Supporting Information

Theoretical Predicted Surface Morphology of FCC Cobalt Nanoparticles Induced by Ru Promoter

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Content

DFT Calculation.

To evaluate the stability of the adsorption structure, the total adsorption energy [$E(\mathrm{Ru}_{n/\mathrm{ads}})$] and the average adsorption energy [$E(\mathrm{Ru}_{\mathrm{ads/av}}$] of Ru_n clusters deposited on the Co substrate were defined as follows:

$$E(\mathrm{Ru}_{\mathrm{n/ads}}) = E(\mathrm{Ru}_{\mathrm{n}}/\mathrm{slab}) - E(\mathrm{slab}) - nE(\mathrm{Ru}) \quad (1)$$

$$E(\mathrm{Ru}_{\mathrm{ads/av}}) = E(\mathrm{Ru}_{n/\mathrm{ads}})/n \quad (2)$$

where n is the total number of adsorbed Ru atoms; $E(\mathrm{Ru}_n/\mathrm{slab})$, E(slab) and E(Ru) are the total energies of the Ru_n/Co system, the bare Co slab and the individual Ru atom in bulk, respectively. Negative adsorption energy corresponds to a stable adsorption structure and the more negative the value, the stronger the adsorption. Meanwhile, the adsorption strength of Co surfaces to Ru atom from gas phase can be revealed by the stepwise adsorption energy, as defined by

$$\Delta E(\mathrm{Ru}_{\mathrm{ads}}) = E(\mathrm{Ru}_{n/\mathrm{ads}}) - E(\mathrm{Ru}_{n\text{-}1/\mathrm{ads}}) \quad (3)$$

where a larger (more negative) stepwise adsorption energy represents a stronger Ru_n adsorption by capturing one Ru atom from gas phase to the $\mathrm{Ru}_{n\text{-}1}$ cluster. For Ru_n clusters on the surface, both n-aggregated Ru clusters and n-dispersed Ru atoms might be stable thermodynamically. To better understand the aggregation behavior of surface Ru_n from isolated Ru atoms, the average aggregation energy [$E_{\mathrm{agg}}(\mathrm{Ru}_{\mathrm{ads}})$] is defined by

$$E_{\mathrm{agg}}(\mathrm{Ru}_{\mathrm{ads}}) = [E(\mathrm{Ru}_{n/\mathrm{ads}}) - nE(\mathrm{Ru}_{\mathrm{ads}})]/n \quad (4)$$

Based on the most preferable adsorption configurations of Ru_n cluster on Co surface, we further investigate the growth process of Ru_n cluster on Co surfaces by the growth energy [$E_{\mathrm{growth}}(\mathrm{Ru}_{\mathrm{ads}})$], as defined by

$$E_{\mathrm{growth}}(\mathrm{Ru}_{\mathrm{ads}}) = E(\mathrm{Ru}_{n/\mathrm{ads}}) - E(\mathrm{Ru}_{n\text{-}1/\mathrm{ads}}) - E(\mathrm{Ru}_{\mathrm{ads}}) \quad (5)$$

here, $E(\mathrm{Ru}_{\mathrm{ads}})$ is the energy that adsorbs a Ru atom to the Co slab. The growth energy is the energy gaining an adsorbed single atom with a $\mathrm{Ru}_{n\text{-}1}$ cluster to form a Ru_n cluster. Negative values of $E_{\mathrm{agg}}(\mathrm{Ru}_{\mathrm{ads}})$ and $E_{\mathrm{growth}}(\mathrm{Ru}_{\mathrm{ads}})$ denote that the aggregation and growth of Ru_n cluster are exothermic and thermodynamically favorable.

"During the growth of Ru_n cluster, the lateral interaction between the adsorbed Ru atoms and the interaction between the cluster/substrate is important to examine the bonding strength of Ru_n

cluster. The lateral interaction energy [E_{int}(Ru$_n$)] between the Ru atoms within the adsorbed Ru$_n$ clusters was calculated as

$$E_{int}(\mathrm{Ru}_n) = E(\mathrm{Ru}_{n/\mathrm{ads}}) - nE(\mathrm{Ru}_{\mathrm{ads}}) \quad (6)$$

where n is the total number of adsorbed Ru atoms. E(Ru$_{n/\mathrm{ads}}$) and E(Ru$_{\mathrm{ads}}$) are the energies of the adsorbed Ru$_n$ cluster and the single adsorbed Ru atom, respectively. The total interaction energy [E_{int}(Ru$_n$/slab)] and the average interaction energy [$E_{int/av}$(Ru$_n$/slab)] between Ru$_n$ cluster and Co slab were calculated as follows

$$E_{int}(\mathrm{Ru}_n/\mathrm{slab}) = E(\mathrm{Ru}_n/\mathrm{slab}) - E(\mathrm{Ru}_n') - E(\mathrm{slab}') \quad (7)$$

$$E_{int/\mathrm{av}}(\mathrm{Ru}_n/\mathrm{slab}) = [E(\mathrm{Ru}_n/\mathrm{slab}) - E(\mathrm{Ru}_n') - E(\mathrm{slab}')]/n \quad (8)$$

where E(Ru$_n$/slab), E(Ru$_n'$) and E(slab′) are the total energies of the Ru$_n$/Co system, the deformed Ru$_n$ clusters and Co slab after Ru$_n$ cluster adsorbed on the Co surface, respectively."

