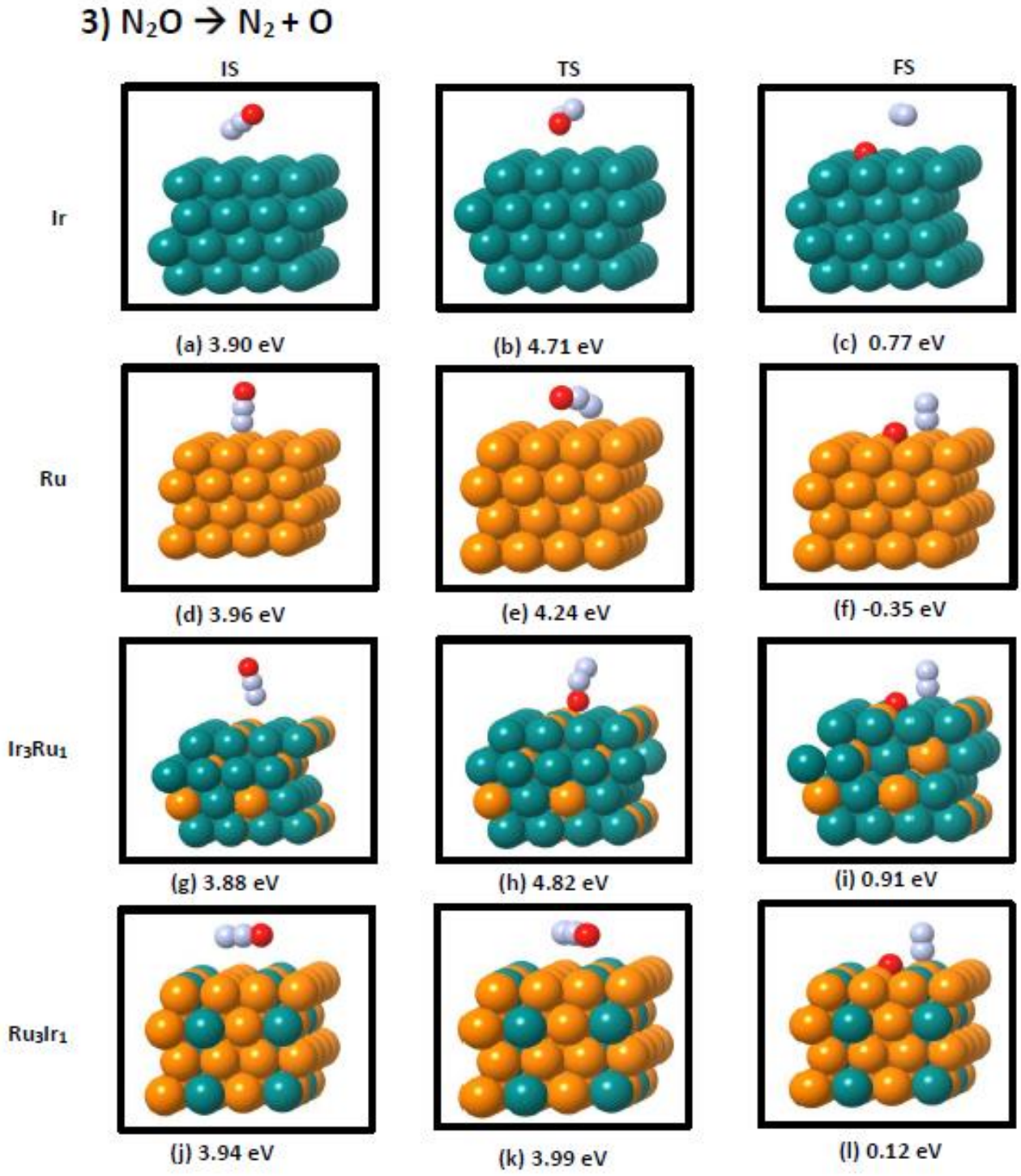

Fig. S26. Optimized geometry and gibbs free formation energy of N_2O decomposition in N_2 formation reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and violet balls represent the Ir, Ru, O, and N, respectively.

