

UCLA

UCLA Previously Published Works

Title

The Crucial Role of Hydrogen Ligation in the Stability of Single Atoms on Rutile TiO₂: A First-Principles Study

Permalink

<https://escholarship.org/uc/item/7s07518p>

Journal

ACS Applied Materials & Interfaces, 18(7)

ISSN

1944-8244

Authors

Ghoshal, Sourav

Ezeakunne, Chidozie

Lee, Yonghyuk

et al.

Publication Date

2026-02-25

DOI

10.1021/acsami.5c24310

Supplemental Material

<https://escholarship.org/uc/item/7s07518p#supplemental>

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

The Crucial Role of Hydrogen Ligation on the Stability of Single-Atoms on Rutile TiO₂: A First-Principles Study

Sourav Ghoshal,^{1,2} Chidozie Ezeakunne,³ Yonghyuk Lee,^{4,5} Anastassia N. Alexandrova,⁵

Shyam Kattel^{3*}

¹Department of Physics, Florida A&M University, Tallahassee, FL 32307, USA

²School of Applied Sciences, Kalinga Institute of Industrial Technology (KIIT)

Deemed to be University, Bhubaneswar, Odisha 751024, India

³Department of Physics, University of Central Florida, Orlando, 32816, USA

⁴Department of Chemical and Biochemical Engineering, Dongguk University, Seoul 04620,

Republic of Korea

⁵Department of Chemistry, University of California, Los Angeles, CA 90095, USA

Corresponding author: Shyam Kattel (shyam.kattel@ucf.edu)

Abstract

Understanding the stability of TiO₂-supported single-atom catalysts (SACs) under H₂ reduction conditions, where hydrogen adsorption on the metal/TiO₂ surface influences metal-support interactions, diffusion, and aggregation, is important for their long-term applications. Using first-principles density functional theory (DFT) calculations, we investigate the thermodynamic and kinetic stability of Rh, Ag, Pt, and Au-based SACs on pristine, oxygen-defective, and hydroxylated rutile TiO₂ (110) surfaces with and without H adsorption on the metal adatom. The thermodynamic driving force for aggregation was assessed by calculating dimerization energies as proxy, while the kinetic stability was quantified in two ways: (i) the total activation energy, E_{total} ($E_f + E_d$), which couples adatom formation (E_f) and diffusion (E_d) energies, serves as a descriptor of ripening kinetics, and (ii) the E_d , used to evaluate diffusion

rate constants and characteristic diffusion times, τ . The results show that Pt consistently exhibits the largest E_{total} and longest τ , reflecting exceptional resistance to sintering, whereas Ag has the smallest values and is intrinsically unstable. Rh presents a distinctive case: although dimerization is thermodynamically favoured, its E_{total} is dominated by the formation energy of two separated Rh atoms on support ($^*\text{Rh}^*\text{Rh}$), giving Rh longer lifetimes than expected from its low diffusion barrier for dimer ($^*\text{Rh}_2$) formation. Au is unstable on oxygen-deficient TiO_2 but is kinetically stabilized upon hydroxylation, which significantly increases both E_{total} and τ . Hydrogen adsorption further modulates stability in a metal-dependent manner—stabilizing Rh but accelerating aggregation of Ag and Au. This combined thermodynamic–kinetic framework provides a quantitative basis for predicting SAC sintering behaviour and guiding strategies for stabilizing late transition metals under hydrogenation conditions.

1. Introduction

Single-atom catalysts (SACs) have emerged as an innovative class of materials in heterogeneous catalysis, offering unparalleled atom efficiency, unique electronic properties, and exceptional catalytic activity and selectivity.^{1–5} By anchoring individual metal atoms onto well-engineered supports, SACs achieve maximum utilization of catalytically active metal atoms, which is crucial for the development of sustainable and cost-effective catalytic processes.^{5–8} However, maintaining the atomic dispersion in SACs remains a significant challenge, especially under reaction conditions, as single atoms can easily migrate/aggregate to form clusters.^{9–13}

Metal oxides-supported SACs have been extensively studied in various thermocatalytic processes, such as the water-gas shift reaction (WGS),¹⁴ CO oxidation,¹⁵ selective hydrogenation¹⁶ and carbon-carbon coupling reactions.^{17,18} The stability of supported SACs is significantly impacted by the metal-support interaction (MSI).^{19–22} Thermally stable SACs on a range of reducible oxides, such as TiO₂,^{17,21–24} CeO₂,^{25–27} MnO₂,²⁸ Fe₂O₃,^{29,30} etc., have been prepared by anchoring isolated metal through M-O bonds, which are stabilized by the transfer of charge from the metal to the supports through hybridization of O-p orbitals with metal-(d/p) orbitals.¹⁷ Among metal oxides, TiO₂ has proven to be one of the most effective supports for SACs due to its robust thermal and chemical stability, high surface area, and ability to form strong MSI.^{31–34} These features enable TiO₂ to stabilize single metal atoms and reduce the likelihood of clustering.^{35,36} Therefore, TiO₂ has been widely used as a support material in numerous catalytic processes, such as hydrogenation, and CO₂ reduction reactions, making it a versatile catalytic material.^{37–40} For example, TiO₂-supported SACs containing transition metal atoms such as Rh, Ag, Pt, and Au have been investigated for water-gas shift reactions, alkene combustion, and hydrogenation reactions.^{41–44} A recent theoretical study demonstrated that Rh-, Ag-, and Pt-based SACs promote homolytic splitting of H₂, thus generating H

necessary for thermo-catalytic hydrogenation reactions.⁴⁵ Similarly, Rh single atoms supported on TiO₂ exhibit high efficiency in CO₂ hydrogenation reaction, delivering excellent selectivity to CO and stability under reaction environments.^{35,36,46} Previous studies have shown that by changing the size of Rh metals from nanoparticles to single atoms over TiO₂, it is possible to steer the selectivity of CO₂ hydrogenation from CH₄ to CO highlighting the unique ability of SACs to tune selectivity.^{47,48} When compared to the other metal oxides, TiO₂-supported Rh is up to an order of magnitude more active than SiO₂- and Al₂O₃-supported Rh, making it one of the most active catalysts for CO₂ methanation.²⁴

Surface vacancies are not only common, but their presence on TiO₂ is also found to be crucial in stabilizing active metal catalyst particles (nanoclusters to single atoms). For instance, Hu et al. elucidated that oxygen-defective TiO₂-supported Ag SAC enhances dissociative H₂ adsorption through a heterolytic mechanism, wherein oxygen vacancies can be advantageously produced in the presence of Ag single atoms.⁴⁹ Similarly, previous experiments and theory combined studies have shown an enhanced thermal stability of Pt and Au SACs on the anatase/rutile TiO₂ surface with oxygen vacancies.^{50,51} Typically, oxygen vacancies (O_{vac}) on TiO₂ surfaces form when bridging oxygen reacts with H atoms of nearby OH groups, generating H₂O.^{52–57} It has been suggested that the TiO₂ surface is covered by OH groups under hydrogen-rich conditions (e. g. CO₂ hydrogenation conditions).^{52–57} Thus, it is anticipated that the surface OH groups play a significant role in the thermodynamic and kinetic stability of SACs formed on TiO₂.^{52–58}

The stability of TiO₂-supported SACs under H₂ reduction reaction conditions^{35,41} remains poorly understood despite their widespread catalytic applications,^{59,60} It is imperative to comprehend the stability/durability of SACs under reduction conditions before their potential technological applications as heterogeneous catalysts. Experimental techniques alone do not provide the atomistic picture of the structure composition of SACs. First principles

density functional theory (DFT) calculations provide an accurate description of the formation and breaking of bonds and thus represent a valuable approach for determining the structure and composition of SACs supported on metal oxides.^{61,62,63,64} In this contribution, we conducted a systematic DFT study to evaluate the thermodynamic and kinetic stability of Rh, Ag, Pt, and Au single atoms on oxygen-defective and hydroxylated rutile TiO₂ (110) surfaces, the thermodynamically most stable low-index surface of TiO₂,^{65,66} under reducing (CO₂ hydrogenation conditions). Pt shows the highest activation energies and diffusion times, making it the most stable, while Ag exhibits the lowest values and readily aggregates. Rh presents a unique case: although mobile once formed, the high cost of adatom formation and facile cluster fragmentation keep it dispersed. Au is unstable on defective surfaces but becomes significantly stabilized by hydroxylation, which increases both total activation energy and diffusion lifetimes. Hydrogen adsorption generally enhances mobility, but its impact is metal-dependent—stabilizing Rh while promoting aggregation of Ag, Au, and to a lesser extent Pt.

2. Computational Methods

2.1. DFT calculations

All results were obtained by performing spin-polarized periodic DFT computations using the Vienna Ab initio Simulation Package (VASP).^{67,68} The projector-augmented wave (PAW) pseudopotentials⁶⁹ were employed to account for interactions between atomic cores and valence electrons. Exchange-correlation energies were calculated using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.⁷⁰ To accurately describe the on-site Coulombic interactions of the 3d electrons in Ti within TiO₂, we employed the DFT+U formalism, where U represents the Hubbard-type correction.^{71,72} Based on previous literature, a U value of 3.5 eV was set for d electrons in Ti.^{73–77} The plane-wave energy cutoff was set at 500 eV, and the self-consistent convergence criterion was 1×10^{-6} .

⁵ eV for atomic position relaxation. Due to the large surface models, a Monkhorst-Pack ($1 \times 1 \times 1$) Γ -centered k-point grid was used for Brillouin zone sampling. The DFT-D3 dispersion correction scheme developed by Grimme et al. was employed to account for van der Waals (vdW) interactions.⁷⁸ Bader charge analysis was performed using the code from the Henkleman group at the University of Texas at Austin^{79,80} to evaluate the charge transfer from metal to oxide support for selected SACs. The climbing image nudged elastic band (CI-NEB) method was employed to locate the transition state of a reaction.⁸¹ Six images, including the initial state (IS) and final state (FS), were used in CI-NEB calculations.

2.2. Structural model of SACs

The rutile TiO_2 (110) surface was modeled as a periodic slab with 12 atomic layers (four tri-layers)³⁵ with a vacuum of ~ 20 Å between slabs along the z-axis. A 4×2 surface cell was utilized, with the bottom two tri-layers fixed at their bulk positions to mimic the bulk-like environment. Each tri-layer consists of 16 Ti and 32 O atoms. To assess the feasibility of single-atom adsorption on TiO_2 surfaces under oxygen-rich and oxygen-poor conditions, we calculated the system's chemical potential ($\mu(\text{System})$) using an approach described elsewhere³⁵ for two different SAC models: TiO_2 -supported ($\perp$) and substituted ($@$) SACs. In the former case, the metal single atom (SA) resides on the TiO_2 surface, while in the latter, the SA replaces a Ti atom in the topmost tri-layer of the $\text{TiO}_2(110)$ slab. Unless otherwise stated, $\text{M}\perp\text{TiO}_2$ and $\text{M}@\text{TiO}_2$ represent supported and substituted SACs on TiO_2 , respectively. To mimic oxygen-poor conditions, we modeled defective TiO_2 surfaces by introducing one- and two-surface oxygen vacancies at the bridging sites of two six-coordinated Ti atoms ($\text{Ti}_{6\text{C}}$) through the removal of 2-coordinated oxygen ($\text{O}_{2\text{C}}$) atoms from the surface. Previous studies have shown that $\text{O}_{2\text{C}}$ vacancies require relatively low formation energy^{82,83} and induce localized electron density on the adjacent Ti atoms, which can facilitate the stabilization of adsorbed metal species.⁸⁴

2.3. Stability assessment parameters

The chemical potential, $\mu(\text{System})$, for $\text{M}\perp\text{TiO}_{2-nx}$ and $\text{M}@\text{TiO}_{2-nx}$ can be determined using Equations (1) and (2), respectively, where 'n' represents the number of oxygen vacancies, ranging from 0 to 2.

$$\mu(\text{System}) = E(\text{M}\perp\text{TiO}_{2-nx}) + n\mu(\text{O}) - E(\text{TiO}_2) - E(\text{Bulk M}) \dots \dots \dots (1)$$

$$\mu(\text{System}) = E(\text{M}@\text{TiO}_{2-nx}) + \mu(\text{Ti}) + n\mu(\text{O}) - E(\text{TiO}_2) - E(\text{Bulk M}) \dots \dots \dots (2)$$

