Density Functional Theory Study on the Metal–Support Interaction between Ru Cluster and Anatase TiO$_2$(101) Surface

Shi-Tong Zhang, Chang-Ming Li, Hong Yan,* Min Wei,* David G. Evans, and Xue Duan

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Supporting Information

ABSTRACT: Density functional theory (DFT) calculations were carried out to study the nucleation and growth mechanism of Ru clusters on the TiO$_2$(101) surface by using supported Ru$_n$ (n = 1–10, 20, 22) cluster models to understand the metal–support interaction and the resulting catalytic performance toward CO oxidation. The results show that the Ru$_n$ cluster prefers a 3D geometry when n ≥ 4 and that the Ru–TiO$_2$ interface is predominantly composed of Ru–O and Ti–O bonds. Calculation studies based on the density of states (DOS), Hirshfeld charge analysis, and electron deformation density (EDD) demonstrate that the electronic interaction is mainly localized at the Ru–TiO$_2$ interface through the electron transfer via the Ru–O bond. Additionally, the investigation on catalytic behavior of Ru$_n$/TiO$_2$ toward CO oxidation reveals the largely enhanced catalytic activity of the supported Ru$_n$ clusters, which originates from the significant reduction of the activation barrier as a result of the electron transfer from Ru to TiO$_2$.

1. INTRODUCTION

The metal–support interaction has attracted considerable attention in the area of supported heterogeneous catalysis because of its significant influence on the catalytic performance. It is generally recognized that the metal–support interaction not only helps to stabilize the fine dispersion of metal particles on a support so as to avoid sintering but also dramatically influences the shape and size of the metal nanoparticles, metal–support charge transfer, optical properties of the semiconductor supports, and electronic structures. Although a number of studies have been devoted to elucidate the metal–support interaction and its effect on the activity and selectivity of catalytic reactions, some key issues remain elusive because of the limitation of experimental techniques. For instance, the structure of the metal–support interface and the growth mechanism of the supported metal particles are still not clear. Therefore, a detailed understanding of the metal–support interaction remains a challenging goal and is essential for the development of high-performance heterogeneous catalysts.

Supported ruthenium catalysts have been widely used in heterogeneous catalysis, owing to their high activity and/or selectivity in many industrially important catalytic processes, including ammonia synthesis and decomposition, hydrogenation, Fischer–Tropsch synthesis, CO oxidation, CO/CO$_2$ methanation, etc. The behavior of Ru-based catalysts for these heterogeneous reactions is strongly dependent on the metal–support interaction, which imposes significant influences on the morphology, surface and electronic structure, and the resulting catalytic performance. As a typical example, the Ru single-crystal surface is least active among noble metals for catalyzing CO oxidation under low-pressure conditions, but it is highly active if it is deposited on oxide supports. In most cases, studies on the Ru–support interaction were carried out using experimental methods, such as X-ray photoelectron spectroscopy, extended X-ray absorption fine structure, and in situ infrared and scanning tunneling microscopy, providing information about the charge transfer, surface morphology, and active sites. However, some important properties, including the Ru–support interface and the electronic structure, are still not fully understood. In addition, the nucleation and growth mechanism of Ru nanoparticles on supports have been rarely revealed, which restricts further insight into the structure–property correlation.

Computational approaches (e.g., density functional theory, DFT) offer an alternative to explore the metal–support interaction at the atomic and electronic level. For instance, DFT has been implemented for elucidating the atom and electron transfer between metal particles and oxide supports, detailed structure of interface, and hydrogenation and oxidation mechanisms. On the basis of this understanding, the essential characteristics for heterogeneous catalysts with good catalytic behavior can be identified. Because a direct full-scale (nano or subnano scale) theoretical simulation including both nanosized metal particles and oxide support is too computationally demanding, the simulation of the nucleation or growth...
of the supported metal particles by using cluster models has been generally accepted to understand the metal–support interface structure and further identify the inherent nature of the metal–support interaction.\textsuperscript{19,40–44} This method has been demonstrated in the studies of several supported metals (e.g., Cu, Au, Pt, and Pd clusters) on oxide supports for potential applications as heterogeneous catalysts.\textsuperscript{8}