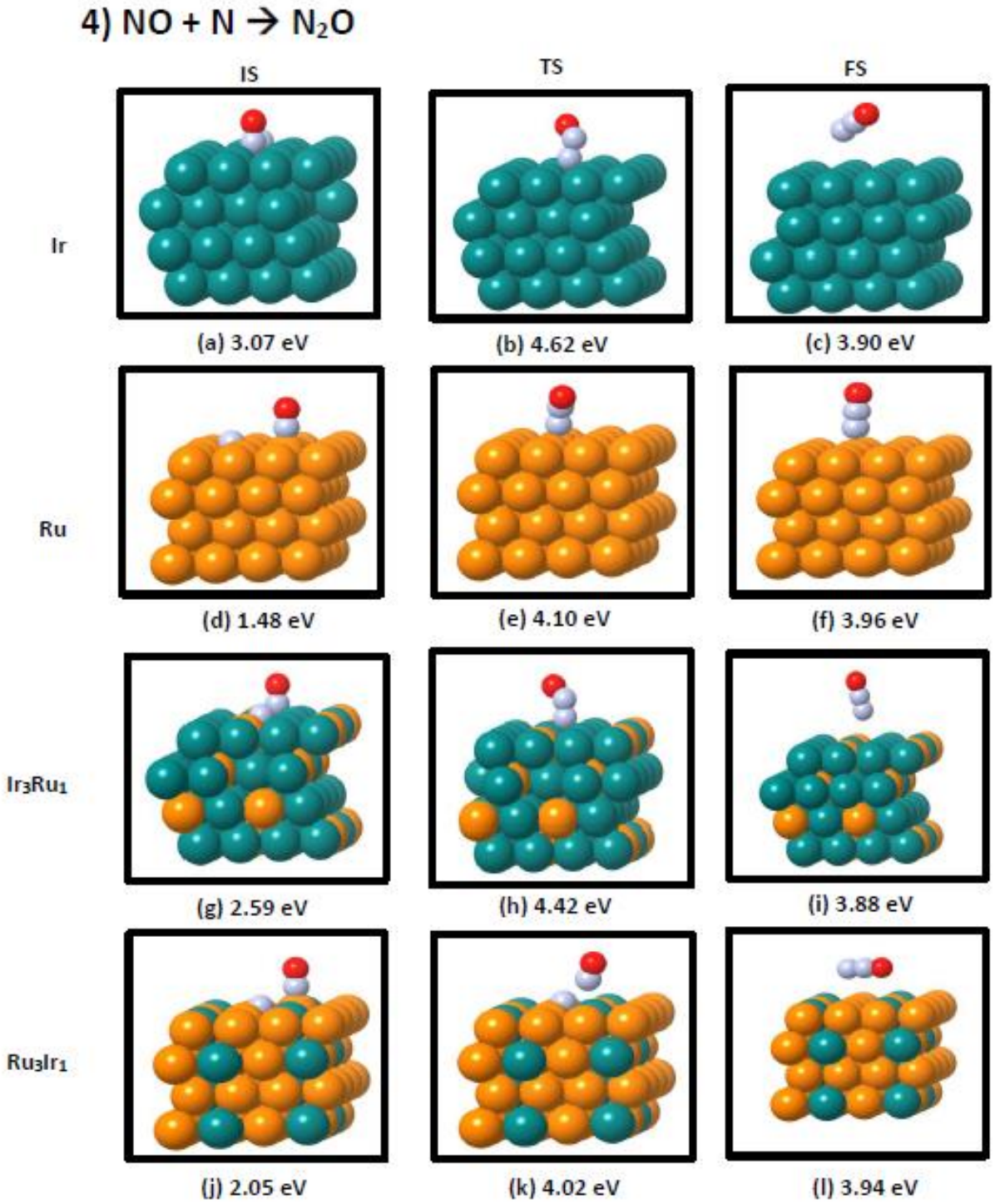

Fig. S27. Optimized geometry and gibbs free formation energy of N_2O formation reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and violet balls represent the Ir, Ru, O, and N, respectively.