Here, $E(\text{M}\perp\text{TiO}_{2-nx})$, $E(\text{M}@\text{TiO}_{2-nx})$, $E(\text{TiO}_2)$, and $E(\text{Bulk M})$ are the DFT calculated total energies of $\text{M}\perp\text{TiO}_{2-nx}$, $\text{M}@\text{TiO}_{2-nx}$, bare TiO_2 surface, and bulk metals, respectively. $\mu(\text{O})$ and $\mu(\text{Ti})$ represent the chemical potential of the atomic O and Ti. $\mu(\text{O})$ and $E(\text{Bulk Ti})$ can be calculated by the following equations

$$\mu(\text{O}) = \frac{E(\text{O}_2)}{2} + \Delta\mu(\text{O}) \dots \dots \dots (3)$$

$$\mu(\text{Ti}) = E(\text{Bulk TiO}_2) - 2\mu(\text{O}) \dots \dots \dots (4)$$

where $E(\text{O}_2)$ and $E(\text{Bulk TiO}_2)$ are the total energies of isolated O_2 gas molecule and bulk TiO_2 , respectively. $\Delta\mu(\text{O})$ is the value of $\mu(\text{O})$ when using half of $E(\text{O}_2)$ as a zero reference, which depends on temperature T and oxygen partial pressure p_{O_2} , and can be calculated using⁸⁵

$$\Delta\mu(\text{O}) = \frac{H_{\text{O}_2}(\text{T},\text{p}) - H_{\text{O}_2}(\text{0K},\text{p}) - TS_{\text{O}_2}(\text{T},\text{p}) + TS_{\text{O}_2}(\text{0K},\text{p}) + k_B T \ln\left(\frac{p_{\text{O}_2}}{p^0}\right)}{2} \dots \dots \dots (5)$$

where various terms on the numerator of the right-hand side of Equation (5) represent the differences in enthalpy (H), entropy (TS) of an O_2 molecule relative to the $T = 0 \text{ K}$ limit, and their pressure dependence. k_B is the Boltzmann constant and p^0 denotes the standard pressure. Next, to determine the optimal hydroxylated TiO_2 structures, we have computed the free energy of various systems with different hydrogen coverages as a function of $\Delta\mu(\text{H})$:

$$\Delta G(\text{System}) = E(\text{System}/m\text{H}) - E(\text{System}) - m(\Delta\mu(\text{H})) - m(E(\text{H}_2)/2) \dots \dots \dots (6)$$

where $E(\text{System}/m\text{H})$, $E(\text{System})$, and m are energies of hydroxylated, bare TiO_2 structures, and the number of H atoms (coverage) attached with bridging O_{2c} atoms, respectively. The approach for determining $\Delta\mu(\text{H})$ follows a similar method to that for $\Delta\mu(\text{O})$. A detailed explanation of the equations used for computing the chemical potential of various systems is provided in the Supporting Information (SI).

The thermodynamic stability of metal single atoms on $\text{TiO}_{2-nx}/m\text{H}$ can be assessed through binding energy (BE) and formation energy (E_f) calculations,^{86,87} as described below:

$$\text{BE} = E(\text{M} \perp \text{TiO}_{2-nx}/m\text{H}) - E(\text{TiO}_{2-nx}/m\text{H}) - E(\text{M}_{\text{iso}}) \dots \dots \dots (7)$$

$$E_f = E(\text{M} \perp \text{TiO}_{2-nx}/m\text{H}) - E(\text{TiO}_{2-nx}/m\text{H}) - E(\text{M}_{\text{Bulk}}) \dots \dots \dots (8)$$

In Equations (7)-(8), $E(\text{M} \perp \text{TiO}_{2-nx}/m\text{H})$, $E(\text{TiO}_{2-nx}/m\text{H})$, $E(\text{M}_{\text{iso}})$, and $E(\text{M}_{\text{Bulk}})$ are the energies of $\text{TiO}_{2-nx}/m\text{H}$ with metal single atom, bare $\text{TiO}_{2-nx}/m\text{H}$ surface, isolated metal, and bulk metal atoms, respectively. Here, n and m denote the number of oxygen vacancies (0-2) and hydrogen coverage (1-8). Finally, to evaluate the kinetic stability of metal atoms at various sites, we calculated the diffusion energy for metal dimerization (E_d) and total activation energy (E_{total}).^{88,89} Using E_d , we also calculated the diffusion rate constant (k) and the corresponding characteristic diffusion time (τ) at 500 K temperature according to the following equation^{49,90}

$$k = \frac{1}{\tau} = \frac{k_B T}{h} \exp\left(-\frac{E_d}{k_B T}\right) \dots \dots \dots (9)$$

As highlighted by Li and co-workers,⁸⁹ ripening kinetics are governed not by diffusion alone but by the combined cost of adatom formation and migration. The resulting total activation energy ($E_{\text{total}} = E_f + E_d$) provides a more realistic descriptor of single-atom stability. Thus, a higher E_{total} exponentially suppresses the probability of single atoms detaching,

migrating, and encountering each other to form a dimer, thereby ensuring longer single-atom lifetimes. This E_{total} energy is defined as the sum of the formation energy (E_f) of two separated metal atoms on support ($*M*M$) and the diffusion barrier (E_d) required for dimer formation ($*M-M$) and is expressed as $E_{\text{total}} = E_f + E_d$. The E_f of $*M*M$ can be calculated by using:

$$E_f = \frac{E(*M * M \perp \text{TiO}_{2-\text{nx}}/\text{mH}) - E(\text{TiO}_{2-\text{nx}}/\text{mH}) - 2E(M_{\text{Bulk}})}{2} \dots \dots (10)$$

To assess the influence of H adsorption on metal dimerization, we extended the definition of total activation energy by including the Gibbs free energy of H adsorption ($\Delta G(\text{H})$). In this case, E_{total} is expressed as: $E_{\text{total}} = E_f + E_d + \Delta G(\text{H})$, where $\Delta G(\text{H})$ is the Gibbs free energy of H adsorption on the metal atom, which can be calculated as:

$$\Delta G(\text{H}) = E_{\text{H}}^{\text{ad}} - (m \times \Delta \mu(\text{H})) \dots \dots (11)$$

In equation (11), E_{H}^{ad} denotes the binding energy of H on the metal, m is the total number of H atoms coordinated to the metal adatom, and $\Delta \mu(\text{H})$ is the chemical potential of H, typically taken as -0.35 eV, corresponding to H_2 pressure of 0.1 atm at 500 K.³⁵ The expression for E_{H}^{ad} in the $*MH * MH \perp \text{TiO}_{2-\text{nx}}/\text{mH}$ system is given by:

$$E_{\text{H}}^{\text{ad}} = E(*MH * MH \perp \text{TiO}_{2-\text{nx}}/\text{mH}) - E(*M * M \perp \text{TiO}_{2-\text{nx}}/\text{mH}) - E(\text{H}_2) \dots (12)$$

In equation (12), $E(*M * M \perp \text{TiO}_{2-\text{nx}}/\text{mH})$ and $E(*MH * MH \perp \text{TiO}_{2-\text{nx}}/\text{mH})$ are the total energies of $\text{TiO}_{2-\text{nx}}/\text{mH}$ surface with two metal atoms adsorbed at distinct sites, in the absence and presence of H adsorption on each metal, respectively, and $E(\text{H}_2)$ is the energy of the H_2 molecule.⁸⁶

3. Results and Discussion

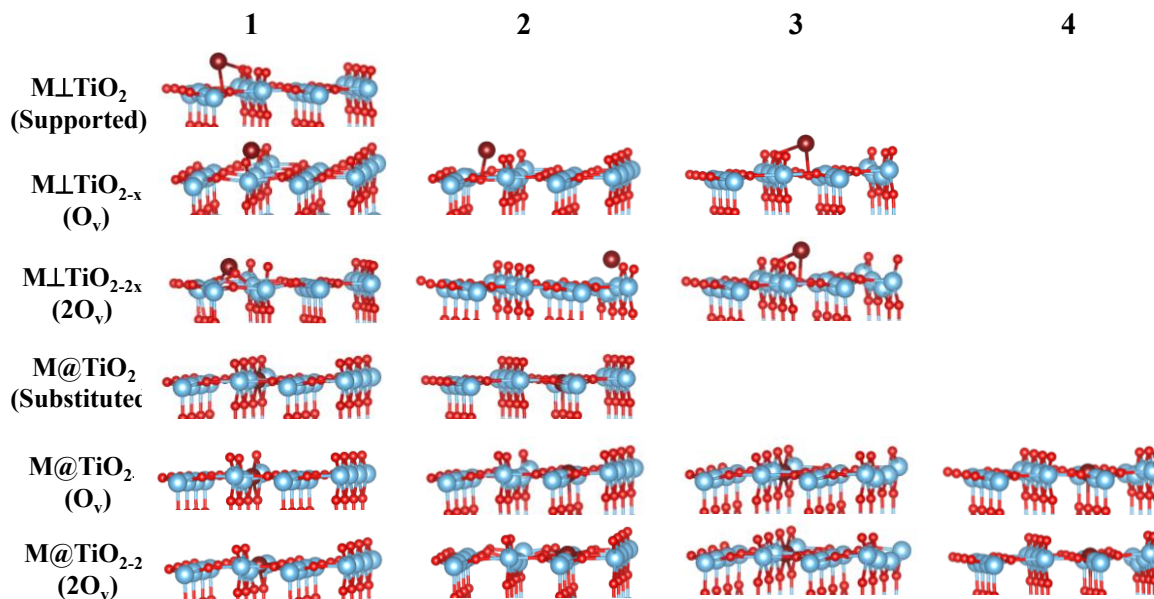


Figure 1. Plausible adsorption sites for TiO_2 -supported ($\perp$) and substituted ($@$) SACs are illustrated. Sites 1 to 4 indicate the possible adsorption locations for the metal atoms on the $\text{TiO}_2(110)$ surface. TiO_2 , TiO_{2-x} , and TiO_{2-2x} refer to pristine, one oxygen-deficient, and two oxygen-deficient TiO_2 surfaces, respectively. O–Red, Ti–Cyan, and M–Brown.

We first identified the most favourable adsorption sites for single-metal atoms on stoichiometric and oxygen vacancy-enriched TiO_2 surfaces. For $\text{M}\perp\text{TiO}_2$, only one adsorption site was found, where the metal interacts with both $\text{O}_{2\text{C}}$ and $\text{O}_{3\text{C}}$ oxygen atoms (Figure 1). In contrast, for $\text{M}@\text{TiO}_2$, two possible adsorption sites were identified, which correspond to the substitution of either six-coordinated Ti ($\text{Ti}_{6\text{C}}$) or four-coordinated Ti ($\text{Ti}_{4\text{C}}$) atoms by the metal atom. On the oxygen-deficient surfaces: $\text{M}\perp\text{TiO}_{2-x}$ and $\text{M}\perp\text{TiO}_{2-2x}$, we considered three potential adsorption sites: directly at the vacancy site, near the vacancy, or slightly away from the $\text{O}_{2\text{C}}$ vacancy (Figure 1). Similarly, for $\text{M}@\text{TiO}_{2-x}$ and $\text{M}@\text{TiO}_{2-2x}$, four adsorption sites were examined by removing nearby and distant $\text{O}_{2\text{C}}$ atoms from two different pristine $\text{M}@\text{TiO}_2$ configurations. The various adsorption sites are illustrated in Figure 1. For the $\text{M}@\text{TiO}_2$, we found that Rh and Pt preferentially replace six-coordinated $\text{Ti}_{6\text{C}}$, whereas Ag and Au favour substitution at the $\text{Ti}_{4\text{C}}$ site (Figures S1-S4). On the $\text{M}\perp\text{TiO}_2$ systems with one or two oxygen

vacancies, all metals, except Rh, prefer to occupy the oxygen vacancy site. However, Rh favours a nearby position (Site 1), which is consistent with previous research.³⁵ On the $M@TiO_{2-x}$ and $M@TiO_{2-2x}$ systems, Site 4 and Site 1 were found to be the most stable adsorption sites for all metal atoms, respectively. The optimized geometries and relative energies of various adsorption sites for all metals are presented in Figures S1–S4.

