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Supplementary Information

The Effect of γ-Al_2O_3 Surface Hydroxylation on the Stability and Nucleation of Ni for Ni/γ-Al_2O_3 Catalyst: A Theoretical Study

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1. Adsorption of Ni_n(n=1–7) Clusters on the Dehydrated γ-Al_2O_3(110) Surface

Ni_n(n=1–7) cluster is placed on a large number of well-defined adsorption sites that are available on the dehydrated γ-Al_2O_3(110) surface, and the most stable adsorption configurations are obtained, as shown in Figure S1.

For the single Ni atom, the Ni atom prefers to bind to O_{2c} and Al_{4c} sites on the dehydrated (110) surface, and forms the Ni–O_{2c-1} (1.815 Å), Ni–O_{2c-2} (1.828 Å) and Ni–Al_{4c} (2.510 Å) bonds, as shown in Figure S1(a). The adsorption energy and the Ni_1-support interaction energy are -269.9 and -359.4 kJ·mol^{-1}, respectively. 0.004 e are transferred to the single Ni atom from support surface. The Ni_1-support interaction energy makes a major contribution to the adsorption energy. The adsorption of the single Ni atom can lead to a strong surface deformation (89.5 kJ·mol^{-1}), and the most stable adsorption configuration of the single Ni atom on the dehydrated (110) surface is in agreement with that of the single Cu atom[1] and Rh atom.[2]

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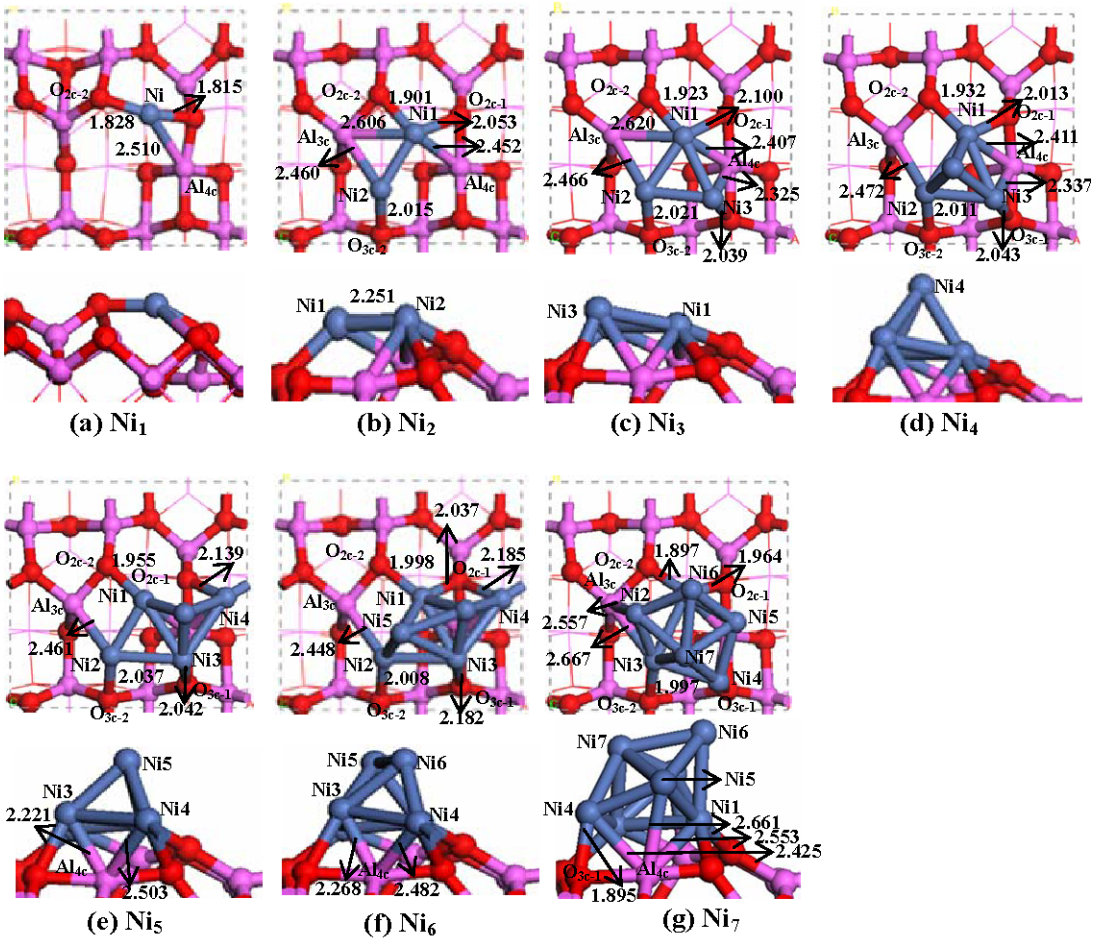