The surface free energy related with the experimental conditions can make it accessible to investigate the morphology evolution on the basis of the Wulff construction. The surface energy $\gamma^0_{\mathrm{Co}(hkl)}$ for a clean Co(hkl) surface is defined as the energy per unit area required for forming the surface relative to the bulk and is determined by

$$\gamma^0_{\mathrm{Co}(hkl)} = [E_{\mathrm{Co}(hkl)} - n_{\mathrm{Co}}E_{\mathrm{Co}(bulk)}]/2\mathrm{A} \quad (9)$$

where $E_{\mathrm{Co}(hlk)}$ and $E_{\mathrm{Co}(bulk)}$ are the total energies of Co(hkl) surface and one bulk Co unit, respectively. n_{Co} is the number of Co bulk units in the system, and A is the surface area exposed by the slab for a given Co(hkl) surface. The adsorption of surface species would result in the change of surface energy, the surface free energy $\gamma^{\mathrm{ads}}_{\mathrm{Co}(hkl)}$ for the Co surface model with different Ru coverage defined as

$$\gamma^{\mathrm{ads}}_{\mathrm{Co}(hkl)} = \gamma^0_{\mathrm{Co}(hkl)} + [n_{\mathrm{Ru}}E(\mathrm{Ru}_{\mathrm{ads/av}})]/\mathrm{A} \quad (10)$$

where n_{Ru} is the number of Ru atoms on the substrate, $[n_{\mathrm{Ru}}E(\mathrm{Ru}_{\mathrm{ads/av}})]/\mathrm{A}$ represents the change of surface energy caused by Ru adsorption.

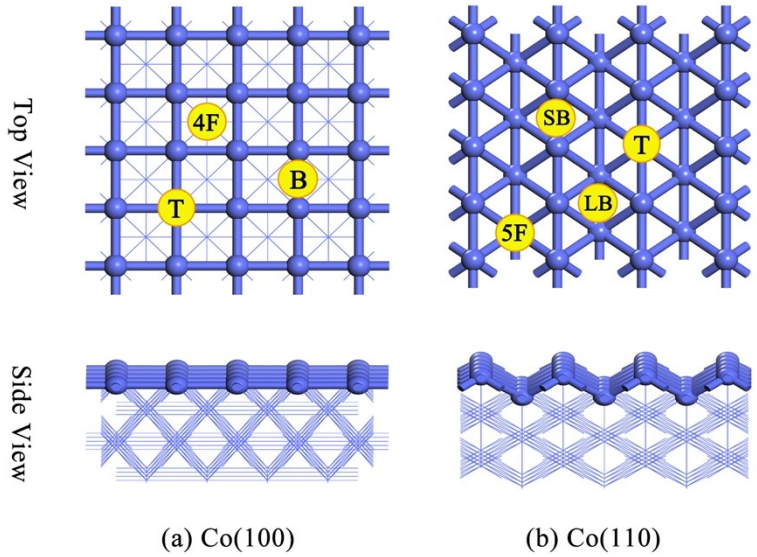
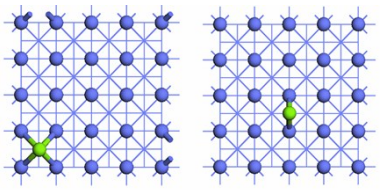


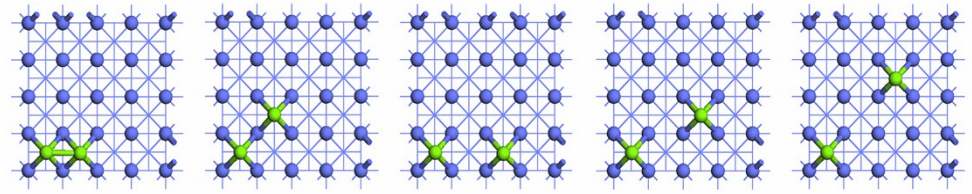
Figure S1. The optimized structures from top and side views of (a) Co(100) and (b) Co(110) surfaces as well as the possible adsorption sites: fourfold site (4F), top site (T), bridge sites (B, LB, SB) and fivefold site (5F). The Co atom is shown as blue balls.