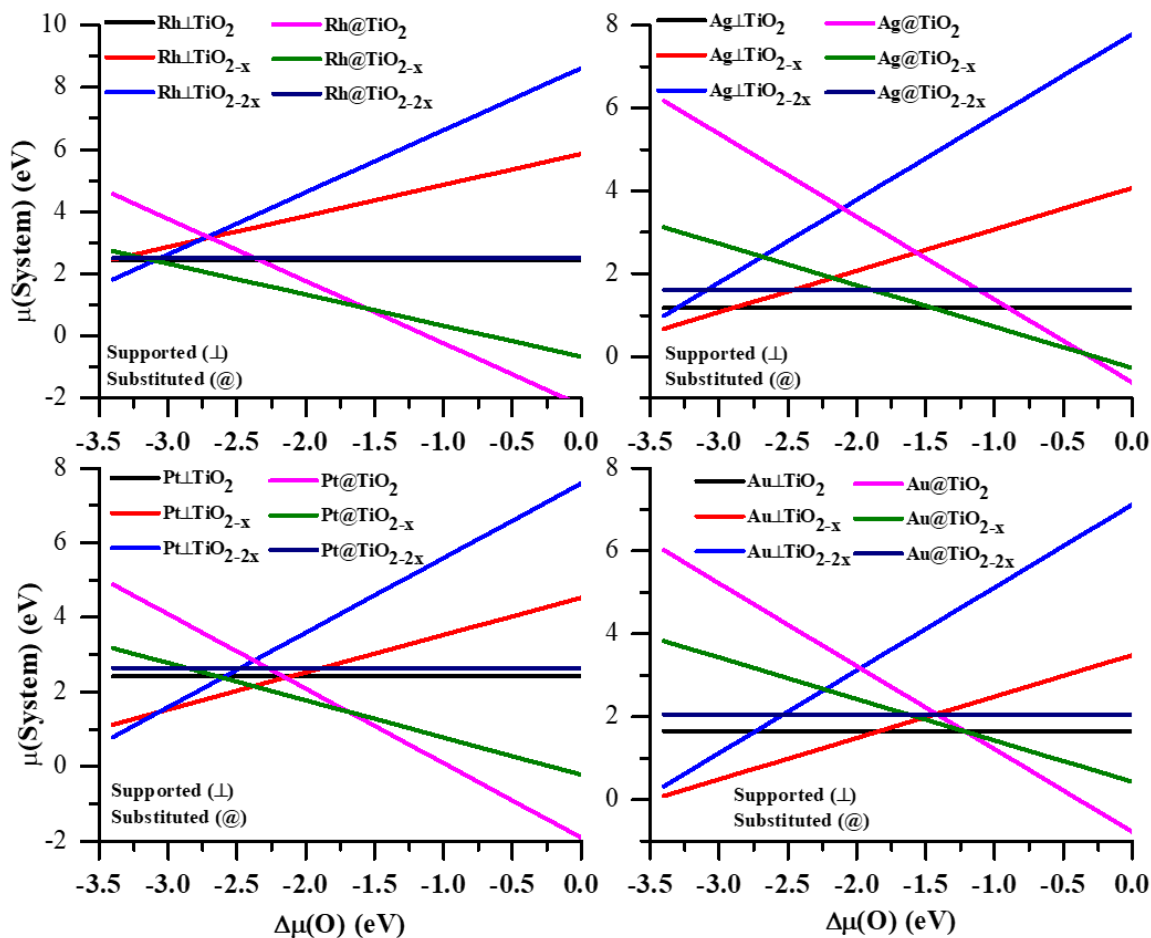


Figure 2. The relative stability of various single-atom catalysts (SACs) as a function of oxygen chemical potential $\Delta\mu(O)$.

Figure 2 presents the relative stability of SACs on pure and oxygen-deficient TiO_2 surfaces as a function of oxygen chemical potential ($\Delta\mu(O)$). The stability of SACs is determined by both their chemical potential, which correlates with the escaping tendency^{91,92} of metal atoms, and their binding energy (BE), which quantifies the strength of metal–support interactions. A higher chemical potential of the SACs (values in the y-axis in Figure 2)

corresponds to a greater escaping tendency, while a lower chemical potential suggests stronger thermodynamic stability. Figure 2 demonstrates that the thermodynamic stability of SACs also depends on oxygen chemical potential, which dictates whether a metal atom prefers a $M@TiO_2$ or $M\perp TiO_2$ configuration. Under oxygen-rich conditions (high μ of oxygen, $-1.0 \text{ eV} < \Delta\mu(O) < 0 \text{ eV}$), the $M@TiO_2$ configuration is thermodynamically the most favourable for all metals. This is because the TiO_2 lattice remains fully oxidized, at the same time, the O-rich condition indicates the Ti-poor conditions, which allow metal atoms to integrate into substitutional sites with strong metal-oxygen coordination, resulting in lower chemical potential (of the system) and enhanced stability. However, as the oxygen chemical potential decreases (oxygen-poor conditions), oxygen vacancies (O_{vac}) begin to form, destabilizing the $M@TiO_2$ and favouring the supported $M\perp TiO_2$ configuration. This transition is metal single atom-dependent and occurs at different $\Delta\mu(O)$ thresholds for each metal: For Rh on TiO_2 , $Rh\perp SAC$ is favourable until $\Delta\mu(O) < -3.2 \text{ eV}$, indicating that Rh remains stable in substitutional sites even under moderately reducing conditions but eventually transitions to a $Rh\perp TiO_2$ configuration at very low oxygen chemical potential. This trend is consistent with, but quantitatively shifted from, the results reported by Tang et al.³⁵, who found that substitutional Rh remains stable only until $\Delta\mu(O) = -2.6 \text{ eV}$, with a supported configuration becoming favourable at more reducing conditions. The slight discrepancy is likely due to the different Hubbard U parameters applied to the Ti 3d states, which affect both oxygen-vacancy formation energies and the relative energetics of metal incorporation. For Ag, the $Ag\perp TiO_2$ model becomes favourable up to the range of $\Delta\mu(O) < -1.5 \text{ eV}$, meaning Ag prefers surface adsorption much earlier than Rh as oxygen vacancies start to form. The results (Figure 2) show that $Pt\perp TiO_2$ is favourable below until $\Delta\mu(O) < -2.3 \text{ eV}$, showing that Pt follows a stability trend between Rh and Ag, favouring $M@TiO_2$ under mildly reducing conditions but transitioning to $M\perp TiO_2$ configurations at more negative $\Delta\mu(O)$. For Au on TiO_2 , $Au\perp TiO_2$, becomes favourable until $\Delta\mu(O) < -1.25 \text{ eV}$,

indicating that Au among all metals has the least potential to move from $M@TiO_2$ to $M\perp TiO_2$ configuration, with decreasing oxygen availability. As a result, metal atoms migrate to the surface, where they interact more favourably with exposed Ti atoms and oxygen vacancy sites, forming stabilized $M\perp TiO_{2-x}$. This effect is further corroborated by the computed binding energy (BE) trends in Figure 3; BE increases for $M\perp TiO_2$ SACs in oxygen-deficient conditions, confirming that vacancies provide stronger anchoring sites for single-metal atoms. While Rh and Pt exhibit strong MSI in both $M\perp TiO_2$ and $M@TiO_2$ configurations, they require highly reducing conditions (lower $\Delta\mu(O)$) before transitioning from the lattice/substitutional site to the surface site. In contrast, Ag and Au, which have inherently weaker metal–oxygen interactions, are much more destabilized by oxygen vacancies and migrate to $M\perp TiO_2$ configurations at higher oxygen chemical potentials (less negative $\Delta\mu(O)$).

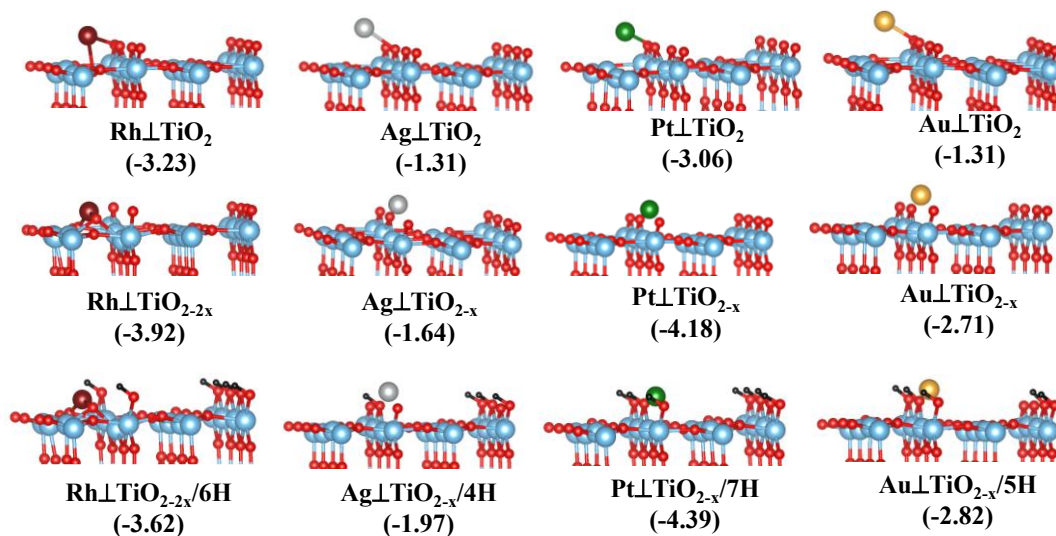
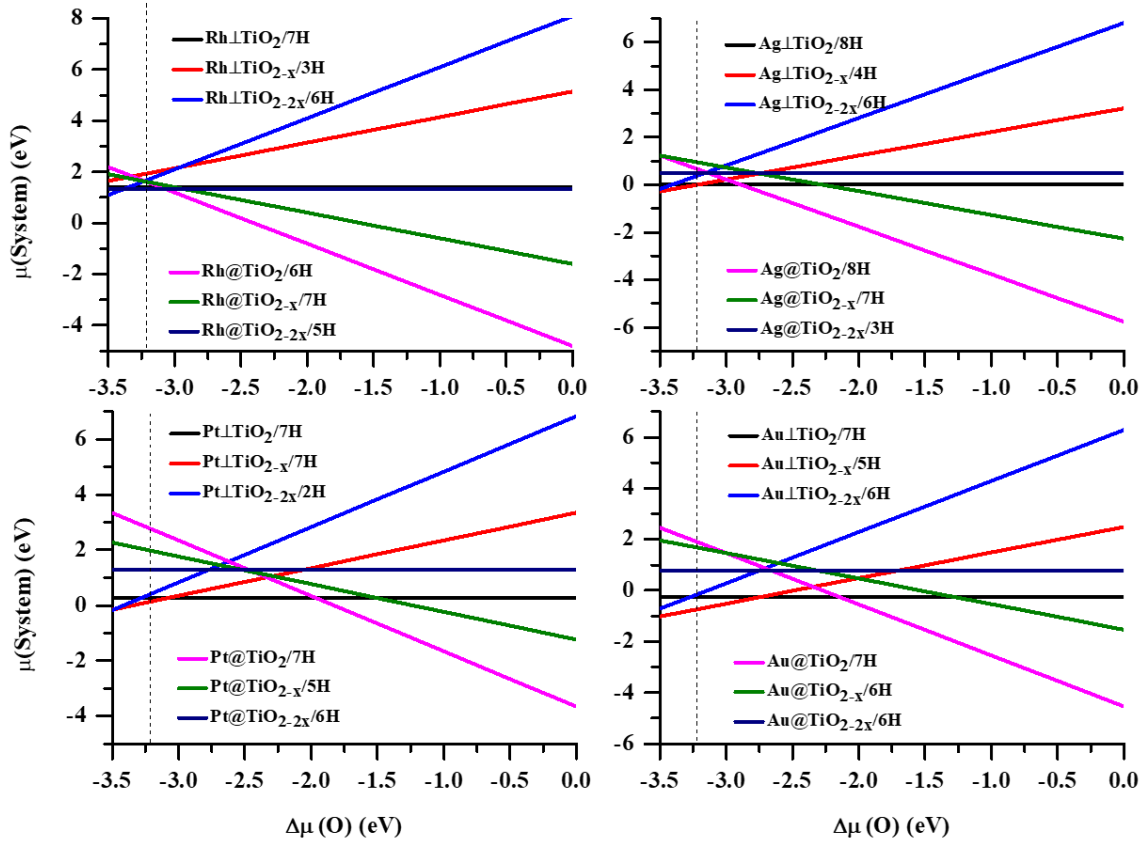


Figure 3. Thermodynamically most stable structures of Rh, Ag, Pt, and Au SACs on perfect, oxygen-defective, and hydroxylated TiO_2 surfaces. The values given in parentheses correspond to the binding energies (in eV) of metal atoms.



M ≡	Rh	Ag	Pt	Au
M⊥TiO ₂	7H (1.40)	8H (0.03)	7H (0.27)	7H (-0.27)
M⊥TiO _{2-x}	3H (1.92)	4H (-0.01)	7H (0.12)	5H (-0.74)
M⊥TiO _{2-2x}	6H (1.64)	6H (0.36)	5H (0.37)	6H (-0.18)
M@TiO ₂	6H (1.65)	8H (0.69)	7H (2.80)	7H (1.92)
M@TiO _{2-x}	7H (1.64)	7H (0.96)	7H (2.00)	6H (1.70)
M@TiO _{2-2x}	5H (1.35)	3H (0.50)	6H (1.31)	6H (0.79)

Figure 4. Relative stability of M⊥TiO₂ and M@TiO₂ (with hydroxylation) as a function of $\Delta\mu(\text{O})$ under a typical condition of H₂ reduction (H₂ pressure of 0.1 atm at 500 K, i.e. $\Delta\mu(\text{H}) = -0.35$ eV). The dashed line represents the specific condition corresponding to water formation equilibrium ($\Delta\mu(\text{H}) = -0.35$ eV and $\Delta\mu(\text{O}) = -3.23$ eV for 0.01% conversion). The DFT predicted optimal H coverages and total system chemical potential (μ_{system}) under above mentioned reduction condition have been supplied in the attached table.