Figure S1. The most stable adsorption configuration of Ni_n(n=1–7) cluster on the dehydrated γ-Al_2O_3(110) surface. Bond lengths are in Å. Pink, red, blue and white balls stand for Al, O, Ni and H atoms, respectively.

For Ni_2 cluster, the most stable adsorption configuration, as shown in Figure S1(b), shows that Ni_2 cluster prefers to adsorb on the dehydrated γ-Al_2O_3(110) surface with the Ni_2 cluster parallel to the surface plane, one Ni atom binds to the surface O_{2c}, Al_{3c} and Al_{4c} sites, and the other binds to the surface $O_{3c\text{-}2}$ and Al_{3c} sites, which is similar to those for Cu_2 cluster[1] and Rh_2 cluster.[2] Upon adsorption, the Ni–Ni bond length in the adsorbed Ni_2 cluster is elongated to 2.251 Å from 2.163 Å in the isolated Ni_2 cluster. The bond lengths of Ni1–$O_{2c\text{-}1}$, Ni1–$O_{2c\text{-}2}$, Ni1–Al_{3c}, Ni1–Al_{4c}, Ni2–$O_{3c\text{-}2}$ and Ni2–Al_{3c} are 2.053, 1.901, 2.606, 2.452, 2.015 and 2.460 Å, respectively. The adsorption energy of Ni_2 cluster and the Ni_2-support interaction energy are -408.8 and -540.7

kJ·mol^{-1}, respectively, which are smaller than those of the single Ni atom (-269.9 and -359.4 kJ·mol^{-1}). 0.043 *e* are transferred to support surface from Ni_2 cluster. The decrease of Ni_2-support interaction energy is responsible for the decrease of the adsorption energy. The surface deformation (128.4 kJ·mol^{-1}) is also stronger than that in the single Ni atom (89.5 kJ·mol^{-1}). Meanwhile, the Ni_2 cluster deformation energy (3.5 kJ·mol^{-1}) has a negligible contribution to the adsorption energy.

For Ni_3 cluster, the most stable adsorption configuration is presented in Figure S1(c). In this configuration, the plane of Ni_3 cluster lies aslant on the surface, and forms two Ni1–O_{2c} bonds (2.100 and 1.923 Å), two Ni–O_{3c} bond (2.021 and 2.039 Å), two Ni–Al_{3c} bond (2.620 and 2.466 Å), and two Ni–Al_{4c} bonds (2.407 and 2.325 Å). The adsorption energy of Ni_3 cluster (-483.6 kJ·mol^{-1}) is smaller than that of Ni_2 cluster (-408.8 kJ·mol^{-1}). 0.015 *e* are transferred to Ni_3 cluster from support surface. The Ni_3-support interaction energy is obviously decreased to -623.2 kJ·mol^{-1} from -540.7 kJ·mol^{-1} of Ni_2 cluster, which is the major component of the adsorption energy. The cluster and surface deformation energies are 6.7 and 132.9 kJ·mol^{-1}, respectively, in which the Ni_3 cluster deformation still has few contributions to the adsorption energy.

For Ni_4 cluster, as shown in Figure S1(d), the most stable adsorption configuration of Ni_4 cluster is similar to the adsorption of Cu_4 cluster on the dehydrated γ-Al_2O_3(110) surface.[3] In this configuration, Ni_4 cluster interacts with the surface through three Ni atoms (Ni1, Ni2 and Ni3), and Ni4 atom is located at the top vertex away from the support surface. The adsorption leads to the formation of two Ni1–O_{2c} bonds (2.013 and 1.932 Å), two Ni–O_{3c} bonds (2.011 and 2.043 Å), Ni–Al_{3c} bond (2.472 Å), and two Ni–Al_{4c} bonds (2.411 and 2.337 Å). The adsorption also causes a strong surface deformation (145.4 kJ·mol^{-1}), however, the Ni_4 cluster deformation (6.0 kJ·mol^{-1})

is negligible. 0.076 *e* are transferred to support surface from Ni_4 cluster. The Ni_4-support interaction energy is -730.3 kJ·mol^{-1}, which is smaller than that for Ni_3 cluster (-623.2 kJ·mol^{-1}). The adsorption energy of Ni_4 cluster is -578.9 kJ·mol^{-1}, which is lower by 95.3 kJ·mol^{-1} than that of Ni_3 cluster. As a result, the decrease of the adsorption energy of Ni_4 cluster is mainly due to the decrease of Ni_4-support interaction energy.