Co(100)-Ru_1



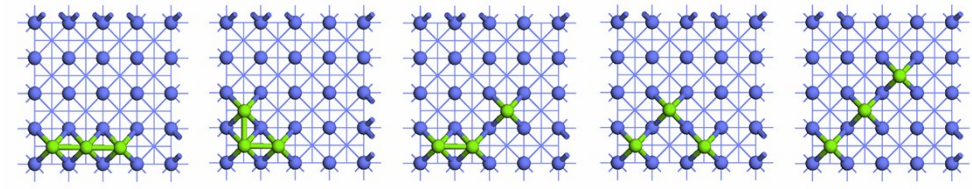
1(-5.26) 2(-4.47)

Co(100)-Ru_2

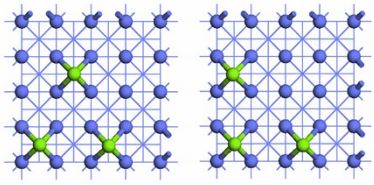


1(-10.76) 2(-10.54) 3(-10.52) 4(-10.52) 5(-10.51)

Co(100)-Ru_3

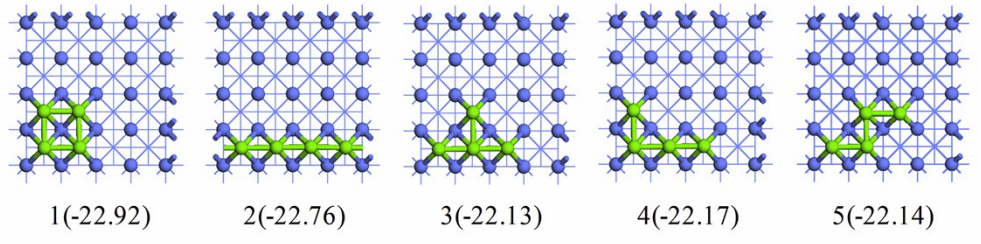


1(-16.51) 2(-16.40) 3(-16.12) 4(-15.83) 5(-15.83)

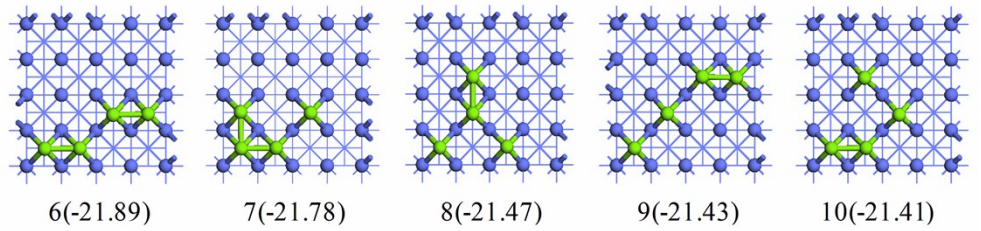


6(-15.78) 7(-15.78)

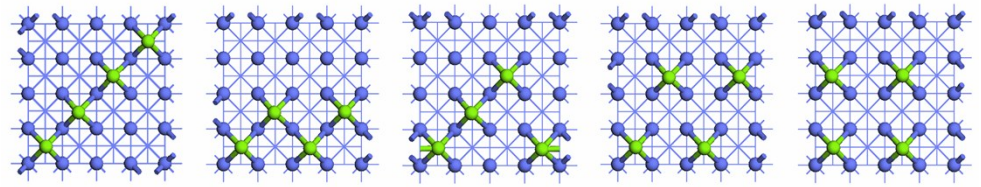
Co(100)-Ru_4



1(-22.92) 2(-22.76) 3(-22.13) 4(-22.17) 5(-22.14)

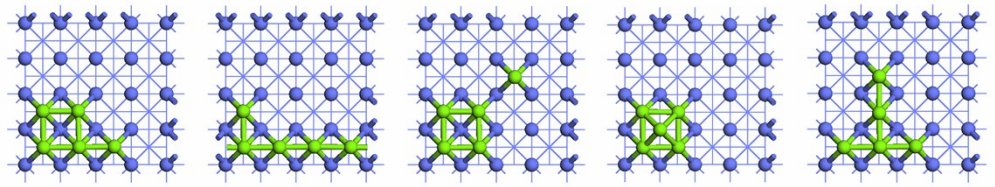


6(-21.89) 7(-21.78) 8(-21.47) 9(-21.43) 10(-21.41)

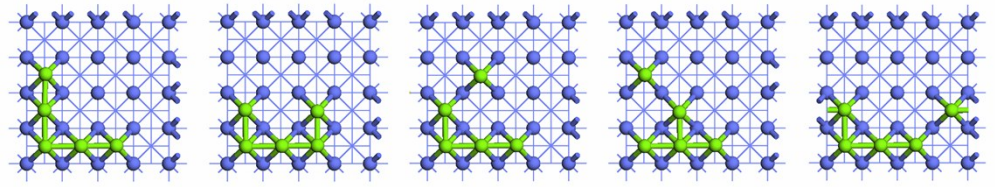


11(-21.19) 12(-21.17) 13(-21.14) 14(-21.04) 15(-21.00)