The attached table in Figure 4 provides the DFT-optimized H coverage on various SACs formed on TiO₂ under hydrogen reduction conditions. The results illustrate how the H coverage on M⊥TiO₂ and M@TiO₂ SACs varies depending on the metal species and the presence of

oxygen vacancies. The optimal H coverages on TiO_2 for various systems were obtained from free energy changes of different coverages vs. $\Delta\mu(\text{H})$ plots, as shown in Figures S5-S8. Understanding these variations is important, as H coverage (presence of surface OH groups) influences the thermodynamic and kinetic stability of SACs by modifying the surface electronic properties, which also affects metal dispersion and MSI. Hydroxyl groups can stabilize isolated atoms and alter the catalytic performance of SACs compared to those supported on TiO_2 without surface OH groups. On the other hand, the presence of surface OH groups may also weaken metal binding, facilitating the migration of metal atoms to form larger metal clusters. The results in Figure 4 indicate that for both pristine $\text{M}\perp\text{TiO}_2$ and $\text{M}@\text{TiO}_2$ configurations, Ag shows the maximum coverage of 8H, while Rh and Pt prefer an H coverage of 7H. When an oxygen vacancy is introduced, the optimal H coverage decreases for $\text{Rh}\perp\text{TiO}_{2-x}$ and $\text{Ag}\perp\text{TiO}_{2-x}$, drastically to 3H and 4H, respectively. This sharp reduction suggests that vacancy formation significantly alters the adsorption environment and electronic structure of the Rh and Ag metals, likely due to charge redistribution and the rearrangement of hydrogen binding sites. For the $\text{M}@\text{TiO}_{2-x}$ configuration, almost all bridging O atoms are prone to hydroxylation, indicating a near-complete saturation of available sites.

DFT-based thermodynamic analysis on the stability of SACs was performed under a typical hydrogen reduction condition (H_2 pressure of 0.1 atm at 500 K, corresponding to $\Delta\mu(\text{H}) = -0.35$ eV).³⁵ Figure 4 plots the relative stability of SACs as a function of $\Delta\mu(\text{O})$. A crucial benchmark in this analysis is $\Delta\mu(\text{O}) = -3.23$ eV, which corresponds to the equilibrium condition for water formation. This value allows us to pinpoint the most favourable SAC structures under realistic catalytic conditions. At $\Delta\mu(\text{O}) = -3.23$ eV, Pt stabilizes in the $\text{Pt}\perp\text{TiO}_{2-x}/7\text{H}$ structure, where a single oxygen vacancy and seven hydroxyl groups contribute to the strongest MSI among all studied metals ($\text{BE} = -4.39$ eV). Compared to $\text{Pt}\perp\text{TiO}_{2-x}$ ($\text{BE} = -4.18$ eV), the increase in BE of $\text{Pt}\perp\text{TiO}_{2-x}/7\text{H}$ suggests that hydroxylation stabilizes Pt by modifying charge

transfer dynamics between the metal and the support. Ag prefers the $\text{Ag}\perp\text{TiO}_{2-x}/4\text{H}$ configuration (BE = -1.97 eV), and Au stabilizes in the $\text{Au}\perp\text{TiO}_{2-x}/5\text{H}$ structure (BE = -2.82 eV). The increase in BE compared to their non-hydroxylated counterparts ($\text{Ag}\perp\text{TiO}_{2-x}$: BE = -1.64 eV, and $\text{Au}\perp\text{TiO}_{2-x}$: BE = -2.71 eV) suggests that hydroxyl groups act as additional anchoring sites, compensating for the inherently weaker metal-TiO₂ interaction of these noble metals. Interestingly, Rh follows a different stability trend. At $\Delta\mu(\text{O}) = -3.23$ eV, the $\text{Rh@TiO}_{2-x}/5\text{H}$ remains more stable than the $\text{Rh}\perp\text{TiO}_{2-2x}/6\text{H}$ configuration. This suggests that under mildly reducing conditions, Rh prefers to remain incorporated into the TiO₂ lattice rather than migrate to surface O vacancy sites. However, as the environment becomes more reducing ($\Delta\mu(\text{O}) < -3.4$ eV), $\text{Rh}\perp\text{TiO}_{2-2x}/6\text{H}$ emerges as the most favourable structure, with a binding energy of -3.62 eV. This transition highlights that substitutional Rh possesses greater thermodynamic stability in moderate reducing environments. Its transition to a supported SAC structure at lower $\Delta\mu(\text{O})$ suggests a potential activation mechanism where Rh atoms gradually migrate to surface sites under highly reducing conditions. Overall, the results in Figure 4, in conjunction with Figure 3, establish that hydroxylation plays a crucial role in stabilizing Ag, Pt, and Au on TiO₂ support. Furthermore, our results predict that the presence of surface OH groups greatly influences the Rh single atom's transition from a substitutional to supported configuration in strongly reducing environments.

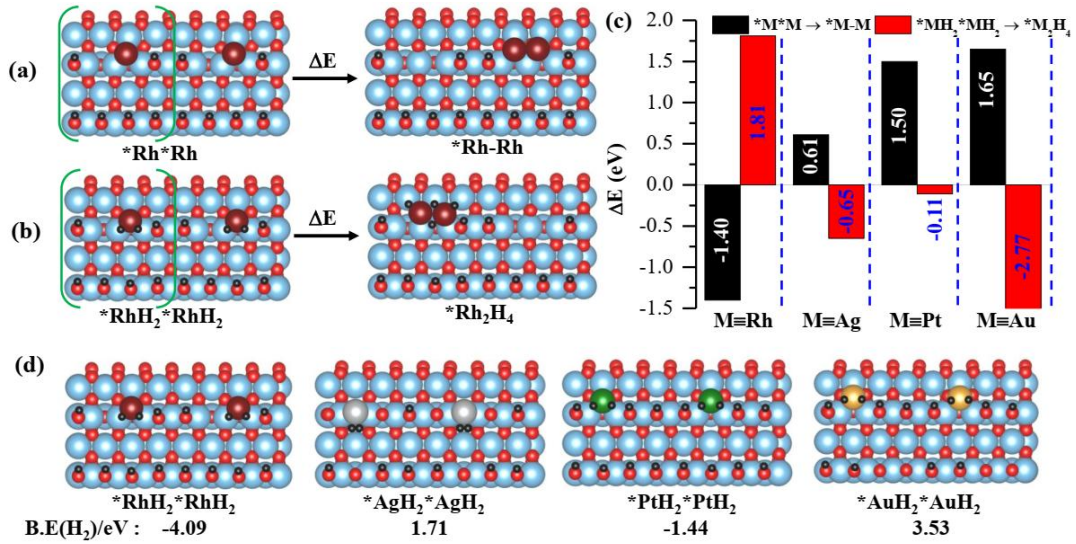


Figure 5. Dimerization energetics of Rh, Pt, Ag, and Au single atoms on hydroxylated and oxygen-deficient TiO₂(110). (a-b) Example of the dimerization pathway for Rh on TiO_{2-2x}/6H, modeled in a supercell doubled along the x direction, in the absence and presence of hydrogen ligands, where two *MH₂ units combine to form an *M₂H₄ dimer. (c) Calculated reaction energies (ΔE, eV) for dimerization of Rh, Pt, Ag, and Au in the absence (black) and presence (red) of H adsorption. (d) Optimized geometries of the most stable *MH₂*MH₂ species with the corresponding H₂ binding energies, BE(H₂).

Next, to assess the thermodynamic stability of metal atoms on hydroxylated, oxygen-deficient TiO₂ surfaces, we investigated the energy change associated with metal dimerization both in the absence and in the presence of H₂ ligands. Figure 5a illustrates the dimerization process for Rh on TiO_{2-x}/6H. To model this, we used a supercell doubled along the x direction, which allowed two isolated monomers (Rh⊥TiO_{2-x}/6H, Pt⊥TiO_{2-x}/7H, Ag⊥TiO_{2-x}/4H, and Au⊥TiO_{2-x}/5H) to be placed in proximity and then transformed into their corresponding dimeric structures, denoted as *M*M and *M-M in the figure (i.e., dimers without H adsorption). Figure 5b shows the analogous pathways with H adsorbed on the metal atoms, where *MH₂*MH₂ transitions to *M₂H₄ dimer. The computed dimerization energies ΔE are summarized in Figure 5c, and the optimized *MH₂*MH₂ geometries and H₂ binding energies (BE(H₂)) are displayed in Figure 5d. In the absence of H₂-adsorption on metal, dimerization is exothermic only for Rh (ΔE = -1.40 eV), indicating a strong thermodynamic driving force for

Rh aggregation on the $\text{TiO}_{2-x}/6\text{H}$ surface. In contrast, Pt and Au dimerization are highly endothermic ($\Delta E \approx +1.50$ to $+1.65$ eV), showing these metals are thermodynamically favoured to remain dispersed; Ag is moderately endothermic ($\Delta E \approx +0.61$ eV). Introducing H ligands dramatically alters these trends. For Rh, dimerization of the H_2 -ligated species becomes strongly endothermic ($\Delta E = +1.81$ eV): H_2 adsorption therefore stabilizes the $^*\text{RhH}_2^*\text{RhH}_2$ monomer relative to the $^*\text{Rh}_2\text{H}_4$ dimer and suppresses aggregation. We would like to note that H coverage was maintained while comparing the energetics of $^*\text{RhH}_2^*\text{RhH}_2$ vs. $^*\text{Rh}_2\text{H}_4$, even though the optimal number of H on Rh_2 may change once the Rh-Rh bond is formed. Pt changes sign and becomes marginally favourable for clustering upon H_2 coordination ($\Delta E = -0.11$ eV), implying that H ligation slightly promotes Pt dimerization. Ag and Au become notably exothermic in the H_2 -ligated case ($\Delta E = -0.65$ eV and -2.77 eV, respectively), indicating that hydrogen-related surface chemistry strongly facilitates aggregation for these two metals. The $\text{BE}(\text{H}_2)$ values given in Figure 5d rationalize these behaviors: H_2 binds most strongly to Rh (-4.09 eV), moderately to Pt (-1.44 eV), and is unfavourable for Ag and Au ($+1.71$ eV and $+3.53$ eV, respectively). The strong H binding on Rh explains why H ligation flips Rh dimerization from exothermic to endothermic. In the case of Pt, the moderate H binding — together with the H-induced displacement of Pt from its preferred vacancy site (see Figure 5d) — weakens the metal–support anchoring and increases Pt mobility, which helps clustering. For Ag and Au, the positive $\text{BE}(\text{H}_2)$ values indicate that direct H_2 adsorption on isolated atoms is not favourable. Nevertheless, when H is present on the hydrogenated support or when H-assisted surface chemistry occurs, the computed energetics show aggregation is favoured, suggesting indirect/cooperative H effects (e.g., H-assisted weakening of metal–support bonds or stabilization of metal–metal bonding) promoting the dimer formation. Overall, these results indicate that H_2 ligation stabilizes Rh single atoms but accelerates aggregation of Ag and Au and, to a lesser extent to Pt — a trend consistent with the dynamic, adsorbate-dependent site

stability reported for Rh/TiO₂ by Tang et al.³⁵ The additional optimized structures are shown in Figures S9–S10.

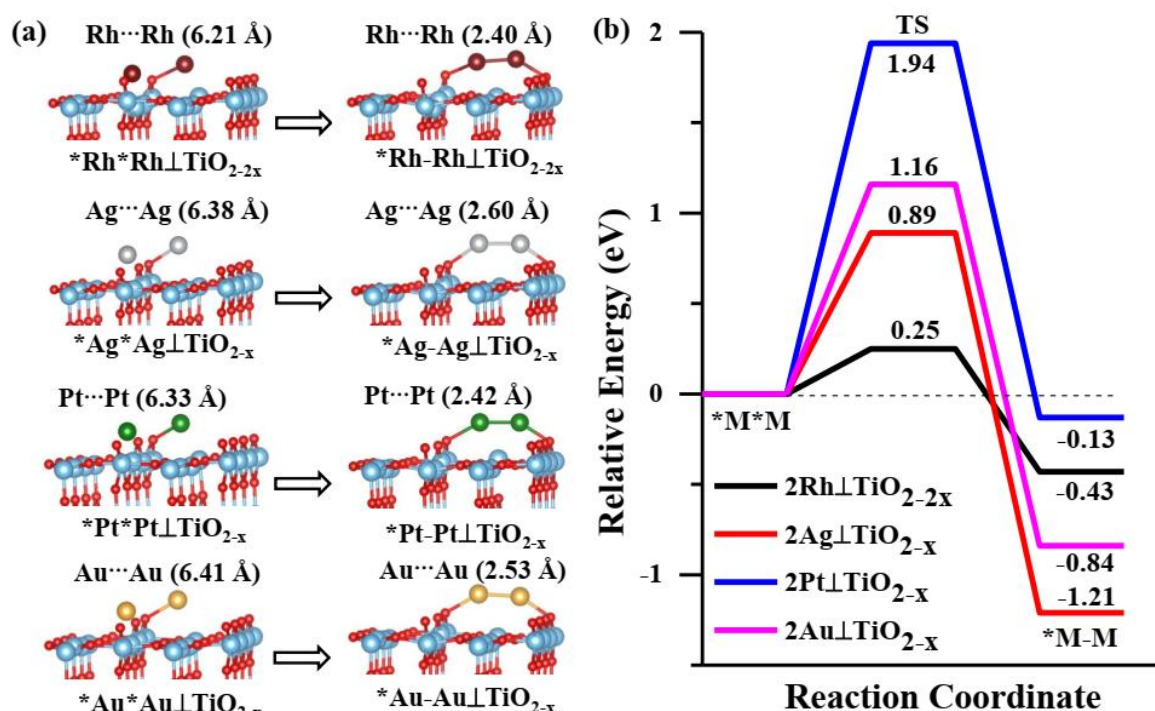


Figure 6. (a) Optimized geometries of isolated metal atoms (*M*M), dimer (*M-M), and (b) potential energy diagrams of metal dimerization on oxygen defective TiO₂ surface (2M⊥TiO_{2-x}, M= Rh, Ag, Pt and Au). The inset figure represents the global minimum structure of two separated Rh atoms on TiO_{2-2x}.