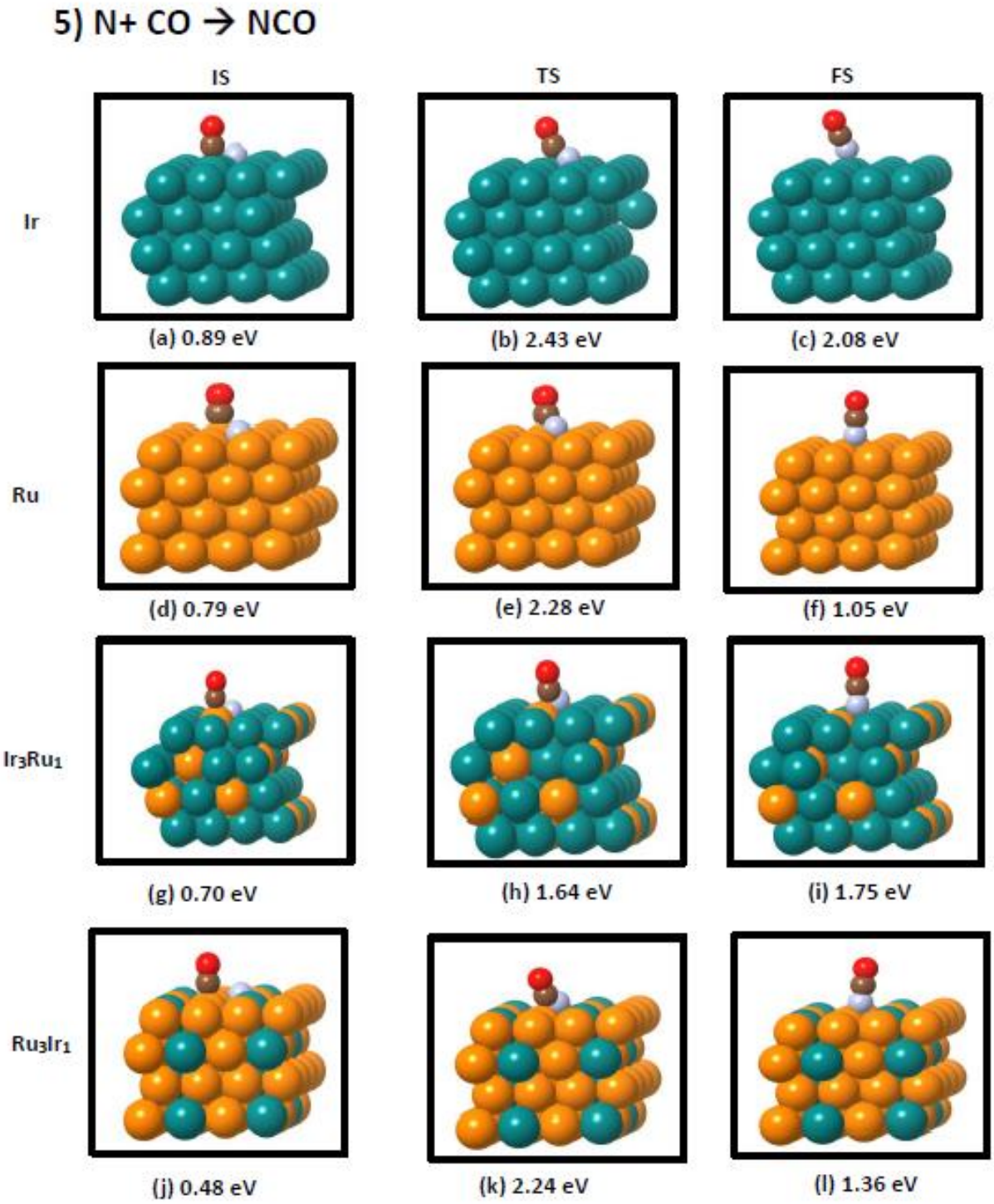

Fig. S28. Optimized geometry and gibbs free formation energy of NCO formation reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, brown, and violet balls represent the Ir, Ru, O, C, and N, respectively.