Co(100)-Ru_5

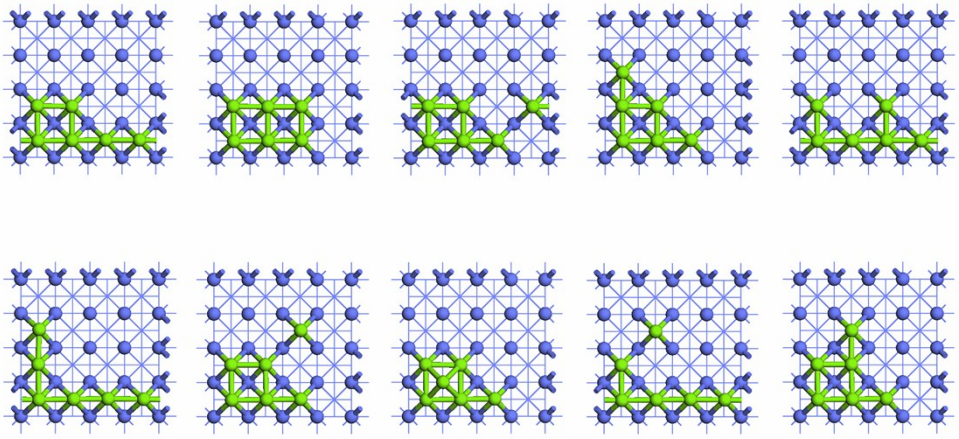


1(-28.64) 2(-28.46) 3(-28.31) 4(-28.16) 5(-27.91)



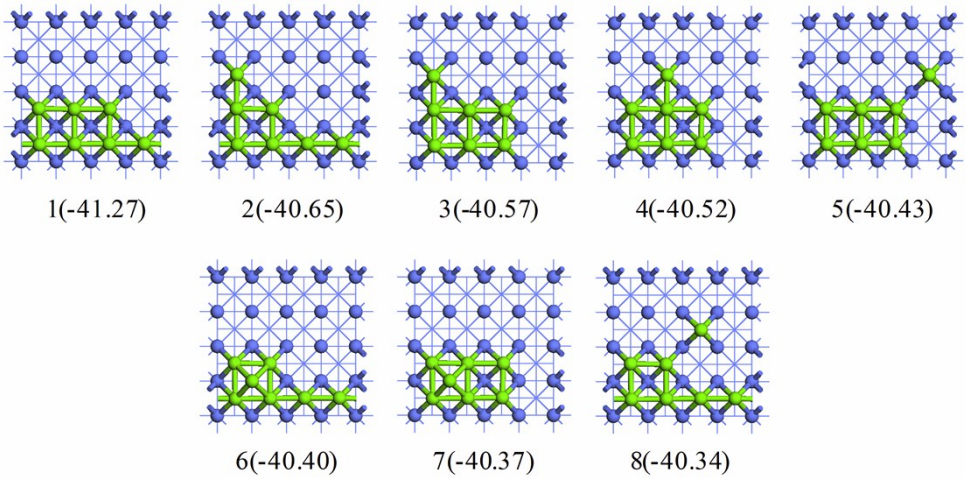
6(-27.90) 7(-27.85) 8(-27.53) 9(-27.37) 10(-26.86)

Co(100)-Ru_6



6(-34.18) 7(-34.01) 8(-33.98) 9(-33.81) 10(-33.35)

Co(100)-Ru_7



1(-41.27) 2(-40.65) 3(-40.57) 4(-40.52) 5(-40.43)

6(-40.40) 7(-40.37) 8(-40.34)