While Figure 5 establishes the thermodynamic driving forces for metal dimerization, it is equally important to evaluate the kinetic stability of isolated atoms, as sintering is governed by both thermodynamics and diffusion barriers. To this end, we computed the activation energies for metal migration leading to dimer formation (Figure 6). Because NEB calculations are computationally prohibitive for the large (doubled) supercell used in the thermodynamic analysis, the kinetic barriers were instead evaluated using a smaller 4×2 surface cell, where two metal atoms were placed at distinct adsorption sites. This approach allows us to probe the kinetic hurdles for dimerization on defective, hydroxylated, and H-liganded TiO₂ surfaces, providing a complementary picture to the thermodynamic results. In Figure 6, the initial state

(*M*M) consists of two isolated metal atoms placed at distinct positions: one at an oxygen vacancy site (defect site) and the other on a four-coordinate Ti atom. The optimized geometries of the initial, final, and intermediate structures of the metal dimerization process on defective TiO₂ surfaces are presented in Figures S11-S14. The choice of this configuration allows us to specifically probe the kinetic stability of metal atoms at defective sites before H exposure. The relative energy diagrams in Figure 6(b) reveal distinct trends in the kinetic stability of various SACs. Among all SACs, Pt exhibits the highest E_d (1.94 eV), followed by Au (1.16 eV), Ag (0.89 eV), and Rh (0.25 eV). The high E_d of Pt suggests strong MSI, making it kinetically stable and resistant to potential sintering. Rh exhibits the lowest E_d, suggesting high mobility and an increased likelihood of aggregation under reaction conditions.

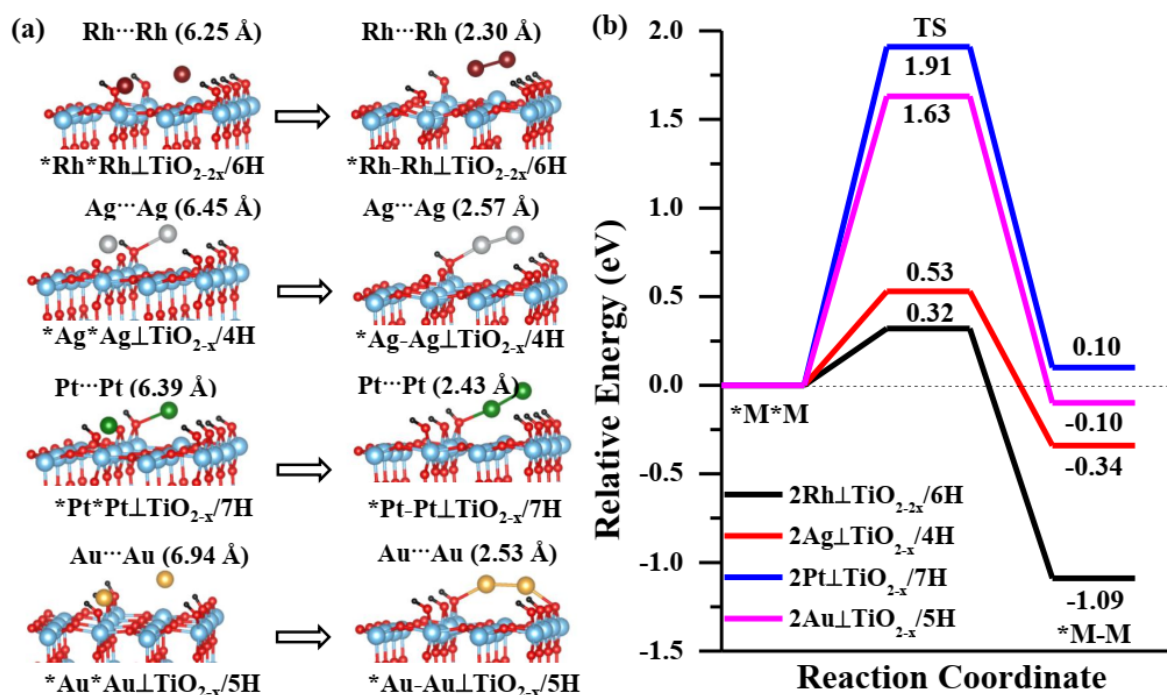


Figure 7. (a) Optimized geometries of isolated metal atoms (*M*M), dimer (*M-M), and (b) potential energy diagrams of metal dimerization on oxygen-defective hydroxylated TiO₂ surface (2M⊥TiO_{2-x}/nH, M= Rh, Ag, Pt and Au). The Inset figure represents the global minimum structure of two Rh atoms on TiO_{2-2x}/6H surface along the reaction coordinate of Rh migration.

The introduction of surface OH groups modifies both the kinetic stability and thermodynamic preference for metal aggregation by influencing the MSI and altering the adsorption environment. The most striking difference between Figures 6 and 7 is the increase in E_d especially for Au, upon hydroxylation, indicating that -OH groups serve as additional anchoring sites that further restrict metal mobility. For Ag, however, hydroxylation does not enhance kinetic stability as effectively—its E_d remains relatively low, indicating that Ag atoms can still migrate and potentially aggregate even in the presence of OH groups. While for Au, dimerization becomes more energy-demanding (1.63 eV) and less exothermic, indicating that hydroxylation introduces a stabilizing effect. In contrast, Pt dimerization remains endothermic, but with an even greater energetic penalty compared to configurations without surface OH groups (Figure 6), further reinforcing their preference for remaining as a single atomic state. The comparison between Figures 6 and 7 highlights that hydroxylation plays a dual role: for Pt, and Au, it enhances both kinetic and thermodynamic stability, reducing their tendency to migrate and aggregate. However, for Rh and Ag, hydroxylation provides limited kinetic stabilization and no significant thermodynamic benefit, meaning Rh and Ag remain highly prone to sintering even on a hydroxylated TiO_2 surface. From the comparison of Figures 5 and 7, we observe a consistent clustering behavior across both the large and small supercells under hydroxylated conditions. As in Figure 5, Pt and Au dimerization remains thermodynamically unfavourable, and Figure 7 further shows that their dimer formation requires substantial activation energy. In contrast, Ag and Rh dimerization follow the same tendencies on both small and extended surfaces, confirming that their aggregation pathways are intrinsic to the system rather than artifacts of cell size. These consistent results indicate that the present model reliably captures the aggregation behavior of late transition metals on oxygen-defective, hydroxylated TiO_2 surfaces.

Table 1. Characteristic diffusion times (τ , sec) for Rh, Ag, Pt, and Au on defective ($M\perp TiO_{2-nx}$), hydroxylated ($M\perp TiO_{2-nx}/mH$) and H-liganded ($MH\perp TiO_{2-nx}/mH$) TiO_2 surfaces.

	$M \equiv Rh$ $n=2$ $m=6$	$M \equiv Ag$ $n=1$ $m=4$	$M \equiv Pt$ $n=1$ $m=7$	$M \equiv Au$ $n=1$ $m=5$
$M\perp TiO_{2-nx}$	3.18×10^{-11}	8.93×10^{-5}	3.40×10^6	4.69×10^{-2}
$M\perp TiO_{2-nx}/mH$	1.61×10^{-10}	2.11×10^{-8}	1.69×10^6	2.56×10^3
$MH\perp TiO_{2-nx}/mH$	1.67×10^{-8}	2.07×10^{-9}	3.79×10^{-1}	2.07×10^{-9}

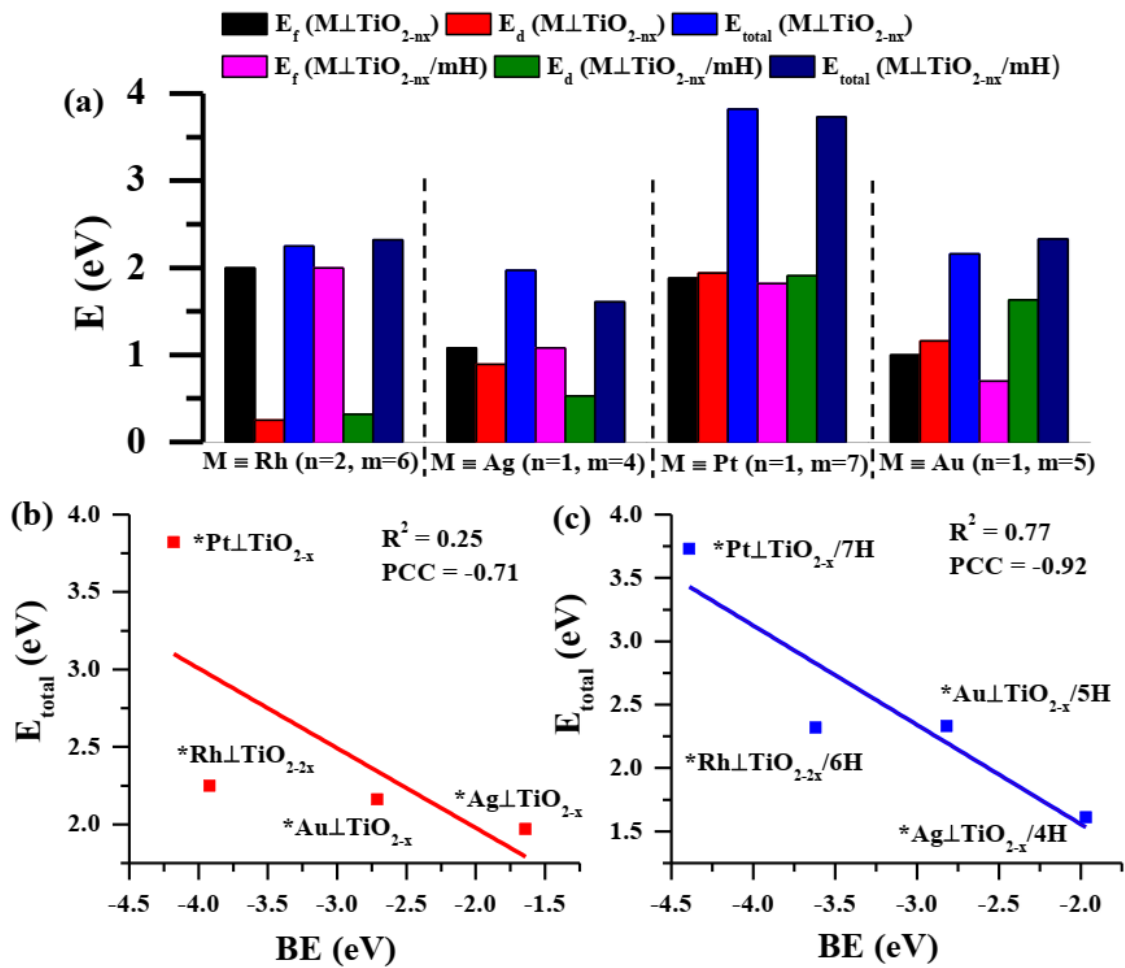


Figure 8. (a) Formation energies (E_f), diffusion barriers (E_d), and total activation energies (E_{total}), (b-c) Correlation between E_{total} (eV) and binding energy (BE) for Rh, Ag, Pt, and Au metals on defective ($M\perp TiO_{2-nx}$) and hydroxylated ($M\perp TiO_{2-nx}/mH$) surfaces..