For Ni_5 cluster, as shown in Figure S1(e), Ni_5 cluster interacts with the surface via four Ni atoms, the adsorption introduces one Ni–Ni bond cleavage in the adsorbed Ni_5 cluster, and the corresponding adsorption energy is -571.2 kJ·mol^{-1}, which is slightly larger than that for Ni_4 cluster (-578.9 kJ·mol^{-1}). 0.036 *e* are transferred to Ni_5 cluster from support surface. However, the Ni_5-support interaction energy (-859.6 kJ·mol^{-1}) is much smaller than that of Ni_4 cluster (-730.3 kJ·mol^{-1}). As a result, the slight increase of the Ni_5 cluster adsorption energy is mainly due to the stronger cluster and surface deformations (95.4 and 193.0 kJ·mol^{-1}) in comparison with those of Ni_4 cluster (6.0 and 145.4 kJ·mol^{-1}). In the adsorption configuration, the bond lengths of Ni1–$O_{2c\text{-}2}$, Ni2–Al_{3c}, Ni2–$O_{3c\text{-}2}$, Ni3–$O_{3c\text{-}1}$ and Ni4–$O_{2c\text{-}1}$ are 1.955, 2.461, 2.037, 2.042 and 2.139 Å, respectively. In addition, Ni3 and Ni4 atoms are bound to the surface Al_{4c} site with the Ni3–Al_{4c} and Ni4–Al_{4c} bond lengths of 2.221 and 2.503 Å, respectively.

For Ni_6 cluster, as shown in Figure S1(f), we can see that the adsorption of Ni_6 cluster can lead to the strong cluster and surface deformations (64.5 and 202.7 kJ·mol^{-1}). However, the Ni_6-support interaction energy (-870.1 kJ·mol^{-1}) is still the main contribution of the adsorption energy. The adsorption energy is -602.9 kJ·mol^{-1}, which is smaller by 31.7 kJ·mol^{-1} than that of Ni_5 cluster. 0.002 *e* are transferred to Ni_6 cluster from the support surface. Four atoms of Ni_6 cluster interact with the surface via three Ni–O_{2c} bonds (2.037, 1.998 and 2.185 Å), two Ni–O_{3c}

bonds (2.008 and 2.182 Å), Ni2–Al_{3c} bond (2.448 Å) and two Ni–Al_{4c} bonds (2.268 and 2.482 Å).

For Ni_7 cluster, the most stable adsorption configuration presented in Figure S1(g) shows that Ni_7 cluster prefers to adsorb on the dehydrated γ-Al_2O_3(110) surface with six Ni atoms. The adsorption also introduces the weaker cluster and surface deformations (52.6 and 198.1 kJ·mol^{-1}) relative to those of Ni_6 cluster (64.5 and 202.7 kJ·mol^{-1}). The adsorption energy and the Ni_7-support interaction energy are -563.1 and -813.8 kJ·mol^{-1}, respectively, which are larger than those of Ni_6 cluster (-602.9 and -870.1 kJ·mol^{-1}), suggesting that the decrease of Ni_7-support interaction energy mainly leads to the decrease of adsorption energy. 0.087 *e* are transferred to Ni_7 cluster from support surface. In the most stable configuration, the bond lengths of Ni1–O_{2c-1}, Ni1–O_{2c-2}, Ni2–Al_{3c}, Ni3–Al_{3c}, Ni3–O_{3c-2} and Ni4–O_{3c-1} bonds are 1.964, 1.897, 2.557, 2.667, 1.997 and 1.895 Å, respectively.