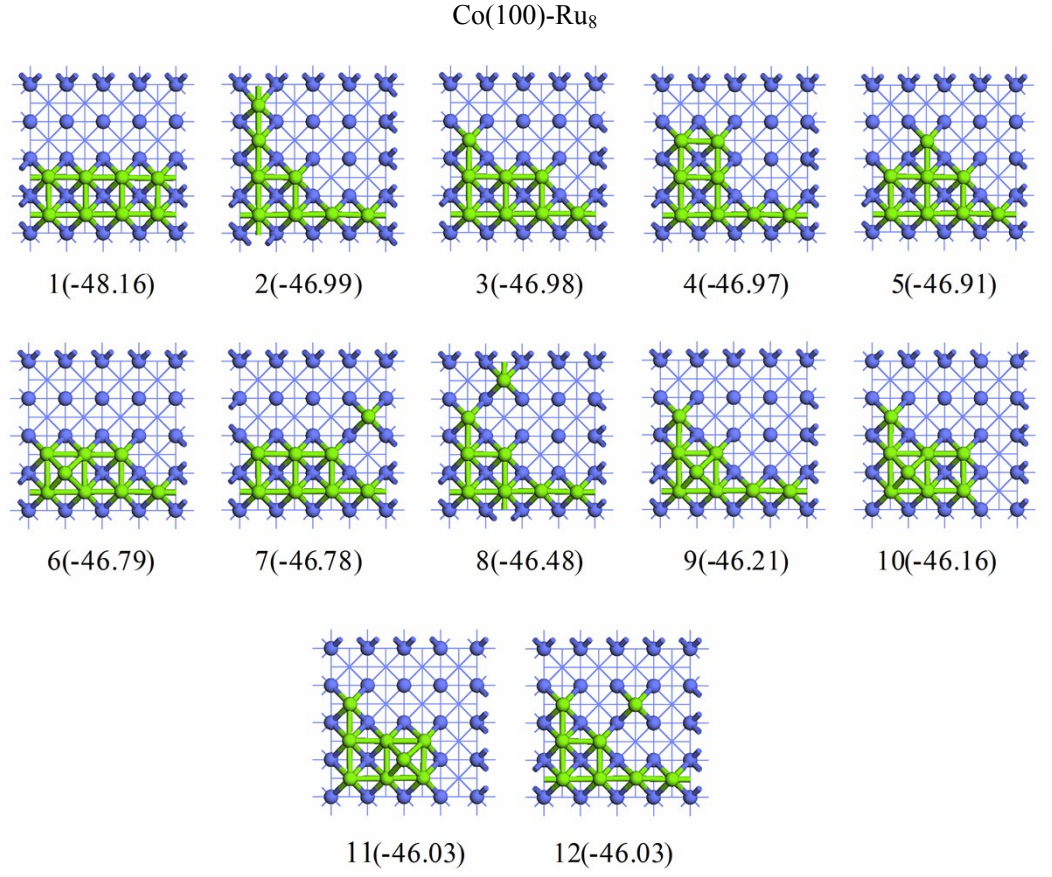
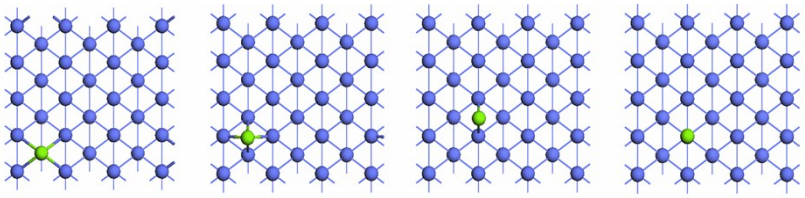


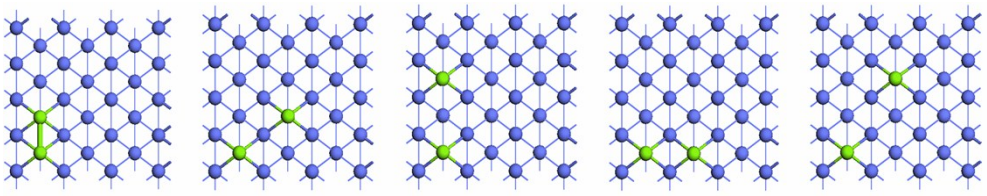
Figure S2. Various structures and adsorption energies for Ru_n (n = 1-8) on the 4×4 Co(100) surface (adsorption energy in eV). The blue and green balls represent Co atoms and Ru atoms, respectively.

Co(110)-Ru_1



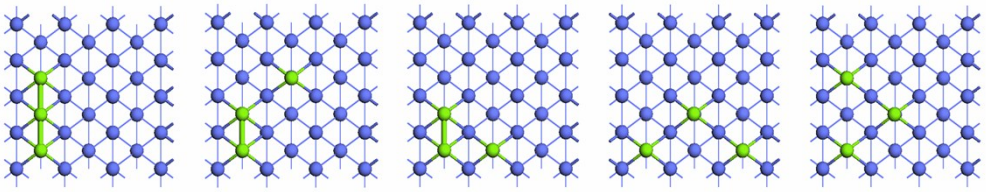
1(-5.42) 2(-5.19) 3(-3.78) 4(-2.45)

Co(110)-Ru_2

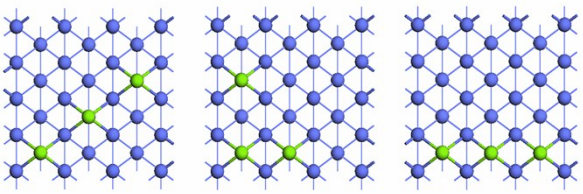


1(-11.45) 2(-10.87) 3(-10.84) 4(-10.84) 5(-10.81)