In the present work, anatase TiO\textsubscript{2} is chosen as the oxide support because Ru/TiO\textsubscript{2} catalysts display excellent catalytic performance in many important chemical processes and have attracted a great deal of attention over the past decades.\textsuperscript{46,47} DFT studies on nucleation and growth mechanism of Ru clusters on the TiO\textsubscript{2}(101) surface were carried out to gain insight into the metal–support interaction; the mechanism of CO oxidation catalyzed by Ru/TiO\textsubscript{2} was also studied to identify the origin of the promoted catalytic activity of Ru catalysts. A number of adsorption models of Ru\textsubscript{n} clusters (\(n = 1–10, 20, 22\)) on the TiO\textsubscript{2}(101) surface were optimized. It was found that Ru\textsubscript{n} cluster prefers a 3D geometry when \(n \geq 4\) and that the electronic interaction is mainly localized at the Ru–TiO\textsubscript{2} interface through the electron transfer from Ru to TiO\textsubscript{2}. This electron transfer was proven to be the main factor that promotes the catalytic activity of the supported Ru cluster toward CO oxidation via reduction of the activation barrier of O and CO association. This work provides a detailed understanding on the Ru–TiO\textsubscript{2} interaction theoretically, which gives helpful instructions in the design and synthesis of supported Ru-based catalysts in heterogeneous catalysis.

2. COMPUTATIONAL METHOD AND DETAILS

The anatase TiO\textsubscript{2}(101) surface was represented as a \(p(3 \times 4)\) slab with a thickness of four titanium layers (16.33x15.10x5.71 Å\(^3\)), and only the bottom atoms in the slab were constrained to their crystal lattice positions. The initial crystal structure of anatase TiO\textsubscript{2} was built according to previous experimental work.\textsuperscript{48} It has been verified that the \(p(3 \times 4)\) slab is large enough to reduce the interactions between neighboring adsorbed metal clusters and to fully release the interfacial strain energy.\textsuperscript{7} The neighboring slabs were separated in the direction perpendicular to the surface by a vacuum region of 20 Å (Figure 1).

First-principle calculations within the DFT framework were performed within the DMol\textsuperscript{3} code in the Materials Studio 5.5 software package.\textsuperscript{49–51} The exchange–correlation potential was described by the Perdew–Burke–Ernzerhof (PBE) generalized gradient approach (GGA).\textsuperscript{52–55} The atomic orbitals were represented by a double numerical basis sets plus polarization function (DNP), which was widely used in many reports concerning the electronic properties of Ru and Ti atoms.\textsuperscript{49–55,56–58} The core electrons for metals were treated by effective core potentials (ECP). The convergence criteria for structure optimizations are based on the following points: (1) an energy tolerance of 5.44x10\(^{-4}\) eV per atom; (2) a maximum force tolerance of 0.11 eV/Å; (3) a maximum displacement tolerance of 4.0x10\(^{-3}\) Å. The \(k\)-space is sampled by the \(\gamma\) point. To study the interactions between Ru clusters and titania surface, adsorption energy is defined as

\[
E_{\text{ads}} = E(\text{Ru}_{n}) + E(\text{TiO}_2) - E(\text{Ru}_{n}/\text{TiO}_2)
\]

where \(n\) is the total number of adsorbed Ru atoms; \(E(\text{Ru}_{n})\), \(E(\text{TiO}_2)\), and \(E(\text{Ru}_{n}/\text{TiO}_2)\) are the total energy of the relaxed free Ru\textsubscript{n} cluster in the gas phase, TiO\textsubscript{2} slab, and Ru\textsubscript{n}/TiO\textsubscript{2} system, respectively. To better understand the effect of metal–support interaction on the growth of Ru\textsubscript{n} clusters, two energies are defined in addition to \(E_{\text{ads}}\): They are the binding energy

\[
E_{\text{bind}} = E(\text{Ru}_{n-1}/\text{TiO}_2) + E(\text{Ru}) - E(\text{Ru}_{n}/\text{TiO}_2)
\]

and the cohesive energy

\[
E_{\text{coh}} = [nE(\text{Ru}) + E(\text{TiO}_2) - E(\text{Ru}_{n}/\text{TiO}_2)]/n
\]

