Supplementary Information

The Effect of γ-Al2O3 Surface Hydroxylation on the Stability and Nucleation of Ni for Ni/γ-Al2O3 Catalyst: A Theoretical Study

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1. Adsorption of Ni\textsubscript{n}(n=1–7) Clusters on the Dehydrated γ-Al2O3(110) Surface

Ni\textsubscript{n}(n=1–7) cluster is placed on a large number of well-defined adsorption sites that are available on the dehydrated γ-Al2O3(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\textsubscript{2c} and Al\textsubscript{4c} sites on the dehydrated (110) surface, and forms the Ni–O\textsubscript{2c-1} (1.815 Å), Ni–O\textsubscript{2c-2} (1.828 Å) and Ni–Al\textsubscript{4c} (2.510 Å) bonds, as shown in Figure S1(a). The adsorption energy and the Ni\textsubscript{1}-support interaction energy are -269.9 and -359.4 kJ·mol\textsuperscript{-1}, respectively. 0.004 e are transferred to the single Ni atom from support surface. The Ni\textsubscript{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\textsuperscript{-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\textsuperscript{1} and Rh atom.\textsuperscript{2}

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Figure S1. The most stable adsorption configuration of Ni$_n$ ($n$=1–7) cluster on the dehydrated $\gamma$-Al$_2$O$_3$(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 $\gamma$-Al$_2$O$_3$(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$_3c-2$ 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$_{2c-1}$, Ni1–O$_{2c-2}$, Ni1–Al$_{3c}$, Ni1–Al$_{4c}$, Ni2–O$_{3c-2}$ 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 $\text{e}$ 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 $\text{e}$ 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 $\gamma$-Al$_2$O$_3$(110) surface. 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 Ni₄ cluster. The Ni₄-support interaction energy is -730.3 kJ·mol⁻¹, which is smaller than that for Ni₃ cluster (-623.2 kJ·mol⁻¹). The adsorption energy of Ni₄ cluster is -578.9 kJ·mol⁻¹, which is lower by 95.3 kJ·mol⁻¹ than that of Ni₃ cluster. As a result, the decrease of the adsorption energy of Ni₄ cluster is mainly due to the decrease of Ni₄-support interaction energy.

For Ni₅ cluster, as shown in Figure S1(e), Ni₅ cluster interacts with the surface via four Ni atoms, the adsorption introduces one Ni–Ni bond cleavage in the adsorbed Ni₅ cluster, and the corresponding adsorption energy is -571.2 kJ·mol⁻¹, which is slightly larger than that for Ni₄ cluster (-578.9 kJ·mol⁻¹). 0.036 e are transferred to Ni₅ cluster from support surface. However, the Ni₅-support interaction energy (-859.6 kJ·mol⁻¹) is much smaller than that of Ni₄ cluster (-730.3 kJ·mol⁻¹). As a result, the slight increase of the Ni₅ 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 Ni₄ cluster (6.0 and 145.4 kJ·mol⁻¹). In the adsorption configuration, the bond lengths of Ni₁–O₂c-2, Ni₂–Al₃c, Ni₂–O₃c-2, Ni₃–O₃c-1 and Ni₄–O₂c-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 Al₄c site with the Ni₃–Al₄c and Ni₄–Al₄c bond lengths of 2.221 and 2.503 Å, respectively.

For Ni₆ cluster, as shown in Figure S1(f), we can see that the adsorption of Ni₆ cluster can lead to the strong cluster and surface deformations (64.5 and 202.7 kJ·mol⁻¹). However, the Ni₆-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 Ni₅ cluster. 0.002 e are transferred to Ni₆ cluster from the support surface. Four atoms of Ni₆ cluster interact with the surface via three Ni–O₂c bonds (2.037, 1.998 and 2.185 Å), two Ni–O₃c...
bonds (2.008 and 2.182 Å), Ni2–Al3c bond (2.448 Å) and two Ni–Al4c bonds (2.268 and 2.482 Å).