Table 1 presents the calculated characteristic diffusion times (τ) of Rh, Ag, Pt, and Au atoms on oxygen-deficient and hydroxylated TiO_2 surfaces. The results highlight the different kinetic regimes that govern single-atom stability. Rh shows the lowest τ values among the four

metals, consistent with its small diffusion barrier ($E_d \approx 0.25$ eV, Fig. 6). However, Rh simultaneously exhibits a relatively large total activation energy (E_{total}), because the formation of mobile Rh adatoms is energetically costly. This indicates that the short τ of Rh mainly reflects its easy mobility once formed, while the high E_{total} underscores that the rate-limiting step is adatom formation rather than diffusion. In contrast, Au exhibits very short τ values on defective TiO_2 , but hydroxylation substantially increases τ by up to three orders of magnitude (10^3 s), showing that surface hydroxyls kinetically stabilize Au atoms against clustering. Pt consistently displays the largest τ values, on the order of 10^6 s, confirming its exceptional kinetic resistance to aggregation. Ag, on the other hand, shows τ values that remain short under both defective and hydroxylated conditions, underscoring its intrinsic instability. These findings align with the analysis of Wan et al.⁸⁸, where the total activation energy was identified as the decisive descriptor of sintering kinetics: although τ differs markedly for Rh and Au but E_{total} is dominated by the formation energy contribution in the case of Rh. Overall, Figures 8a emphasize that both E_d and E_f must be considered simultaneously, as their relative magnitudes dictate whether diffusion or formation controls the sintering process. Figure 8b-c establishes a moderate to strong correlation between E_{total} and the BE of SAC on TiO_2 , highlighting how MSI governs the kinetic stability. For oxygen-defective surfaces (Figure 8b), the Pearson correlation coefficient (PCC) is obtained as -0.71, indicates moderately strong negative correlation, where metals with higher BE, such as Pt and Rh, exhibit higher E_{total} , making them more resistant to aggregation. Conversely, Ag, with lower BE, has a significantly lower activation barrier, indicating higher mobility and a greater tendency to sinter and form a cluster. This correlation suggests that thermodynamic stability is a key predictor of kinetic resistance to migration. However, when hydroxylation is introduced (Figure 8c), the correlation becomes stronger. For Au, E_{total} increases, reflecting enhanced kinetic stability, whereas for Ag it decreases, consistent with its weak anchoring. The relative order of E_{total} before and after

hydroxylation is Pt (3.82 eV) > Rh (2.25 eV) > Au (2.16 eV) > Ag (1.97 eV) and Pt (3.73 eV) > Rh (2.33 eV) $\approx$ Au (2.32 eV) > Ag (1.61 eV), respectively. This comparison indicates that hydroxylation enhances the kinetic stability of Au, has only a minor effect on Rh and Pt, and does not stabilize Ag, while Pt remains the most stable metal irrespective of surface hydroxylation.

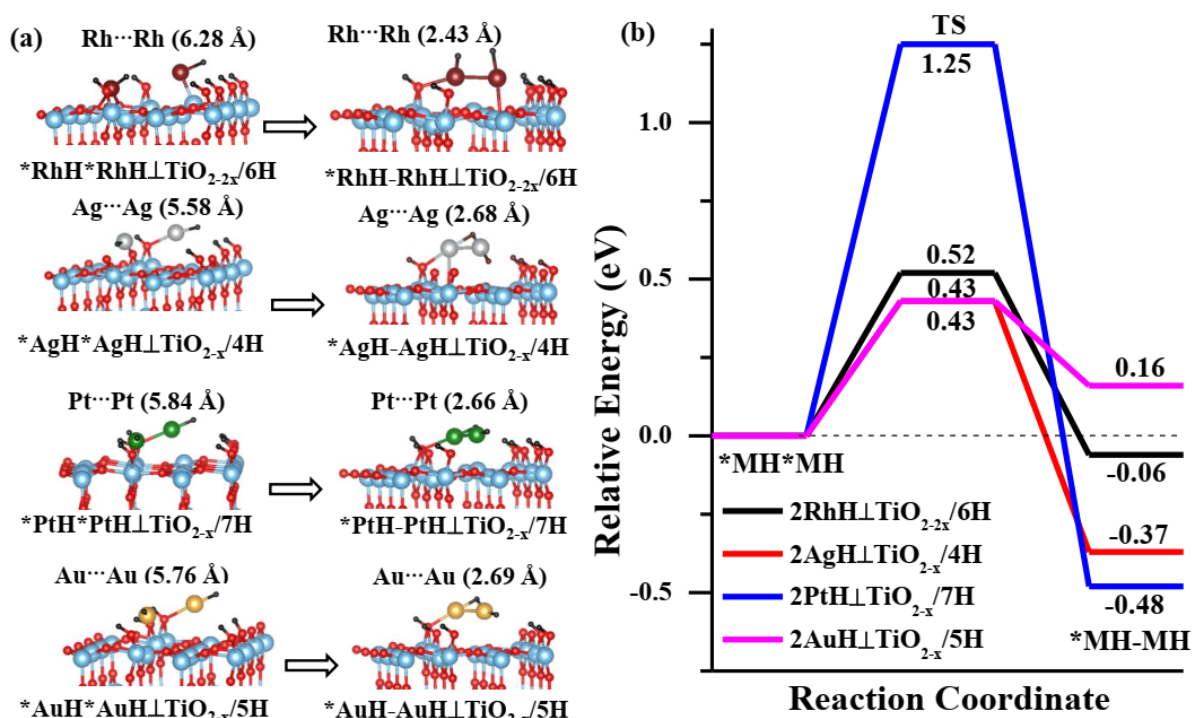


Figure 9. (a) Optimized geometries of isolated metal atoms (*M*M), dimer (*M-M), and (b) potential energy diagrams of metal dimerization on oxygen defective hydroxylated TiO₂ surface in presence of H-adsorption on metal (2MH $\perp$ TiO_{2-x}/nH, M = Rh, Ag, Pt and Au)).

The impact of H-ligands on the dimerization behavior/kinetic stability of SACs supported on oxygen-defective hydroxylated TiO₂ surfaces is shown in Figure 9a. Figure 9b shows the E_{act} for metal dimerization on hydroxylated TiO₂ surfaces in the presence of one H atom bound to each metal center. The corresponding optimized geometries of initial, final, and intermediate structures are presented in Figures S19-S22. The introduction of H-ligands on M provides insight into how H adsorption on metal further modifies metal mobility, electronic structure, and aggregation behavior. Compared with the H-free case (Figure 7), the diffusion

barriers change from 0.32 (Rh), 0.53 (Ag), 1.91 (Pt), and 1.63 eV (Au) to 0.52 (Rh), 0.43 (Ag), 1.25 (Pt), and 0.43 eV (Au) upon H adsorption. This indicates that, except for Rh, hydrogen ligation substantially decreases the kinetic barriers and facilitates dimerization. The effect is particularly strong for Au, where the barrier drops from 1.63 to 0.43 eV, making dimerization both kinetically and thermodynamically favourable. Ag also shows an appreciable reduction in barrier height, reinforcing its intrinsic tendency to sinter. For Pt, the barrier remains the highest among the four metals but is still reduced by ~ 0.7 eV relative to the H-free case. Interestingly, Rh behaves differently: its barrier increases slightly upon H adsorption, consistent with the thermodynamic results from the large supercell (Figure 5), where H_2 ligation stabilizes isolated Rh atoms. Overall, these findings confirm that H ligation accelerates aggregation of Ag and Au, and to a lesser extent Pt, while providing a stabilizing effect for Rh.

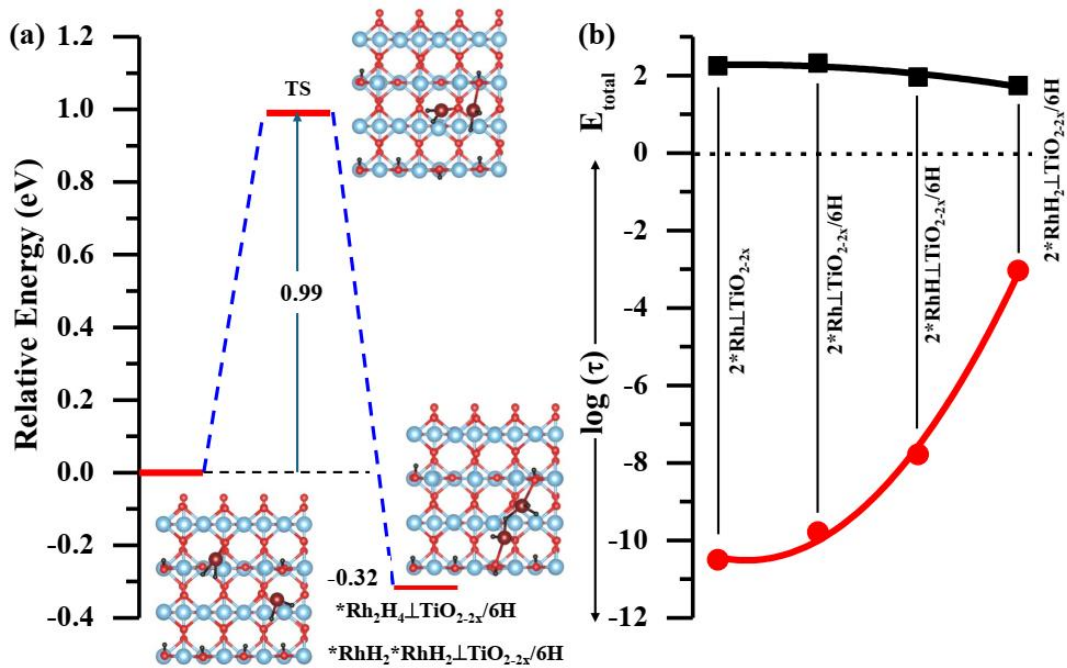


Figure 10. (a) Relative energy for Rh dimerization on oxygen-defective hydroxylated TiO_2 surface in presence of H_2 -adsorption on metal ($2 * RhH_2 \perp TiO_{2-x}/6H$) (b) Variation of total activation energy (E_{total} , eV, in black) and characteristic diffusion time (τ , sec^{-1} , in red) with increasing hydrogen concentration, from the H-free surface to hydroxylated TiO_2 and one- and two-H adsorbed Rh species.

Figure 10 highlights the unique behavior of Rh single atoms under increasing hydrogen coverage. In Figure 10(a), the E_{act} for Rh dimerization increases by nearly 1.0 eV upon H_2 adsorption, indicating that higher H-dosage progressively suppresses Rh mobility and disfavours aggregation. To further quantify this effect, Figure 10(b) presents the variation of total activation energy (E_{total}) and the corresponding characteristic diffusion time (τ) as a function of H_2 concentration. Interestingly, τ increases exponentially with hydrogen dosage, reflecting the strong kinetic stabilization of Rh under H-rich conditions. At the same time, E_{total} decreases because, for exothermic adsorption ($\Delta G(\text{H}_2) < 0$), the concentration of mobile adatoms increases exponentially and the effective activation energy is reduced, as predicted in the atomistic ripening framework by Li and co-workers.⁸⁹ This contrasting trend underscores the dual role of hydrogen: while it enhances the apparent diffusion probability by lowering E_{total} , it simultaneously prolongs the atomic residence time, thereby kinetically stabilizing isolated Rh atoms. Together with the thermodynamic insights from the large supercell, these results reveal that Rh maintains remarkable dispersion in H-rich environments, in sharp contrast to Ag, Au, and Pt, which tend to agglomerate when ligated with hydrogen (Figure 9).

4. Conclusions

Using first-principles density functional theory (DFT) calculations, we systematically studied the role of oxygen vacancies, hydroxylation, and H adsorption on the thermodynamic and kinetic stability of Pt, Rh, Ag, and Au SACs on TiO_2 . Two descriptors were employed: (i) the total activation energy (E_{total}), which reflects the combined cost of adatom formation and diffusion and is likely the driving force of Ostwald ripening kinetics, and (ii) the activation barrier (E_{act}), obtained from NEB calculations, which directly determines diffusion rate constants and characteristic diffusion times (τ). The E_{total} analysis shows the stability in the order $\text{Pt} > \text{Rh} \approx \text{Au} > \text{Ag}$, with hydroxylation markedly enhancing the kinetic protection of Au. Pt's large E_{total} indicates exceptional resistance to ripening, while Ag's low E_{total} highlights its

inherent instability. Rh represents a unique case where dimerization is thermodynamically favourable, yet E_{total} is dominated by a high formation energy; hence, Rh is kinetically hindered from sintering despite a low diffusion barrier. The τ results derived from E_{act} provide a complementary perspective on kinetic stability. Pt exhibits the longest diffusion times, Rh the shortest due to its small diffusion barrier, while Ag and Au show intermediate values that decrease rapidly with temperature. Importantly, hydroxylation extends the diffusion times of Au by several orders of magnitude, making it significantly more stable than on defective TiO_2 . Hydrogen ligation modifies these trends in a metal-specific fashion: stabilizing Rh but accelerating aggregation for Ag and Au, with Pt remaining comparatively resilient. Together, these insights highlight that the long-term stability of SACs on TiO_2 arises from the interplay of formation energetics, diffusion barriers, and adsorbate effects. Pt and hydroxylated Rh/Au emerge as the most promising candidates under hydrogen-rich conditions, whereas Ag may require alternative stabilization strategies such as dopants, alloying, or ligand coordination.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge.

It contains optimized geometries of SACs on $\text{TiO}_2(110)$, equations used to calculate chemical potentials, and plots of system chemical potential vs. $\Delta\mu(\text{H})$.