Here, \(E(\text{Ru})\), \(E(\text{TiO}_2)\), and \(E(\text{Ru}_{n}/\text{TiO}_2)\) are the total energies of the individual Ru\textsubscript{n} bare TiO\textsubscript{2} substrate, and Ru\textsubscript{n}/TiO\textsubscript{2} cluster, respectively. \(E_{\text{bind}}\) gives the adsorption energy of the nth adsorbed Ru atom on the Ru\textsubscript{n-1}/TiO\textsubscript{2} system; \(E_{\text{coh}}\) represents the ability of metal atoms growing together.\textsuperscript{5,19} Positive values of \(E_{\text{ads}}\), \(E_{\text{bind}}\), and \(E_{\text{coh}}\) correspond to energetically stable adsorption, binding, and cohesive systems, respectively.

The metal–support interaction can dramatically influence the heterogeneous catalytic performance of the supported metal particles. Moreover, the optical properties, reaction dynamics, and charge dynamics upon photoexcitation of the oxide supports are also dependent on the metal–support interaction, which have been reported in the system of TiO\textsubscript{2} and CeO\textsubscript{2}.\textsuperscript{8,9} In this study, we focus on the improved catalytic performance of the supported metal particles. Therefore, the transition states (TS) of the CO oxidation on different models are searched with the complete LST/QST method.\textsuperscript{56} This method begins by performing a liner synchronous transit (LST)/optimization calculation. The transition state (TS) approximation obtained was used to perform a quadratic synchronous transit (QST) maximization. On the basis of that maximization point, another constrained minimization was performed, and the cycle was repeated until a stationary point was located.

3. RESULTS AND DISCUSSION

3.1. Adsorptions. Adsorption of Single Ru. Various possible adsorption sites for a single Ru adatom on the anatase TiO\textsubscript{2}(101) surface have been searched. The most stable structure is shown in Figure 2a, in which the Ru atom binds at a bridge site of two edge O\textsubscript{2} atoms along the [101] direction, with the Ru–O\textsubscript{2} bond length of \(\sim 2.05\) Å (configuration Ru\textsubscript{1}). This value is similar to the case of a single Pt or Pd atom adsorbed at the anatase TiO\textsubscript{2}(101)
The adsorption energy of a Ru adatom on the anatase TiO$_2$(101) surface in this structure is 3.59 eV, which is much larger than that of the reported noble metal atom (0.39 eV for Au, 2.84 eV for Pt, and 2.67 eV for Pd). The Ru atom also shows a preferable bonding with both an O$_2$c and an O$_3$c atom at the O$_2$c$-$Ti$_5$c$-$O$_3$c bridge site (configuration Ru$_{1,b}$) as shown in Figure 2b. The length of Ru$-$O$_2$c (or Ru$-$O$_3$c) bond slightly shortens by $\sim$0.1 Å in this structure compared with that in the Ru$_{1,a}$ configuration, indicating that the Ru atom exhibits an interaction with the surface oxygen atoms in Ru$_{1,b}$ that is stronger than that in the Ru$_{1,a}$ configuration. However, the calculated adsorption energy of configuration Ru$_{1,b}$ (Figure 2b) is less stable than that of Ru$_{1,a}$ (Figure 2a) by 1.07 eV. This is mainly related to the fact that the Ru atom is 3-coordinated with O atoms in Ru$_{1,b}$ whereas it is 4-coordinated in Ru$_{1,a}$.