Co(110)-Ru_3

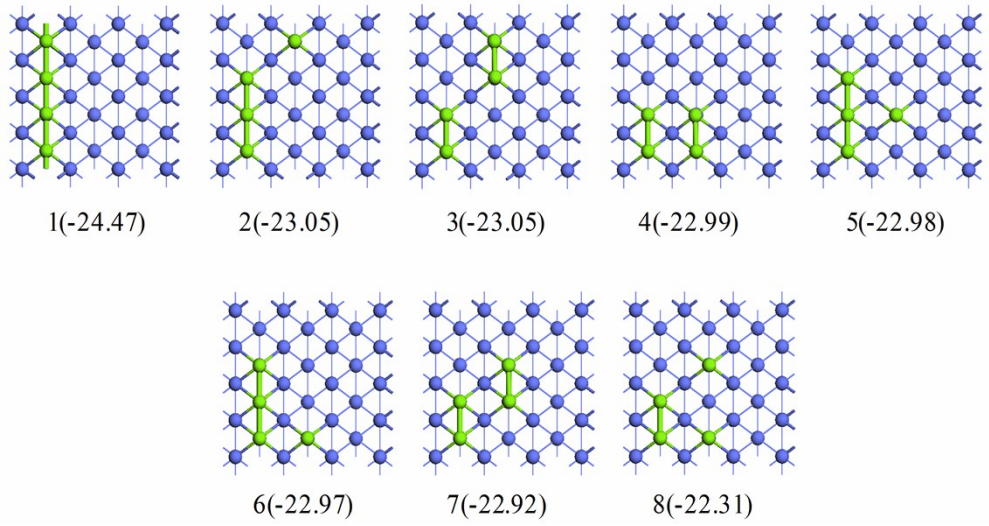


1(-17.56) 2(-16.89) 3(-16.87) 4(-16.35) 5(-16.31)

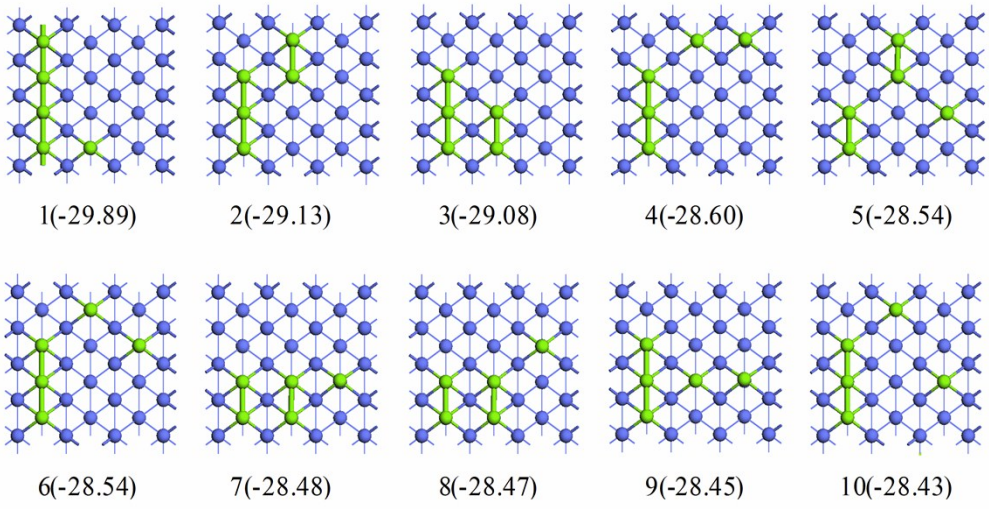


6(-16.30) 7(-16.23) 8(-14.71)

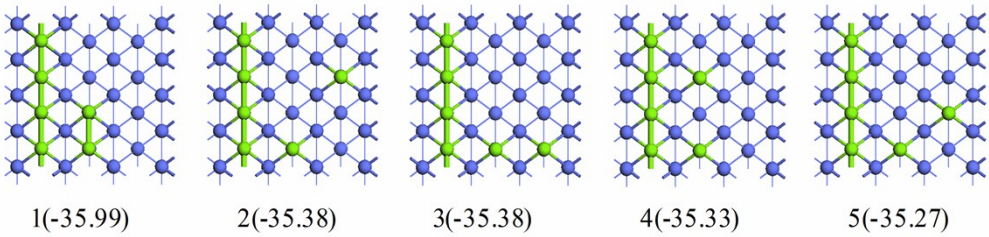
Co(110)-Ru_4



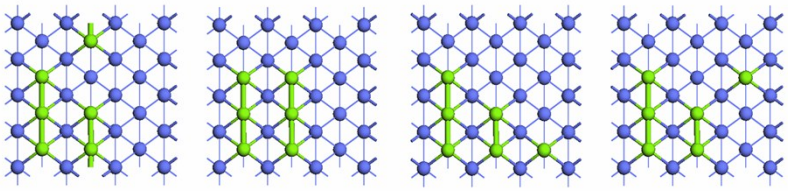
Co(110)-Ru_5



Co(110)-Ru_6

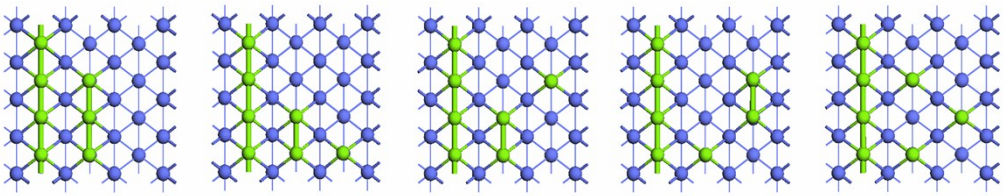


1(-35.99) 2(-35.38) 3(-35.38) 4(-35.33) 5(-35.27)