Acknowledgments

This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy (DOE) as part of the Accelerate Innovations in Emerging Technologies initiative FWP 101064. This work used computational resources at the San Diego Supercomputer Center (SDSC) and Texas Advanced Computing Center (TACC) The University of Texas at Austin through allocation CHE200036 from the

Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by National Science Foundation grants #2138259, #2138286, #2138307, #2137603, and #2138296. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a Department of Energy Office of Science User Facility using NERSC award BES-ERCAP27318. This research also used the Theory and Computation facility of the Center for Functional Nanomaterials (CFN), which is a US Department of Energy Office of Science User Facility at Brookhaven National Laboratory under Contract No. DE-SC0012704.

References

- (1) Kment, S.; Bakandritsos, A.; Tantis, I.; Kmentová, H.; Zuo, Y.; Henrotte, O.; Naldoni, A.; Otyepka, M.; Varma, R. S.; Zbořil, R. Single Atom Catalysts Based on Earth-Abundant Metals for Energy-Related Applications. *Chem Rev* **2024**, *124* (21), 11767–11847.
- (2) Cui, T.; Li, L.; Ye, C.; Li, X.; Liu, C.; Zhu, S.; Chen, W.; Wang, D. Heterogeneous Single Atom Environmental Catalysis: Fundamentals, Applications, and Opportunities. *Adv Funct Mater* **2022**, *32* (9), 2108381.
- (3) Wang, Y.; Mao, J.; Meng, X.; Yu, L.; Deng, D.; Bao, X. Catalysis with Two-Dimensional Materials Confining Single Atoms: Concept, Design, and Applications. *Chem Rev* **2018**, *119* (3), 1806–1854.
- (4) Chen, Y.; Lin, J.; Jia, B.; Wang, X.; Jiang, S.; Ma, T. Isolating Single and Few Atoms for Enhanced Catalysis. *Advanced materials* **2022**, *34* (39), 2201796.
- (5) Zhuo, H.-Y.; Zhang, X.; Liang, J.-X.; Yu, Q.; Xiao, H.; Li, J. Theoretical Understandings of Graphene-Based Metal Single-Atom Catalysts: Stability and Catalytic Performance. *Chem Rev* **2020**, *120* (21), 12315–12341.
- (6) Yan, H.; Su, C.; He, J.; Chen, W. Single-Atom Catalysts and Their Applications in Organic Chemistry. *J Mater Chem A Mater* **2018**, *6* (19), 8793–8814.
- (7) Chen, F.; Sun, Y.-J.; Huang, X.-T.; Bai, C.-W.; Zhang, Z.-Q.; Duan, P.-J.; Chen, X.-J.; Yang, Q.; Yu, H.-Q. Embedding Electronic Perpetual Motion into Single-Atom Catalysts for Persistent Fenton-like Reactions. *Proceedings of the National Academy of Sciences* **2024**, *121* (4), e2314396121.
- (8) Ghoshal, S.; Ghosh, A.; Roy, P.; Ball, B.; Pramanik, A.; Sarkar, P. Recent Progress in Computational Design of Single-Atom/Cluster Catalysts for Electrochemical and Solar-Driven N₂ Fixation. *ACS Catal* **2022**, *12* (24), 15541–15575.

- (9) Zhang, H.; Liu, G.; Shi, L.; Ye, J. Single-atom Catalysts: Emerging Multifunctional Materials in Heterogeneous Catalysis. *Adv Energy Mater* **2018**, *8* (1), 1701343.
- (10) Singh, B.; Sharma, V.; Gaikwad, R. P.; Fornasiero, P.; Zbořil, R.; Gawande, M. B. Single-atom Catalysts: A Sustainable Pathway for the Advanced Catalytic Applications. *Small* **2021**, *17* (16), 2006473.
- (11) Rong, H.; Ji, S.; Zhang, J.; Wang, D.; Li, Y. Synthetic Strategies of Supported Atomic Clusters for Heterogeneous Catalysis. *Nat Commun* **2020**, *11* (1), 5884.
- (12) Jeong, H.; Shin, S.; Lee, H. Heterogeneous Atomic Catalysts Overcoming the Limitations of Single-Atom Catalysts. *ACS Nano* **2020**, *14* (11), 14355–14374.
- (13) Wang, A.; Li, J.; Zhang, T. Heterogeneous Single-Atom Catalysis. *Nat Rev Chem* **2018**, *2* (6), 65–81.
- (14) Chen, Y.; Lin, J.; Li, L.; Qiao, B.; Liu, J.; Su, Y.; Wang, X. Identifying Size Effects of Pt as Single Atoms and Nanoparticles Supported on FeO_x for the Water-Gas Shift Reaction. *ACS Catal* **2018**, *8* (2), 859–868.
- (15) Liang, J.-X.; Yang, X.-F.; Wang, A.; Zhang, T.; Li, J. Theoretical Investigations of Non-Noble Metal Single-Atom Catalysis: Ni₁/FeO_x for CO Oxidation. *Catal Sci Technol* **2016**, *6* (18), 6886–6892.
- (16) Zhou, H.; Yang, X.; Wang, A.; Miao, S.; Liu, X.; Pan, X.; Su, Y.; Li, L.; Tan, Y.; Zhang, T. Pd/ZnO Catalysts with Different Origins for High Chemoselectivity in Acetylene Semi-Hydrogenation. *Chinese Journal of Catalysis* **2016**, *37* (5), 692–699.
- (17) Lang, R.; Du, X.; Huang, Y.; Jiang, X.; Zhang, Q.; Guo, Y.; Liu, K.; Qiao, B.; Wang, A.; Zhang, T. Single-Atom Catalysts Based on the Metal–Oxide Interaction. *Chem Rev* **2020**, *120* (21), 11986–12043.
- (18) Wang, L.; Zhang, W.; Wang, S.; Gao, Z.; Luo, Z.; Wang, X.; Zeng, R.; Li, A.; Li, H.; Wang, M. Atomic-Level Insights in Optimizing Reaction Paths for Hydroformylation Reaction over Rh/CoO Single-Atom Catalyst. *Nat Commun* **2016**, *7* (1), 14036.
- (19) Han, B.; Guo, Y.; Huang, Y.; Xi, W.; Xu, J.; Luo, J.; Qi, H.; Ren, Y.; Liu, X.; Qiao, B. Strong Metal–Support Interactions between Pt Single Atoms and TiO₂. *Angewandte Chemie International Edition* **2020**, *59* (29), 11824–11829.
- (20) Tian, S.; Gong, W.; Chen, W.; Lin, N.; Zhu, Y.; Feng, Q.; Xu, Q.; Fu, Q.; Chen, C.; Luo, J. Regulating the Catalytic Performance of Single-Atomic-Site Ir Catalyst for Biomass Conversion by Metal–Support Interactions. *ACS Catal* **2019**, *9* (6), 5223–5230.
- (21) Hu, P.; Huang, Z.; Amghouz, Z.; Makkee, M.; Xu, F.; Kapteijn, F.; Dikhtiarenko, A.; Chen, Y.; Gu, X.; Tang, X. Electronic Metal–Support Interactions in Single-atom Catalysts. *Angewandte Chemie International Edition* **2014**, *53* (13), 3418–3421.

- (22) Chen, L.; Unocic, R. R.; Hoffman, A. S.; Hong, J.; Braga, A. H.; Bao, Z.; Bare, S. R.; Szanyi, J. Unlocking the Catalytic Potential of TiO₂-Supported Pt Single Atoms for the Reverse Water–Gas Shift Reaction by Altering Their Chemical Environment. *JACS Au* **2021**, *1* (7), 977–986.
- (23) Yurtsever, A.; Fernández-Torre, D.; Onoda, J.; Abe, M.; Morita, S.; Sugimoto, Y.; Pérez, R. The Local Electronic Properties of Individual Pt Atoms Adsorbed on TiO₂ (110) Studied by Kelvin Probe Force Microscopy and First-Principles Simulations. *Nanoscale* **2017**, *9* (18), 5812–5821.
- (24) Solymosi, F.; Erdöhelyi, A. +; Bánsági, T. Methanation of CO₂ on Supported Rhodium Catalyst. *J Catal* **1981**, *68* (2), 371–382.
- (25) Pereira-Hernández, X. I.; DeLaRiva, A.; Muravev, V.; Kunwar, D.; Xiong, H.; Sudduth, B.; Engelhard, M.; Kovarik, L.; Hensen, E. J. M.; Wang, Y. Tuning Pt–CeO₂ Interactions by High-Temperature Vapor-Phase Synthesis for Improved Reducibility of Lattice Oxygen. *Nat Commun* **2019**, *10* (1), 1358.
- (26) Ma, Y.; Chi, B.; Liu, W.; Cao, L.; Lin, Y.; Zhang, X.; Ye, X.; Wei, S.; Lu, J. Tailoring of the Proximity of Platinum Single Atoms on CeO₂ Using Phosphorus Boosts the Hydrogenation Activity. *ACS Catal* **2019**, *9* (9), 8404–8412.
- (27) Wang, Y.; Arandiyán, H.; Scott, J.; Aguey-Zinsou, K.-F.; Amal, R. Single Atom and Nanoclustered Pt Catalysts for Selective CO₂ Reduction. *ACS Appl Energy Mater* **2018**, *1* (12), 6781–6789.
- (28) Ni, S.; Zhang, H.; Zhao, Y.; Li, X.; Sun, Y.; Qian, J.; Xu, Q.; Gao, P.; Wu, D.; Kato, K. Single Atomic Ag Enhances the Bifunctional Activity and Cycling Stability of MnO₂. *Chemical Engineering Journal* **2019**, *366*, 631–638.
- (29) Lang, R.; Xi, W.; Liu, J.-C.; Cui, Y.-T.; Li, T.; Lee, A. F.; Chen, F.; Chen, Y.; Li, L.; Li, L. Non Defect-Stabilized Thermally Stable Single-Atom Catalyst. *Nat Commun* **2019**, *10* (1), 234.
- (30) Chen, W.; Ma, Y.; Li, F.; Pan, L.; Gao, W.; Xiang, Q.; Shang, W.; Song, C.; Tao, P.; Zhu, H. Strong Electronic Interaction of Amorphous Fe₂O₃ Nanosheets with Single-atom Pt toward Enhanced Carbon Monoxide Oxidation. *Adv Funct Mater* **2019**, *29* (42), 1904278.
- (31) Serp, P.; Minh, D. P. *Supported Metal Single Atom Catalysis*; John Wiley & Sons, 2022.
- (32) Qi, K.; Chhowalla, M.; Voiry, D. Single Atom Is Not Alone: Metal–Support Interactions in Single-Atom Catalysis. *Materials Today* **2020**, *40*, 173–192.
- (33) Li, R.; Luo, L.; Ma, X.; Wu, W.; Wang, M.; Zeng, J. Single Atoms Supported on Metal Oxides for Energy Catalysis. *J Mater Chem A Mater* **2022**, *10* (11), 5717–5742.
- (34) Lang, R.; Du, X.; Huang, Y.; Jiang, X.; Zhang, Q.; Guo, Y.; Liu, K.; Qiao, B.; Wang, A.; Zhang, T. Single-Atom Catalysts Based on the Metal–Oxide Interaction. *Chem Rev* **2020**, *120* (21), 11986–12043.