2. Adsorption of Ni_n(n=1–7) Clusters on the Hydrated γ-Al_2O_3(110) Surface

Ni_n(n=1–7) cluster is placed on a large number of well-defined adsorption sites that are available on the hydrated γ-Al_2O_3(110) surface, and the most stable adsorption configurations are obtained, as shown in Figure S2.

For the single Ni atom, as shown in Figure S2(a), the single Ni atom prefers to bind to the surface O_{2c-1}, O_{2c-2} and Al_{4c} sites, which is similar to that on dehydrated γ-Al_2O_3(110) surface. However, it is different from the adsorption of the single Cu atom on hydrated γ-Al_2O_3(110) surface, in which the single Cu atom prefers to bind to O_w and O_{3c-2} sites.[1] The bond lengths of Ni–O_{2c-1}, Ni–O_{2c-2} and Ni–Al_{4c} are 1.840, 1.844 and 2.500 Å, respectively. The adsorption energy (-277.6 kJ·mol^{-1}) on the hydrated γ-Al_2O_3(110) surface is slightly smaller than that on the dehydrated γ-Al_2O_3(110) (-269.9 kJ·mol^{-1}). 0.081 *e* are transferred to the single Ni atom from

support surface. The Ni_1-support interaction energy (-331.6 kJ·mol^{-1}) is larger than that for the single Ni atom on the dehydrated γ-Al_2O_3(110) surface (-359.4 kJ·mol^{-1}), which makes a major contribution to the adsorption energy. The adsorption of the single Ni atom leads to a weaker surface deformation (54.0 kJ·mol^{-1}) than that for the dehydrated γ-Al_2O_3(110) surface (89.5 kJ·mol^{-1}), suggesting that the presence of surface hydroxyls can increase the stability of the γ-Al_2O_3(110) surface.