Adsorption of Ru$_2$. Different adsorptions of Ru dimer (Ru$_2$) on the anatase TiO$_2$(101) surface were investigated, and three energetically stable adsorptions of the Ru$_2$ cluster are shown in Figure 3. Figure 3a displays the most stable structure of Ru$_2$ adsorption on the anatase TiO$_2$(101) surface (Ru$_{2,a}$), in which each of the individual Ru atoms binds with one O$_2$c and one O$_3$c atom and the Ru$-$Ru bond is parallel to the [010] direction. The adsorption configurations in Figure 3b (Ru$_{2,b}$) and Figure 3c (Ru$_{2,c}$) are constructed by adding the second Ru atom to the most stable single Ru adsorption (Ru$_{1,a}$) and allowing the structures to relax again. It is found that Ru$_{2,b}$ and Ru$_{2,c}$ (Figure 3b,c) are structurally and energetically close: the Ru$_1$ atom in these two configurations binds near the O$_3$c top site, and the Ru$_2$ atom in Ru$_{2,b}$ has only a slight displacement toward the O$_2$c$-$Ti$_5$c$-$O$_3$c bridge site from the Ti$_5$c top site compared with that in Ru$_{2,c}$. The adsorption energy of Ru$_{2,b}$ is only 0.04 eV higher than that of Ru$_{2,c}$, indicating that Ru$_{2,a}$ and Ru$_{2,c}$ can easily transfer between each other. As discussed in Adsorption of Single Ru, the most active site on the anatase TiO$_2$(101) surface for a single Ru adsorption is the O$_2$c$-$O$_2$c bridge site (Figure 2a); however, in the case of a Ru dimer, the most active site on the TiO$_2$(101) surface becomes the O$_2$c$-$Ti$_5$c$-$O$_3$c bridge site. This can be further confirmed by studying four triangles (Figure 4a,b,c,e) and two line models (Figure 4d,f). The most stable structure of Ru$_3$ cluster on the TiO$_2$(101) surface (Ru$_{3,a}$) is presented in Figure 4a with an adsorption energy of 5.46 eV. In this configuration, the Ru1 and Ru2 atom are adsorbed at the O$_2$c$-$Ti$_5$c$-$O$_3$c bridge site and the third Ru atom (Ru$_3$) binds at the O$_2$c$-$Ti$_5$c$-$O$_3$c bridge site. The adsorption energy of Ru$_{3,b}$ (5.24 eV) is quite close to that of Ru$_{3,a}$, indicating that the Ru$_{3,a}$ and Ru$_{3,b}$ may transfer between each other. The configuration in Figure 4c (Ru$_{3,c}$) is obtained by adding a third Ru atom to the configuration Ru$_{1,b}$ with an
Adsorption energy of 4.97 eV, which is slightly lower than that of Ru$_{10a}$ and Ru$_{10b}$. This structure can also be viewed as the intermediate phase between Ru$_{10a}$ and Ru$_{10b}$. Configuration Ru$_{10c}$ is a triangle model, but its adsorption energy is much lower than that of other triangle models because Ru2 atom is far from the TiO$_2$ surface and the interaction is rather weak. Line models adsorbed on the TiO$_2$ surface (Ru$_{1a}$ and Ru$_{1c}$) are shown in Figure 4d and Figure 4f, respectively, with rather low adsorption energies, suggesting these line adsorption structures are not favorable.