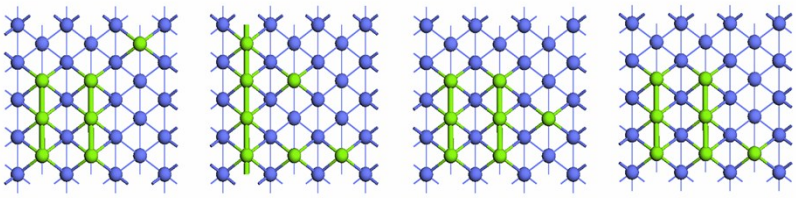


6(-35.26) 7(-35.21) 8(-34.56) 9(-34.54)

Co(110)-Ru_7



1(-42.11) 2(-41.47) 3(-41.46) 4(-41.46) 5(-40.86)



6(-40.86) 7(-40.77) 8(-40.67) 9(-40.67)

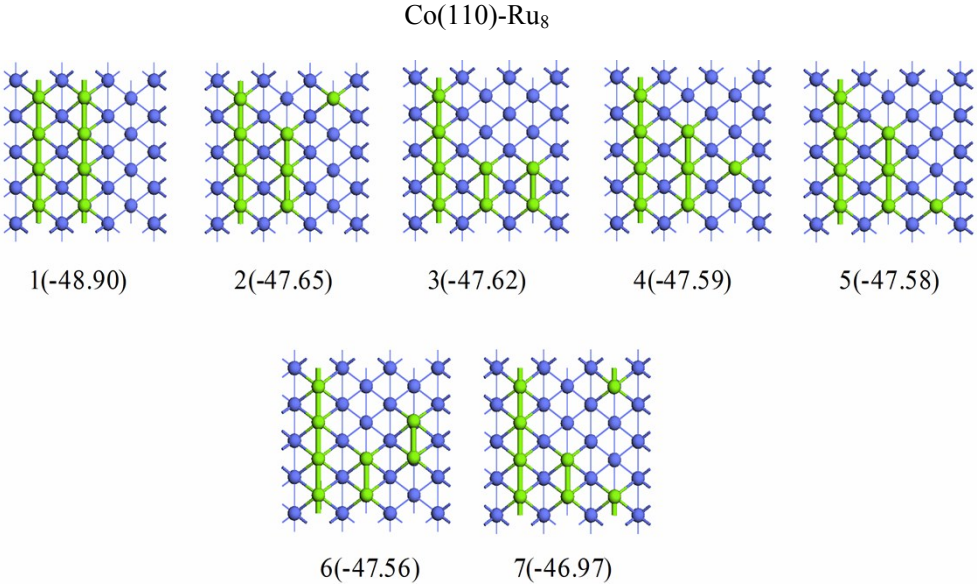


Figure S3. Various structures and adsorption energies for Ru_n (n = 1-8) on the 3×4 Co(110) surface (adsorption energy in eV).The blue and light green balls represent Co atoms and Ru atoms, respectively.

Co(100)-Ru_{11}

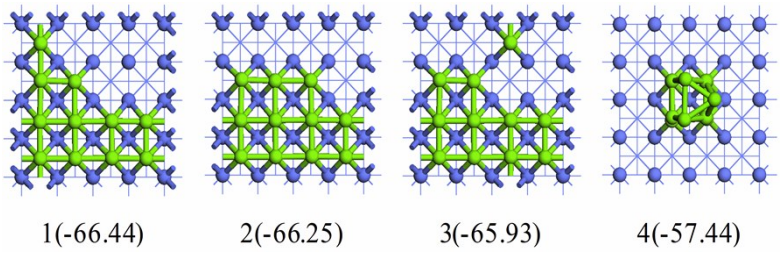


Figure S4. Various structures and adsorption energies for Ru_{11} on the Co(100) surface (adsorption energy in eV).

Co(110)-Ru_{11}

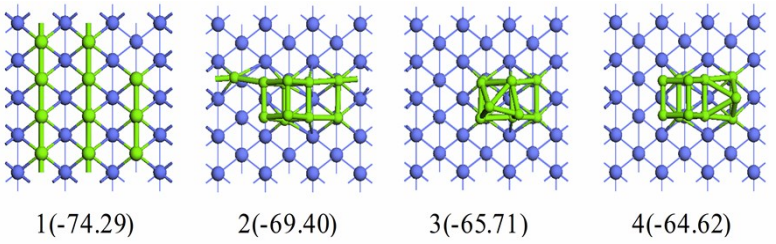


Figure S5. Various structures and adsorption energies for Ru_{11} on the Co(110) surface (adsorption energy in eV).