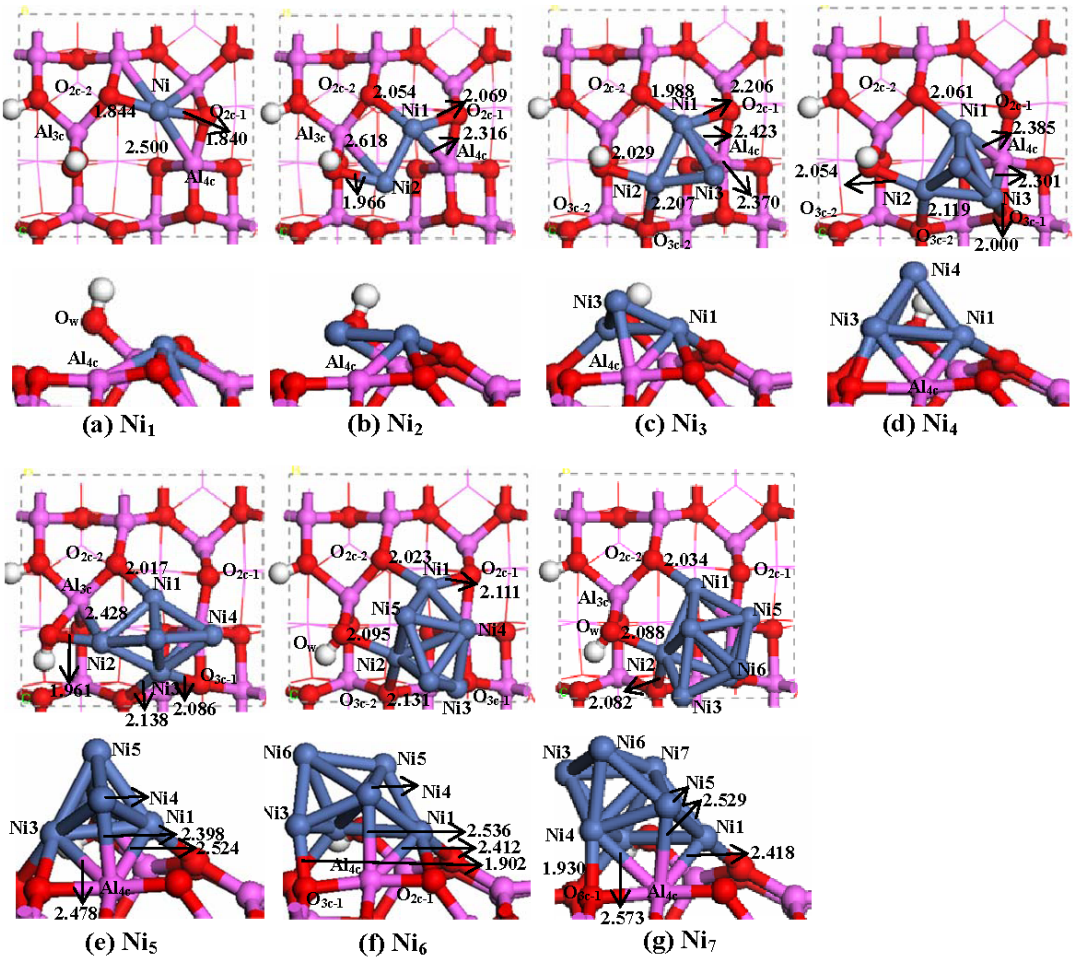

Figure S2. The most stable adsorption configuration of Ni_n(n=1–7) cluster on the hydrated γ-Al_2O_3(110) surface. Bond lengths are in Å. See Fig. S1 for color coding.

For Ni_2 cluster, one Ni atom bounds to the surface $O_{2c\text{-}1}$, $O_{2c\text{-}2}$ and Al_{4c} sites, and the other Ni atom bounds to the surface O_w and Al_{3c} sites, as illustrated in Figure S2(b), the corresponding adsorption energy and the Ni_2-support interaction energy are -349.9 and -449.6 kJ·mol^{-1},

respectively. 0.040 *e* are transferred from Ni_2 cluster to support surface. Due to the presence of surface hydroxyls, both energies are larger than those for the dehydrated (110) surface (-408.8 and -540.7 kJ·mol^{-1}). The Ni_2 cluster is adsorbed parallel to the surface plane with the Ni1–Ni2 bond length of 2.204 Å, which is longer than that for the isolated Ni_2 cluster (2.163 Å). The bond lengths of Ni1–O_{2c-1}, Ni1–O_{2c-2}, Ni1–Al_{4c}, Ni2–O_w and Ni2–Al_{3c} are 2.069, 2.054, 2.316, 1.966 and 2.618 Å, respectively. Compared to the dehydrated (110) surface, the increase of Ni_2-support interaction energy is responsible for the increase of the adsorption energy. Meanwhile, the hydrated γ-Al_2O_3(110) surface deformation energy (98.9 kJ·mol^{-1}) is smaller than the dehydrated (110) surface (128.4 kJ·mol^{-1}), suggesting that the presence of surface hydroxyls is still in favor of the stability of γ-Al_2O_3(110) surface. Further, the deformation of Ni_2 cluster (0.8 kJ·mol^{-1}) has a negligible contribution to the adsorption energy.

For Ni_3 cluster, as shown in Figure S2(c), the average bond length of Ni–Ni (2.281 Å) is larger than that for the isolated Ni_3 cluster (2.277 Å). The bond lengths of two Ni–Al_{4c} bonds are 2.423 and 2.370 Å, respectively. The bond lengths of Ni1–O_{2c-1}, Ni1–O_{2c-2}, Ni2–O_w and Ni2–O_{3c-2} bonds are 2.206, 1.988, 2.029 and 2.207 Å, respectively. Owing to the presence of surface hydroxyls, the adsorption ability of Ni_3 cluster (-470.3 kJ·mol^{-1}), the Ni_3-support interaction (-572.0 kJ·mol^{-1}) and the surface deformation (100.3 kJ·mol^{-1}) become weaker in comparison with those on the dehydrated (110) surface (-483.6, -623.2 and 132.9 kJ·mol^{-1}). 0.093 *e* are transferred to Ni_3 cluster from support surface. The Ni_3 cluster deformation (1.4 kJ·mol^{-1}) has few contributions to the adsorption energy. The increases of Ni_3-support interaction and surface deformation are the major contributions to the increase of the Ni_3 cluster adsorption ability.