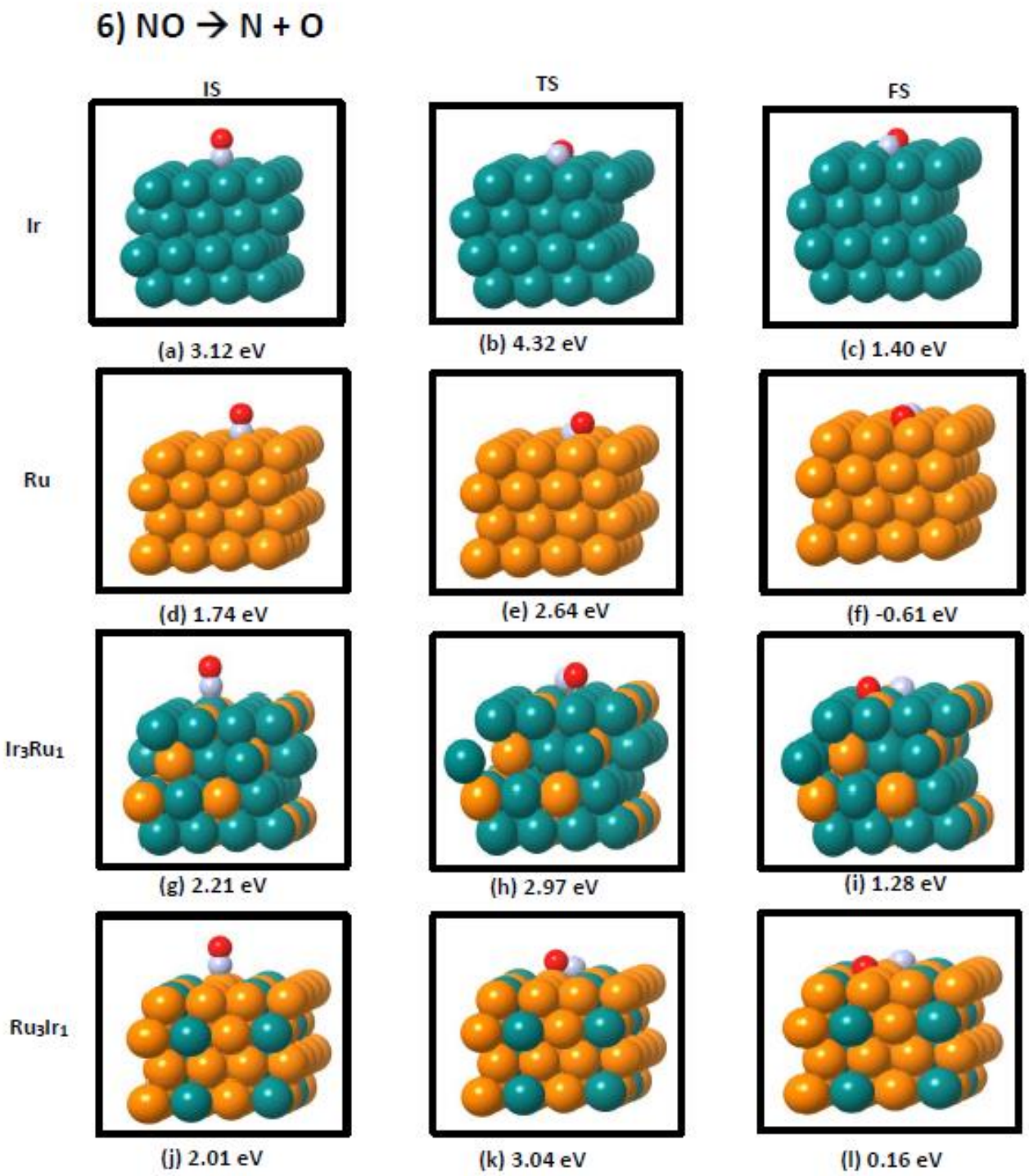

Fig. S29. Optimized geometry and gibbs free formation energy of NO decomposition reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and violet balls represent the Ir, Ru, O, and N, respectively.