For Ni7 cluster, the most stable adsorption configuration presented in Figure S1(g) shows that Ni7 cluster prefers to adsorb on the dehydrated γ-Al2O3(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 Ni6 cluster (64.5 and 202.7 kJ·mol⁻¹). The adsorption energy and the Ni7-support interaction energy are -563.1 and -813.8 kJ·mol⁻¹, respectively, which are larger than those of Ni6 cluster (-602.9 and -870.1 kJ·mol⁻¹), suggesting that the decrease of Ni7-support interaction energy mainly leads to the decrease of adsorption energy. 0.087 e are transferred to Ni7 cluster from support surface. In the most stable configuration, the bond lengths of Ni1–O2c-1, Ni1–O2c-2, Ni2–Al3c, Ni3–Al3c, Ni3–O3c-2 and Ni4–O3c-1 bonds are 1.964, 1.897, 2.557, 2.667, 1.997 and 1.895 Å, respectively.

2. Adsorption of Niₙ (n=1–7) Clusters on the Hydrated γ-Al₂O₃(110) Surface

Niₙ (n=1–7) cluster is placed on a large number of well-defined adsorption sites that are available on the hydrated γ-Al₂O₃(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 O₂c-1, O₂c-2 and Al₄c sites, which is similar to that on dehydrated γ-Al₂O₃(110) surface. However, it is different from the adsorption of the single Cu atom on hydrated γ-Al₂O₃(110) surface, in which the single Cu atom prefers to bind to Ow and O₃c-2 sites. The bond lengths of Ni–O₂c-1, Ni–O₂c-2 and Ni–Al₄c are 1.840, 1.844 and 2.500 Å, respectively. The adsorption energy (-277.6 kJ·mol⁻¹) on the hydrated γ-Al₂O₃(110) surface is slightly smaller than that on the dehydrated γ-Al₂O₃(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 \text{kJ} \cdot \text{mol}^{-1}) is larger than that for the single Ni atom on the dehydrated $\gamma$-Al$_2$O$_3$(110) surface (-359.4 \text{kJ} \cdot \text{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 \text{kJ} \cdot \text{mol}^{-1}) than that for the dehydrated $\gamma$-Al$_2$O$_3$(110) surface (89.5 \text{kJ} \cdot \text{mol}^{-1}), suggesting that the presence of surface hydroxyls can increase the stability of the $\gamma$-Al$_2$O$_3$(110) surface.

**Figure S2.** The most stable adsorption configuration of Ni$_n$($n=1$–7) cluster on the hydrated $\gamma$-Al$_2$O$_3$(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$_{2c-1}$, O$_{2c-2}$ 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 \text{kJ} \cdot \text{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$_2$O$_3$(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$_2$O$_3$(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 Ni₄ cluster, as shown in Figure S2(d), it interacts with the surface through three Ni atoms (Ni1, Ni2 and Ni3), and forms Ni1–O₂c-2 bond (2.061 Å), Ni2–O₆ bond (2.054 Å), Ni2–O₃c-2 bond (2.119 Å), Ni3–O₃c-1 bond (2.000 Å) and two Ni–Al₄c bonds (2.385 and 2.301 Å). The adsorption energy and the Ni₄-support interaction energy are -524.2 and -625.5 kJ·mol⁻¹, respectively. 0.082 e are transferred from Ni₄ 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 Ni₄-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 Ni₄ cluster deformation energy (9.3 kJ·mol⁻¹) makes a negligible contribution to the adsorption energy.

For Ni₅ cluster, as shown in Figure S2(e), it reorients into a square pyramidal geometry after the adsorption. The adsorption of Ni₅ cluster leads to the strong deformation of both Ni₅ 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 Ni₅-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 Ni₅ cluster from support surface. The Ni₅ cluster interacts with the surface via four Ni atoms (Ni1, Ni2, Ni3, and Ni4), and forms Ni1–O₂c-2 bond (2.017 Å), Ni2–Al₃c bond (2.428 Å), Ni2–O₆ bond (1.961 Å), Ni3–O₃c-1 bond (2.086 Å), Ni3–O₃c-2 bond (2.138 Å) and three Ni–Al₄c 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.
References