**Adsorption of Ru$_n$ (n = 4−10, 20, 22).** The optimized geometries of Ru$_n$ (n = 4−10, 20, 22) on anatase TiO$_2$(101) with adsorption energies are shown in Figure 5. The geometry of each Ru$_n$/TiO$_2$(101) (n = 4−10, 20, 22) was selected from several possible configurations and has the most favorable adsorption energy. For the Ru$_4$ cluster on the TiO$_2$(101) surface, several 2D and 3D clusters were taken into consideration, and the results show that Ru$_4$ cluster prefers a tetrahedral structure (Figure 5a) by adding the fourth Ru atom on the top of the triangle Ru ring based on configuration Ru$_4_{1a}$. The Ru$_5$ cluster also prefers a 3D geometry (Figure 5b) with two Ru atoms binding at the O$_{1i}$−Ti$_{1m}$−O$_{2s}$ bridge site, another two Ru atoms binding at the O$_{1m}$−Ti$_{2m}$−O$_{2s}$ bridge site, and the fifth atom binding with the latter two Ru atoms. For Ru$_6$ (n = 6−10) clusters on the anatase TiO$_2$(101) surface, the last Ru atom was introduced based on the structure of Ru$_5_{1a}$, indicating that a relatively stable Ru−TiO$_2$ interface has been formed. With the increase of atom number, the Ru$_n$ cluster transforms from 2D (n < 4) to 3D geometry (n ≥ 4), which shows a trend similar to that of Au, Pt, and Pd on the TiO$_2$(101) surface. Because a full-scale simulation including both metal particles and oxide support is too computationally demanding, a Ru strip model loaded on the titania surface (Figure 5h) and a Ru$_{22}$ cluster supported on TiO$_2$ (Figure 5i) were used to explore the Ru−TiO$_2$ interaction. These two models share the same packed-manner with the Ru$_{10}$ cluster (Figure 5g), and one Ru atom fully coordinated by 12 Ru atoms is contained in the Ru$_{22}$/TiO$_2$ model. It has been reported that noble metal particles are prone to highly disperse on the surface of TiO$_2$, and even metal clusters containing 4 atoms were observed experimentally. Therefore, it is expected that the TiO$_2$-supported Ru$_{10}$, Ru$_{20}$, and Ru$_{22}$ cluster models can reasonably reflect the chemical and physical properties (e.g., interface structure, charge distribution, and atom transfer) of practical Ru/TiO$_2$ system. Structurally, it is found that the Ru$_{10}$ structure (Figure 5g) may be a basic unit for building the Ru nanoparticles on the TiO$_2$ surface. The Ru$_{10}$ and Ru$_{22}$ cluster (Figure 5h,i) mainly expose the Ru(001) and Ru(101) surface, which is in agreement with experimental findings.

To further understand the growth and metal–support interaction of Ru clusters on the TiO$_2$(101) surface, the binding energies ($E_{\text{bind}}$) and the cohesive energies ($E_{\text{coh}}$) of Ru$_n$ (n = 1−10) clusters supported on the TiO$_2$(101) surface were calculated (Figure 6). As shown in Figure 6a, $E_{\text{bind}}$ increases from n = 1 to n = 3, decreases sharply at the point n = 4, and then increases again from n = 4 to n = 6. This is because the Ru−Ru and Ru−TiO$_2$ interaction jointly dominate the growth behavior of Ru$_n$ cluster in the ranges n = 1−3 and n = 4−6; at the point n = 4, only the Ru−Ru interaction drives the formation of Ru$_4$/TiO$_2$ from Ru$_3$/TiO$_2$. In the range n = 6−10, $E_{\text{bind}}$ shows an even−odd oscillation, which reflects the variation of the driving force for the growth of Ru clusters. At the point n = 7 or 9, the seventh or ninth Ru atom binds at the metal−support contact layer; at the point n = 6 or 8, the sixth or eighth Ru atom binds mainly via Ru−Ru interaction. For the Ru$_{10}$/TiO$_2$, both the metal−support and Ru−Ru interaction contribute to the growth of Ru$_{10}$ cluster because the 10th Ru atom binds at the Ru/TiO$_2$ interface. As can be seen in Figure 6b, $E_{\text{coh}}$ increases gradually with the increase of cluster size because of the formation of Ru−Ru bonds which stabilizes the adsorbed Ru cluster. $E_{\text{coh}}$ shows a sharp increase in the range n = 2−6 and approaches a constant value as n = 6−10, indicating that the Ru tends to form bigger cluster as n < 6 and that the packing ability of Ru$_n$ cluster becomes stable when n ≥ 6.