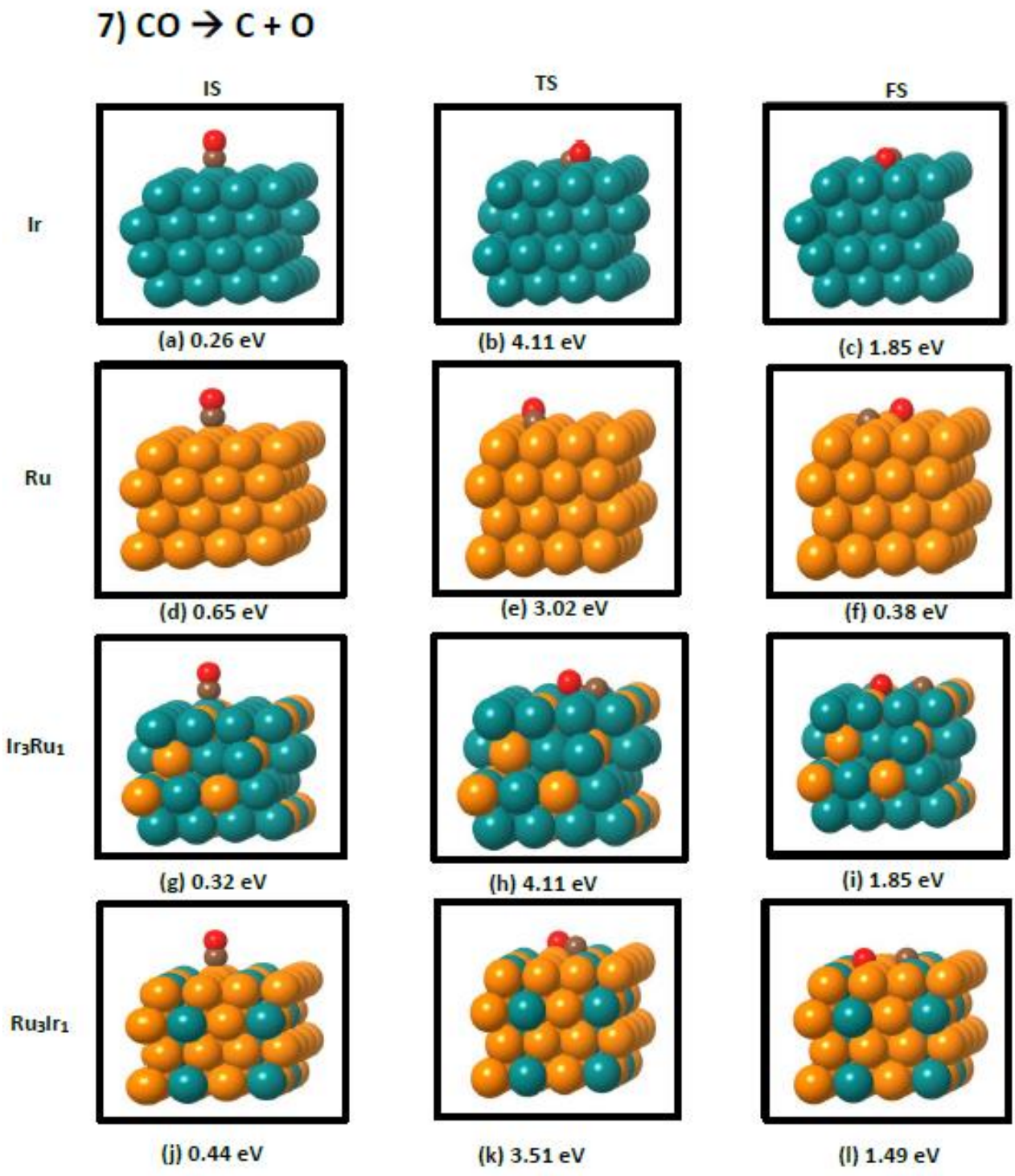

Fig. S30. Optimized geometry and gibbs free formation energy of CO decomposition reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and brown balls represent the Ir, Ru, O, and C, respectively.