For Ni_4 cluster, as shown in Figure S2(d), it interacts with the surface through three Ni atoms (Ni1, Ni2 and Ni3), and forms Ni1–O_{2c-2} bond (2.061 Å), Ni2–O_w bond (2.054 Å), Ni2–O_{3c-2} bond (2.119 Å), Ni3–O_{3c-1} bond (2.000 Å) and two Ni–Al_{4c} bonds (2.385 and 2.301 Å). The adsorption energy and the Ni_4-support interaction energy are -524.2 and -625.5 kJ·mol^{-1}, respectively. 0.082 *e* are transferred from Ni_4 cluster to support surface. Due to the presence of surface hydroxyls, both energies are larger than those (-578.9 and -730.3 kJ·mol^{-1}) for the dehydrated (110) surface. Moreover, the increase of Ni_4-support interaction energy mainly leads to the increase of the adsorption energy. The decrease of the surface deformation energy from 145.4 kJ·mol^{-1} for the dehydrated (110) surface to 92.0 kJ·mol^{-1} for the hydrated (110) surface still indicates that the presence of surface hydroxyls is in favor of the stability of the (110) surface. Similarly, the Ni_4 cluster deformation energy (9.3 kJ·mol^{-1}) makes a negligible contribution to the adsorption energy.

For Ni_5 cluster, as shown in Figure S2(e), it reorients into a square pyramidal geometry after the adsorption. The adsorption of Ni_5 cluster leads to the strong deformation of both Ni_5 cluster and the surface with the corresponding deformation energies of 29.4 and 123.4 kJ·mol^{-1}, respectively, which are weaker than those (95.4 and 193.0 kJ·mol^{-1}) for the dehydrated (110) surface due to the presence of surface hydroxyls. Moreover, the adsorption energy (-504.1 kJ·mol^{-1}) and the Ni_5-support interaction energy (-656.9 kJ·mol^{-1}) are increased relative to those for the dehydrated (110) surface (-571.2 and -859.6 kJ·mol^{-1}). 0.003 *e* are transferred to Ni_5 cluster from support surface. The Ni_5 cluster interacts with the surface via four Ni atoms (Ni1, Ni2, Ni3, and Ni4), and forms Ni1–O_{2c-2} bond (2.017 Å), Ni2–Al_{3c} bond (2.428 Å), Ni2–O_w bond (1.961 Å), Ni3–O_{3c-1} bond (2.086 Å), Ni3–O_{3c-2} bond (2.138 Å) and three Ni–Al_{4c} bonds (2.524,

2.478 and 2.398 Å).

For Ni_6 cluster, as shown in Figure S2(f), the Ni_6 cluster is adsorbed on the hydrated (110) surface via Ni1–O_{2c} bonds (2.111 and 2.023 Å), Ni2–O_w bond (2.095 Å), Ni2–O_{3c-2} bond (2.131 Å), Ni3–O_{3c-1} bond (1.902 Å) and two Ni–Al_{4c} bonds (2.412 and 2.536 Å). Due to the presence of surface hydroxyls, the adsorption of Ni_6 cluster can lead to the weaker deformation of cluster (41.8 kJ·mol^{-1}) and surface (136.2 kJ·mol^{-1}) in comparison with those (64.5 and 202.7 kJ·mol^{-1}) for the dehydrated (110) surface, indicating that the presence of surface hydroxyls can still improve the stability of surface. Meanwhile, the adsorption energy (-524.0 kJ·mol^{-1}) and the Ni_6-support interaction energy (-702.0 kJ·mol^{-1}) also increased due to the presence of surface hydroxyls. 0.066 *e* are transferred from Ni_6 cluster to support surface. The increase of the Ni_6-support interaction energy makes a major contribution to the increase of adsorption energy for Ni_6 cluster on the hydrated (110) surface.

For Ni_7 cluster, the Ni_7 cluster interacts with the surface though five Ni atoms, as shown in Figure S2(g), and forms Ni1–O_{2c-2} bond (2.034 Å), Ni2–O_w bond (2.088Å), two Ni–O_{3c} bonds (2.082 and 1.930 Å) and three Ni–Al_{4c} bonds (2.418, 2.573 and 2.529 Å). Due to the presence of surface hydroxyls, the adsorption energy and the Ni_7-support interaction energy (-500.5 and -652.0 kJ·mol^{-1}) are larger than those on the dehydrated (110) surface (-563.1 and -813.8 kJ·mol^{-1}), respectively. 0.015 *e* are transferred from Ni_7 cluster to support surface. Meanwhile, the adsorption of Ni_7 cluster leads to the weaker cluster and surface deformations (40.1 and 111.4 kJ·mol^{-1}) relative to those (52.6 and 198.1 kJ·mol^{-1}) on the dehydrated (110) surface, suggesting that the presence of surface hydroxyls is beneficial to the stability of the (110) surface.

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