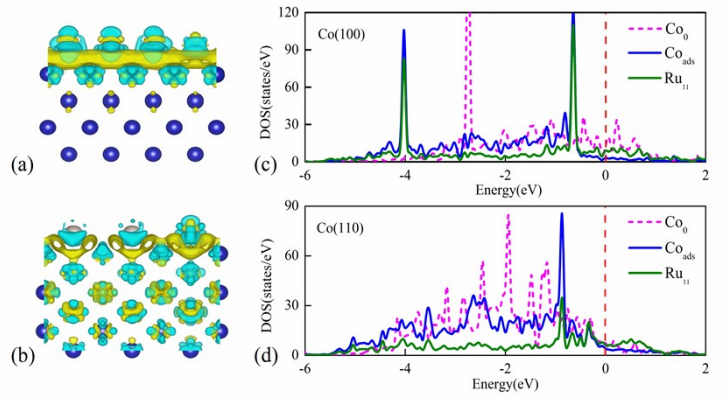
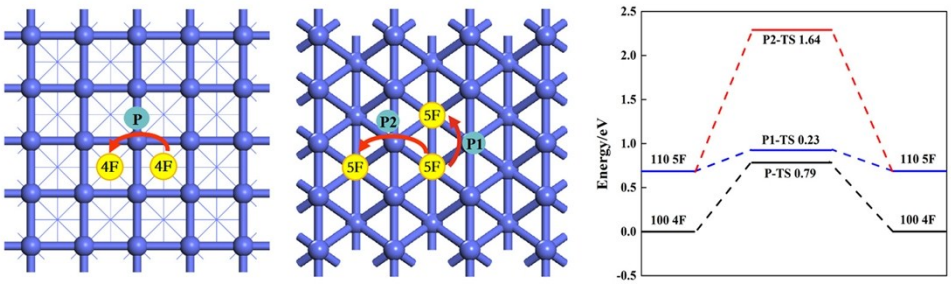


Figure S6. (a) and (b): Differential charge density distribution for Ru_{11} clusters on Co(100) and Co(110) surfaces. The yellow and green regions represent electronic charge accumulation and depletion, respectively. (c) and (d): Density of states (DOS) projected onto the d orbitals of adsorbed Ru_{11} cluster (green line) and the surface Co atoms (pink dashed line denotes clean Co surfaces and blue solid line denotes the Co surfaces adsorbed Ru_{11}) of the Co(100) and Co(110) surfaces. The zero of energy is set at the Fermi level shown by dashed red lines.

The electron transfer from Co surfaces can be quantified by Bader charge analysis and visualized from the differential charge density (Figure 6a and 6b). The result shows that the Co surfaces are positively charged and the adsorbed Ru_{11} cluster is negatively charged by 0.10 |e| on Co(100) surface and 0.14 |e| on Co(110) surface per Ru atom. Such unidirectional charge transfer between substrate and adsorbate is in agreement with the fact that electrons transfer from less electronegative element (1.88 for Co) to more electronegative element (2.28 for Pt, 2.20 for Ru). The projected d-orbital density of states of adsorbed Ru_{11} cluster and the surface Co atoms are presented in Figure 6c and 6d. Both the d orbitals of Co(100) and Co(110) surfaces shifted towards the lower energy after Ru_n adsorption, leading to the electronic loss of Co surfaces. In addition, there is a stronger d-orbital mixing near Fermi level between the adsorbed Ru_{11} cluster on Co(110) surface than that of Co(100) surface, implying the stronger interaction between the Co(110) surface and Ru_{11} cluster, coincides with the trend of adsorption energies.



(a) Co(100) (b) Co(110) (c) Diffusion pathways

Figure S7. Diffusion pathways of a single Ru atom on the Co(100) and Co(110) surfaces.

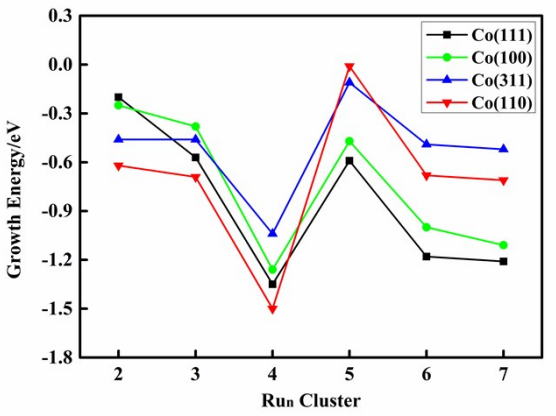


Figure S8. The growth energy with respect to the size of Ru_n cluster on fcc Co surfaces.

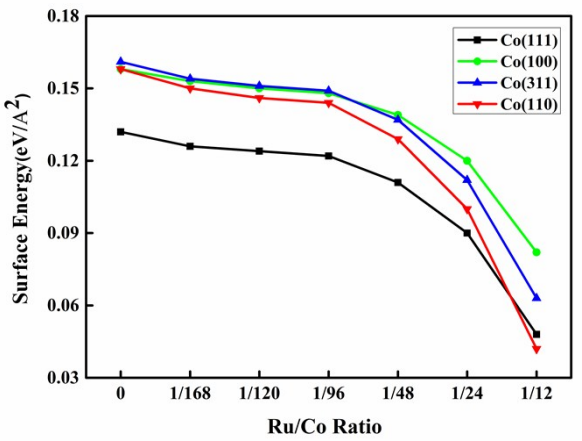


Figure S9. Surface energies of four FCC Co surfaces as functions of surface Ru/Co atomic ratio.