**3.2. Electronic Interaction.** The total densities of states (TDOS) and local densities of states (LDOS) for the clean TiO$_2$(101) surface as well as Ru$_n$/TiO$_2$ systems (n = 10, 20,
and 22) were calculated (Figure 7) to further understand the interaction between Ru and the TiO$_2$ support in the view of electronic structure. For the clean TiO$_2$(101) surface (Figure 7a), significant hybridization takes place between the O 2p and Ti 3d state because of the Ti$-$O bonding. The valence band (VB) is dominated by O 2p orbitals while the conduction band (CB) is dominated by Ti 3d orbitals, with the calculated band gap of $\sim$2.5 eV. This value is lower than the reported one (3.2 eV)$^{63}$ because of the underestimation of band gap by the PBE functional. As a result of the introduction of Ru clusters, the band gap disappeared (Figure 7b$-$d) and the Fermi level moved from the VB top (Figure 7a) to the bottom of the bands contributed by the unoccupied Ru 4d orbitals. The local density of states of the interface Ru atoms as well as the neighboring O and Ti atom are shown in the inset illustrations. It is noteworthy that the 4d orbitals of the interface Ru atoms show significant hybridization with the adjacent O 2p orbitals and Ti 3d orbitals in the region from $-2.0$ to $0$ eV (inset illustrations

**Figure 7.** Total density of states (DOS) and partial density of states (PDOS) of (a) the clean TiO$_2$(101) surface, (b) Ru$_{10}$/TiO$_2$ system, (c) Ru$_{20}$/TiO$_2$ system, and (d) Ru$_{22}$/TiO$_2$ system. The inset in (a) shows the local density of states (LDOS) of the surface O and Ti atom, and those in (b), (c), and (d) show the LDOS of the interface Ru atoms and the neighboring O and Ti atom (the distance cutoff is 4.0 Å).

**Figure 8.** Hirshfeld charge analysis on different layers of (a) Ru$_{10}$/TiO$_2$, (b) Ru$_{20}$/TiO$_2$, and (c) Ru$_{22}$/TiO$_2$ (cyan, Ru; red, O; white, Ti). The value of the Hirshfeld charge is denoted by the black text.
of Figure 7b–d). This indicates the bonded interaction occurs among the interface Ru, O, and Ti atoms. Further confirmation was performed by mapping the electron density of the Ru

\[ \text{TiO}_2 (n = 10, 20, 22) \]  system (Figure S2 of the Supporting Information). It is found that the electron density of both Ru–O and Ti–O bond is much higher than that of the Ti–Ru bond. The high degree of electron delocalization indicates that the metal–support interface is predominantly composed of Ru–O and Ti–O bonds, with the absence of metallic Ti–Ru bond.

Hirshfeld charge analysis shows that the total charge of each adsorbed Ru

\[ \text{Ru}_n \]  cluster (n = 1–10, 20, 22) is positive, and the value increases with the enhancement of n (Figure S3 of the Supporting Information), suggesting that charge transfer occurs from the Ru cluster to the TiO

\[ _2 \]  surface. This has also been observed in our previous experimental work. As shown in Figure 8, the electronic interaction is mainly localized in the layer of Ru atoms that are in direct contact with the TiO

\[ _2 (101) \]  surface; Ru atoms in noncontacting layers, the middle and top layers in Ru clusters, are less affected by the electronic interaction. Electron deformation density (EDD) pattern of the Ru

\[ _{10} / \text{TiO}_2 (101) \]  system was also studied in this work, which shows the regions where electron density increases or decreases (Figure S4 of the Supporting Information). According to the EDD calculations, the Ru–O bond is polarized, in which electrons move away from the Ru atom to the surface O atom. This depletion of electron density from Ru reduces the Pauli repulsion that the metal atoms experienced and thus leads to a strong attractive interaction at the metal–support interface. On the basis of the DOS calculations, Hirshfeld charge analysis, and EDD results, it is concluded that the electronic interaction is mainly localized at the Ru–TiO

\[ _2 \]  interface with electron transfer from Ru to TiO

\[ _2 \]  via the Ru–O bond.