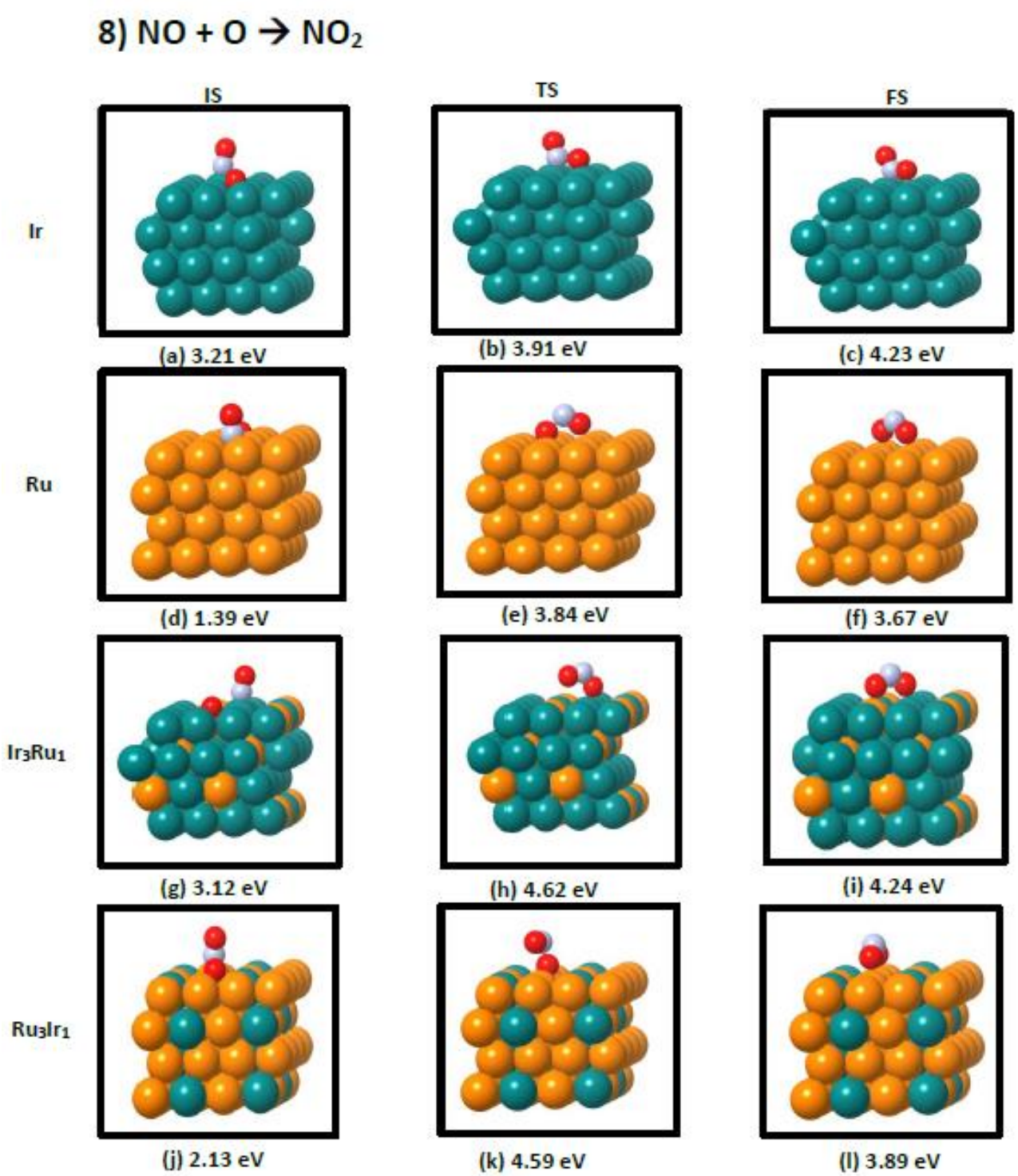

Fig. S31. Optimized geometry and gibbs free formation energy of NO_2 formation reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and violet balls represent the Ir, Ru, O, and N, respectively.