- (35) Tang, Y.; Asokan, C.; Xu, M.; Graham, G. W.; Pan, X.; Christopher, P.; Li, J.; Sautet, P. Rh Single Atoms on TiO₂ Dynamically Respond to Reaction Conditions by Adapting Their Site. *Nat Commun* **2019**, *10* (1), 4488.
- (36) Ma, S.; Song, W.; Liu, B.; Zheng, H.; Deng, J.; Zhong, W.; Liu, J.; Gong, X.-Q.; Zhao, Z. Elucidation of the High CO₂ Reduction Selectivity of Isolated Rh Supported on TiO₂: A DFT Study. *Catal Sci Technol* **2016**, *6* (15), 6128–6136.
- (37) Hu, G.; Wu, Z.; Jiang, D. First Principles Insight into H₂ Activation and Hydride Species on TiO₂ Surfaces. *The Journal of Physical Chemistry C* **2018**, *122* (35), 20323–20328.
- (38) Ghoshal, S.; Roy, P.; Pramanik, A.; Sarkar, P. Ru/Rh Catalyzed Selective Hydrogenation of CO₂ to Formic Acid: A First Principles Microkinetics Analysis. *Catal Sci Technol* **2022**, *12* (23), 7219–7232.
- (39) Rivera-Cárcamo, C.; Scarfiello, C.; García, A. B.; Tison, Y.; Martinez, H.; Baaziz, W.; Ersen, O.; Le Berre, C.; Serp, P. Stabilization of Metal Single Atoms on Carbon and TiO₂ Supports for CO₂ Hydrogenation: The Importance of Regulating Charge Transfer. *Adv Mater Interfaces* **2021**, *8* (8), 2001777.
- (40) Li, R.; Li, T.; Zhou, Q. Impact of Titanium Dioxide (TiO₂) Modification on Its Application to Pollution Treatment—a Review. *Catalysts* **2020**, *10* (7), 804.
- (41) Li, Q.; Yan, G.; Vlachos, D. G. Theoretical Insights into H₂ Activation over Anatase TiO₂ Supported Metal Adatoms. *ACS Catal* **2024**, *14* (2), 886–896.
- (42) Jin, C.; Dai, Y.; Wei, W.; Ma, X.; Li, M.; Huang, B. Effects of Single Metal Atom (Pt, Pd, Rh and Ru) Adsorption on the Photocatalytic Properties of Anatase TiO₂. *Appl Surf Sci* **2017**, *426*, 639–646.
- (43) Wang, X.; Zhang, L.; Bu, Y.; Sun, W. Interplay between Invasive Single Atom Pt and Native Oxygen Vacancy in Rutile TiO₂ (110) Surface: A Theoretical Study. *Nano Res* **2022**, *15* (1), 669–676.
- (44) Li, L.; Li, W.; Zhu, C.; Mao, L.-F. A DFT+ U Study about Agglomeration of Au Atoms on Reduced Surface of Rutile TiO₂ (110). *Mater Chem Phys* **2021**, *271*, 124944.
- (45) Li, Q.; Yan, G.; Vlachos, D. G. Theoretical Insights into H₂ Activation over Anatase TiO₂ Supported Metal Adatoms. *ACS Catal* **2024**, *14* (2), 886–896.
- (46) Doherty, F.; Goldsmith, B. R. Rhodium Single-Atom Catalysts on Titania for Reverse Water Gas Shift Reaction Explored by First Principles Mechanistic Analysis and Compared to Nanoclusters. *ChemCatChem* **2021**, *13* (13), 3155–3164.
- (47) Karelovic, A.; Ruiz, P. Mechanistic Study of Low Temperature CO₂ Methanation over Rh/TiO₂ Catalysts. *J Catal* **2013**, *301*, 141–153.
- (48) Yang, Y.; Liu, J.; Liu, F.; Wu, D. Reaction Mechanism of CO₂ Methanation over Rh/TiO₂ Catalyst. *Fuel* **2020**, *276*, 118093.

- (49) Hu, J.; Kim, E. M.; Janik, M. J.; Alexopoulos, K. Hydrogen Activation and Spillover on Anatase TiO₂-Supported Ag Single-Atom Catalysts. *The Journal of Physical Chemistry C* **2022**, *126* (17), 7482–7491.
- (50) Thang, H. V.; Pacchioni, G.; DeRita, L.; Christopher, P. Nature of Stable Single Atom Pt Catalysts Dispersed on Anatase TiO₂. *J Catal* **2018**, *367*, 104–114.
- (51) Wu, Z.; Hwang, I.; Cha, G.; Qin, S.; Tomanec, O.; Badura, Z.; Kment, S.; Zboril, R.; Schmuki, P. Optimized Pt Single Atom Harvesting on TiO₂ Nanotubes—Towards a Most Efficient Photocatalyst. *Small* **2022**, *18* (2), 2104892.
- (52) Kowalski, P. M.; Meyer, B.; Marx, D. Composition, Structure, and Stability of the Rutile TiO₂ (110) Surface: Oxygen Depletion, Hydroxylation, Hydrogen Migration, and Water Adsorption. *Physical Review B—Condensed Matter and Materials Physics* **2009**, *79* (11), 115410.
- (53) Wendt, S.; Matthiesen, J.; Schaub, R.; Vestergaard, E. K.; Lægsgaard, E.; Besenbacher, F.; Hammer, B. Formation and Splitting of Paired Hydroxyl Groups on Reduced TiO₂ (110). *Phys Rev Lett* **2006**, *96* (6), 066107.
- (54) Schaub, R.; Thostrup, P.; Lopez, N.; Lægsgaard, E.; Stensgaard, I.; Nørskov, J. K.; Besenbacher, F. Oxygen Vacancies as Active Sites for Water Dissociation on Rutile TiO₂ (110). *Phys Rev Lett* **2001**, *87* (26), 266104.
- (55) Kunat, M.; Burghaus, U.; Wöll, C. The Adsorption of Hydrogen on the Rutile TiO₂ (110) Surface. *Physical Chemistry Chemical Physics* **2004**, *6* (16), 4203–4207.
- (56) Suzuki, S.; Fukui, K.; Onishi, H.; Iwasawa, Y. Hydrogen Adatoms on TiO₂ (110)–(1× 1) Characterized by Scanning Tunneling Microscopy and Electron Stimulated Desorption. *Phys Rev Lett* **2000**, *84* (10), 2156.
- (57) Bikondoa, O.; Pang, C. L.; Ithnin, R.; Muryn, C. A.; Onishi, H.; Thornton, G. Direct Visualization of Defect-Mediated Dissociation of Water on TiO₂ (110). *Nat Mater* **2006**, *5* (3), 189–192.
- (58) Yin, X.; Calatayud, M.; Qiu, H.; Wang, Y.; Birkner, A.; Minot, C.; Wöll, C. Diffusion versus Desorption: Complex Behavior of H Atoms on an Oxide Surface. *ChemPhysChem* **2008**, *9* (2), 253–256.
- (59) Zhang, W.; Fu, Q.; Luo, Q.; Sheng, L.; Yang, J. Understanding Single-Atom Catalysis in View of Theory. *JACS Au* **2021**, *1* (12), 2130–2145.
- (60) Li, L.; Chang, X.; Lin, X.; Zhao, Z.-J.; Gong, J. Theoretical Insights into Single-Atom Catalysts. *Chem Soc Rev* **2020**, *49* (22), 8156–8178.
- (61) Wan, J.; Chen, W.; Jia, C.; Zheng, L.; Dong, J.; Zheng, X.; Wang, Y.; Yan, W.; Chen, C.; Peng, Q. Defect Effects on TiO₂ Nanosheets: Stabilizing Single Atomic Site Au and Promoting Catalytic Properties. *Advanced Materials* **2018**, *30* (11), 1705369.

- (62) Chang, T.-Y.; Tanaka, Y.; Ishikawa, R.; Toyoura, K.; Matsunaga, K.; Ikuhara, Y.; Shibata, N. Direct Imaging of Pt Single Atoms Adsorbed on TiO₂ (110) Surfaces. *Nano Lett* **2014**, *14* (1), 134–138.
- (63) Thang, H. V.; Pacchioni, G.; DeRita, L.; Christopher, P. Nature of Stable Single Atom Pt Catalysts Dispersed on Anatase TiO₂. *J Catal* **2018**, *367*, 104–114.
- (64) Addou, R.; Senftle, T. P.; O'Connor, N.; Janik, M. J.; Van Duin, A. C. T.; Batzill, M. Influence of Hydroxyls on Pd Atom Mobility and Clustering on Rutile TiO₂ (011)-2×1. *ACS Nano* **2014**, *8* (6), 6321–6333.
- (65) Ranade, M. R.; Navrotsky, A.; Zhang, H. Z.; Banfield, J. F.; Elder, S. H.; Zaban, A.; Borse, P. H.; Kulkarni, S. K.; Doran, G. S.; Whitfield, H. J. Energetics of Nanocrystalline TiO₂. *Proceedings of the National Academy of Sciences* **2002**, *99* (suppl_2), 6476–6481.
- (66) Ramamoorthy, M.; Vanderbilt, D.; King-Smith, R. D. First-Principles Calculations of the Energetics of Stoichiometric TiO₂ Surfaces. *Phys Rev B* **1994**, *49* (23), 16721.
- (67) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys Rev B* **1996**, *54* (16), 11169.
- (68) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput Mater Sci* **1996**, *6* (1), 15–50.
- (69) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys Rev B* **1999**, *59* (3), 1758.
- (70) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys Rev Lett* **1996**, *77* (18), 3865.
- (71) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+ U Study. *Phys Rev B* **1998**, *57* (3), 1505.
- (72) Anisimov, V. I.; Aryasetiawan, F.; Lichtenstein, A. I. First-Principles Calculations of the Electronic Structure and Spectra of Strongly Correlated Systems: The LDA+ U Method. *Journal of Physics: Condensed Matter* **1997**, *9* (4), 767.
- (73) Zhang, D.; Yang, M.; Dong, S. Hydroxylation of the Rutile TiO₂ (110) Surface Enhancing Its Reducing Power for Photocatalysis. *The Journal of Physical Chemistry C* **2015**, *119* (3), 1451–1456.
- (74) Zhao, Y.; Hou, T.; Li, Y.; Chan, K. S.; Lee, S.-T. Effective Increasing of Optical Absorption of TiO₂ by Introducing Trivalent Titanium. *Appl Phys Lett* **2013**, *102* (17).
- (75) Hu, G.; Wu, Z.; Jiang, D. First Principles Insight into H₂ Activation and Hydride Species on TiO₂ Surfaces. *The Journal of Physical Chemistry C* **2018**, *122* (35), 20323–20328.

- (76) Liu, J.-Y.; Gong, X.-Q.; Alexandrova, A. N. Mechanism of CO₂ Photocatalytic Reduction to Methane and Methanol on Defected Anatase TiO₂ (101): A Density Functional Theory Study. *The Journal of Physical Chemistry C* **2019**, *123* (6), 3505–3511.
- (77) Haa, M.-A.; Alexandrova, A. N. Oxygen Vacancies of Anatase (101): Extreme Sensitivity to the Density Functional Theory Method. *J Chem Theory Comput* **2016**, *12* (6), 2889–2895.
- (78) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J Chem Phys* **2010**, *132* (15).
- (79) Tang, W.; Sanville, E.; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias. *Journal of Physics: Condensed Matter* **2009**, *21* (8), 084204.
- (80) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. Improved Grid-based Algorithm for Bader Charge Allocation. *J Comput Chem* **2007**, *28* (5), 899–908.
- (81) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J Chem Phys* **2000**, *113* (22), 9901–9904.
- (82) Matsunaga, K.; Tanaka, Y.; Toyoura, K.; Nakamura, A.; Ikuhara, Y.; Shibata, N. Existence of Basal Oxygen Vacancies on the Rutile TiO₂ (110) Surface. *Phys Rev B* **2014**, *90* (19), 195303.
- (83) Wang, F.; Wei, S.; Zhang, Z.; Patzke, G. R.; Zhou, Y. Oxygen Vacancies as Active Sites for H₂S Dissociation on the Rutile TiO₂ (110) Surface: A First-Principles Study. *Physical Chemistry Chemical Physics* **2016**, *18* (9), 6706–6712.
- (84) Morgan, B. J.; Watson, G. W. A DFT+ U Description of Oxygen Vacancies at the TiO₂ Rutile (1 1 0) Surface. *Surf Sci* **2007**, *601* (21), 5034–5041.
- (85) Reuter, K.; Scheffler, M. Composition and Structure of the RuO₂ (110) Surface in an O₂ and CO Environment: Implications for the Catalytic Formation of CO₂. *Phys Rev B* **2003**, *68* (4), 045407.
- (86) Lv, X.; Wei, W.; Huang, B.; Dai, Y.; Frauenheim, T. High-Throughput Screening of Synergistic Transition Metal Dual-Atom Catalysts for Efficient Nitrogen Fixation. *Nano Lett* **2021**, *21* (4), 1871–1878.
- (87) Guo, X.; Gu, J.; Lin, S.; Zhang, S.; Chen, Z.; Huang, S. Tackling the Activity and Selectivity Challenges of Electrocatalysts toward the Nitrogen Reduction Reaction via Atomically Dispersed Biatom Catalysts. *J Am Chem Soc* **2020**, *142* (12), 5709–5721.
- (88) Wan, Q.; Hu, S.; Dai, J.; Chen, C.; Li, W.-X. First-Principles Kinetic Study for Ostwald Ripening of Late Transition Metals on TiO₂ (110). *The Journal of Physical Chemistry C* **2018**, *123* (2), 1160–1169.

- (89) Ouyang, R.; Liu, J.-X.; Li, W.-X. Atomistic Theory of Ostwald Ripening and Disintegration of Supported Metal Particles under Reaction Conditions. *J Am Chem Soc* **2013**, *135* (5), 1760–1771.
- (90) Su, Y.-Q.; Zhang, L.; Wang, Y.; Liu, J.-X.; Muravev, V.; Alexopoulos, K.; Filot, I. A. W.; Vlachos, D. G.; Hensen, E. J. M. Stability of Heterogeneous Single-Atom Catalysts: A Scaling Law Mapping Thermodynamics to Kinetics. *NPJ Comput Mater* **2020**, *6* (1), 144.
- (91) Toro-Labbé, A. Characterization of Chemical Reactions from the Profiles of Energy, Chemical Potential, and Hardness. *J Phys Chem A* **1999**, *103* (22), 4398–4403.
- (92) Cárdenas-Jirón, G. I.; Letelier, J. R.; Toro-Labbé, A. The Internal Rotation of Hydrogen Thioperoxide: Energy, Chemical Potential, and Hardness Profiles. *J Phys Chem A* **1998**, *102* (40), 7864–7871.

Table of Contents (TOC) Image