**3.3. Mechanism Studies of CO Oxidation on Ru/TiO

\[ _2 \] .** Ru single crystal is the least active noble metal catalysts for CO oxidation under ultrahigh vacuum conditions, but it becomes rather active under oxidizing state or high-pressure conditions. Intensive studies of the CO oxidation over Ru single-crystal surface have been carried out, but supported Ru nanoparticle catalysts for this reaction have been rarely reported. According to the discussion above, Ru

\[ _{10} \]  is the smallest species featuring a 3D structure and exposed Ru(001) and Ru(101) surface. Herein, to understand the effect of Ru–TiO

\[ _2 \]  interaction on catalytic performance, the oxidation mechanism of CO to CO

\[ _2 \]  was studied on the Ru

\[ _{10} / \text{TiO}_2 \]  system, Ru

\[ _{10} ^0 \]  cluster, and Ru

\[ _{10} ^+ \]  cluster. The two Ru clusters were placed in 3D lattices that were the same as those of the Ru

\[ _{10} / \text{TiO}_2 \]  system. The charged species is treated by assigning a total charge to the system in which the atomic charge is not fixed. The Ru atoms in the bottom layer of Ru

\[ _{10} ^0 \]  and Ru

\[ _{10} ^+ \]  cluster are fixed, but the adsorption structures of reactants and products are fully optimized to search for the most stable state rather than being determined artificially. As shown in Figure 9a, the oxygen atoms are dissociatively adsorbed at the Ru–Ru bridge site while the CO molecule is adsorbed at the 4-fold hollow (4f) site on Ru

\[ _{10} / \text{TiO}_2 \]  the energy barrier required for this reaction is 0.43 eV with an exothermic energy of 0.16 eV. This reaction over Ru

\[ _{10} ^0 \]  cluster is also exothermic by 0.18 eV, but the reaction barrier is as high as 1.10 eV. This demonstrates that the anatase TiO

\[ _2 \]  support dramatically promotes the catalytic activity of Ru clusters toward CO oxidation. To further confirm whether this dramatically improved catalytic performance is attributed to the oxidation state of the supported Ru, the CO oxidation process catalyzed by Ru

\[ _{10} ^+ \]  cluster was also studied (Figure 9c). The total charge for Ru

\[ _{10} ^+ \]  in the calculations is actually set to be 1.07 e, which is identical to that of the Ru

\[ _{10} \]  cluster in the Ru

\[ _{10} / \text{TiO}_2 (101) \]  system. In the initial state, O

\[ _2 \]  is also dissociatively adsorbed at the Ru–Ru bridge site and CO is at the 4f site. The CO oxidation on Ru

\[ _{10} ^+ \]  shows an energy barrier of 0.33 eV with an exothermic energy of 0.13 eV, both of which are slightly lower than those on the Ru

\[ _{10} / \text{TiO}_2 \]  system (0.43 and 0.16 eV, respectively). Therefore, the results provide indications that the significant improvement in catalytic activity of Ru clusters for CO oxidation mainly originates from the charge transfer between the Ru cluster and TiO

\[ _2 \]  support. Assmann et al. investigated various Ru catalysts for CO oxidation from bulk single crystals to supported nanoparticles and found that the metallic Ru surface under oxidation state will convert to catalytically active species. According to the present calculation results, it is noteworthy that in the initial state of CO oxidation over Ru

\[ _{10} / \text{TiO}_2 \]  and Ru

\[ _{10} ^+ \]  clusters, the C–O distance is 3.07 and 2.76 Å, respectively, much shorter than that on the Ru

\[ _{10} ^0 \]  cluster (4.09 Å). This indicates a shorter reaction distance for CO

\[ _2 \]  formation from CO and O on Ru

\[ _{10} / \text{TiO}_2 \]  and Ru

\[ _{10} ^+ \]  surface. In addition, Hirshfeld charge analysis shows that the coadsorbed CO molecule and two O atoms on these three Ru

\[ _{10} \]  systems are negatively charged with −0.18 and −0.50e, respectively. However, the charge distributions are different. In the Ru

\[ _{10} ^0 \]  cluster, the positive charge is mainly localized at the three Ru atoms around the adsorbed species; in the cases of the Ru