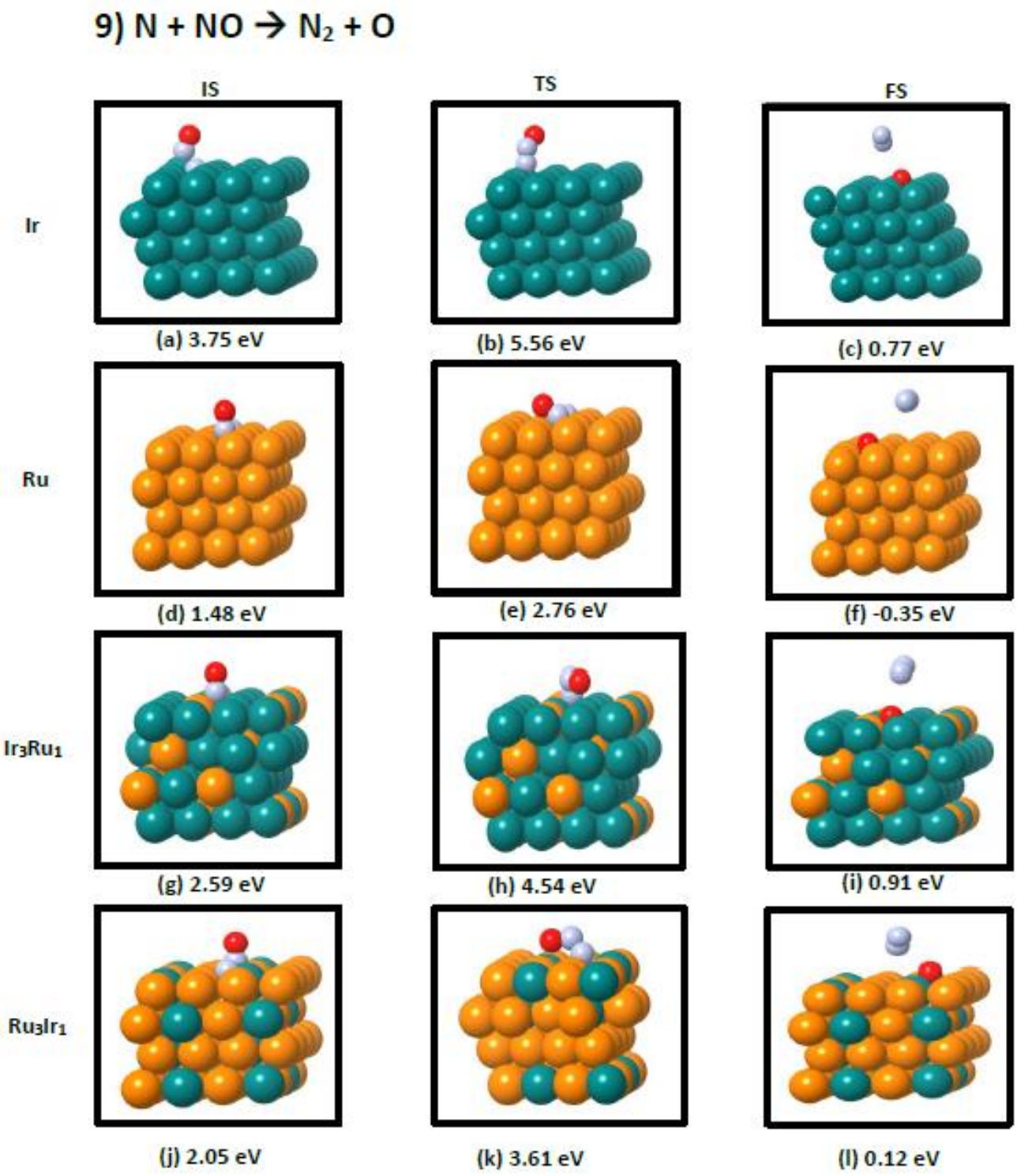

Fig. S32. Optimized geometry and gibbs free formation energy of N_2 formation reaction over Ir, Ru and their alloy surfaces at T = 200 °C and P = 0.1 MPa . To calculate the formation energy, we used H_2O, N_2, CH_4, and H_2 as standard electronic energies. Green, orange, red, and violet balls represent the Ir, Ru, O, and N, respectively.