\[ _{10} / \text{TiO}_2 \]  and Ru

\[ _{10} ^+ \]  clusters, the charge distribution is more uniform and most Ru atoms are positively charged above 0.10e. The variation in initial C–O distance can be attributed to the different charge distributions. Furthermore, the more uniform charge distribution on the Ru

\[ _{10} / \text{TiO}_2 \]  and Ru

\[ _{10} ^+ \]  clusters results in a decreased Coulomb force that CO and O could overcome to produce CO

\[ _2 \]  in comparison with that on the Ru

\[ _{10} ^0 \]  surface (Figure S5 of the Supporting Information). This decreased Coulomb force accounts for the much lower energy barrier on the Ru

\[ _{10} / \text{TiO}_2 (0.43 \text{ eV}) \]  and Ru

\[ _{10} ^+ \]  surface (0.33 eV) relative to the
Ru$_{10}$ surface (1.10 eV). It should be noted that the charge-transfer effect is essential for small clusters studied in this work, but it would be less relevant for large aggregates.

4. CONCLUSIONS

DFT calculations were carried out to investigate the metal–support interaction between Ru and the TiO$_2$(101) surface, and its influence on the catalytic performance toward CO oxidation was also revealed. The nucleation and growth mechanism of Ru clusters on the TiO$_2$(101) surface was studied, the most energetically stable adsorption structure was identified, and the electronic interaction between Ru and TiO$_2$ was discussed. It is found that the active site for Ru cluster growth on the anatase TiO$_2$(101) surface shifts from the bridge site of two O$_{2c}$ atoms to the O$_{2c}$–Ti$_{6c}$–O$_{3c}$ bridge site and finally to the O$_{2c}$–Ti$_{6c}$–O$_{3c}$ bridge site. The Ru$_n$ cluster prefers a 3D geometry when $n \geq 4$, and a stable interface is formed between Ru$_n$ and TiO$_2$ when $n \geq 6$. The electronic calculations show that electron transfer from the Ru clusters to the TiO$_2$ support via the Ru–O bond, which is mainly localized at the contact layer of Ru clusters. It is worth noting that the electron transfer between metal and support is discussed only on the stoichiometric TiO$_2$(101) surface in this work. Some studies have demonstrated that the charge transfer may occur in an opposite direction on a defect surface, especially when the Fermi energy of the metal is localized below the defect-related state in the band gap.$^{68,69}$ Therefore, the interaction between the metal and nonstoichiometric TiO$_2$ surface deserves further study in our future work. To investigate the nature of the promoted catalytic performance by Ru–TiO$_2$ interaction, the CO oxidation to CO$_2$ was chosen as probe reaction over Ru$_{10}$/TiO$_2$ system, Ru$_{10}$ cluster, and Ru$_{10}^{++}$ cluster, respectively. The results show that the significant promotion in catalytic activity of Ru$_{10}$ cluster and Ru$_{10}$/TiO$_2$ toward CO oxidation originates from the oxidation state of the Ru clusters. This work provides a computational insight into the metal–support interaction between Ru clusters and the TiO$_2$ surface, which may give helpful information for the design of Ru-based catalysts.

**ASSOCIATED CONTENT**

5 Supporting Information

Most stable geometries of the Ru$_n$ clusters (Figure S1); electron density contour maps of metal–support interface (Figure S2); Hirshfeld charge of Ru$_n$ ($n = 1$–10) cluster models as a function of $n$ (Figure S3); electronic deformation density of Ru$_{10}$/TiO$_2$ system (Figure S4); Hirshfeld charge analysis on the initial states of Ru$_{10}$/TiO$_2$, Ru$_{10}^{++}$, and Ru$_{10}^{4+}$ (Figure S5); lattice vectors and fractional coordinates of the optimized Ru$_n$/TiO$_2$ ($n = 1$–10, 20, 22) systems (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Authors**

Tel.: +86-10-64412131. Fax: +86-10-64425385. E-mail: yanhong@mail.buct.edu.cn.

Tel.: +86-10-64412131. Fax: +86-10-64425385. E-mail: weimin@mail.buct.edu.cn.

**Notes**

The authors declare no competing financial interest.

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