Ru-Catalyzed Steam Methane Reforming: Mechanistic Study from First Principles Calculations

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Supporting Information

ABSTRACT: Elucidating the reaction mechanism of steam methane reforming (SMR) is imperative for the rational design of catalysts for efficient hydrogen production. In this paper, we provide mechanistic insights into SMR on Ru surface using first principles calculations based on dispersion-corrected density functional theory. Methane activation (i.e., C–H bond cleavage) was found to proceed via a thermodynamically exothermic dissociative adsorption process, resulting in $(\text{CH}_y + \text{zH})^*$ species ($^*$ denotes a surface-bound state, and $y + z = 4$), with $\text{C}^*$ and $\text{CH}^*$ being the most stable adsorbates. The calculation of activation barriers suggests that the conversion of $\text{C}^*$ into O-containing species via $\text{C}=\text{O}$ bond formation is kinetically slow, indicating that the surface reaction of carbon intermediates with oxygen is a possible rate-determining step. The results suggest the importance of subsequent elementary reactions following methane activation in determining the formation of stable carbon structures on the surface that deactivates the catalyst or the conversion of carbon into O-containing species.

1. INTRODUCTION

The emerging shift to another viable source of energy in the so-called hydrogen-based society creates a tremendous demand for hydrogen. Until now, the steam reforming of methane is one of the most used processes in the production of hydrogen.\(^1\) Because methane is thermodynamically very stable, steam methane reforming (SMR) is a highly endothermic process that requires a temperature of 900 K or higher.\(^2\) SMR proceeds via the reaction

$$\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$$

A number of mechanisms have been proposed for this reaction. Some models assume that the rate-determining step is the decomposition of methane that forms chemisorbed $\text{CH}_y$ ($y = 0–3$) radicals.\(^3–5\) Another model considers the surface reaction of carbon intermediates with adsorbed oxygen as the rate-determining step.\(^6\) Despite these theoretical and other experimental studies, the elementary steps that comprise the overall reaction still remain unclear. Thus, it is imperative to understand the thermodynamics of the elementary steps of SMR at the atomic scale.

Although only a few theoretical studies have been carried out to elucidate the reaction mechanism of SMR, most of these studies have used Ni, Rh, and Pt.\(^7–10\) On the other hand, to the best of our knowledge, only methane activation on Ru(0001) has been studied.\(^11\) This is surprising as Ru-catalyzed SMR is significant from industrial and scientific points of view. First, there is a general consensus from experiments that precious metals such as Ru, Rh, Pt, and Pd have high activity for SMR, although Ni is most frequently used because of its lower cost.\(^12–15\) Second, experiments have shown that Ru is catalytically active for both carbon formation on the surface that leads to catalyst deactivation and SMR.\(^12,14,15\) Thus, it is scientifically interesting to explore new mechanistic insights into the catalytic pathways toward carbon formation and SMR on Ru. These results will provide significant insights into the rational design of catalysts that promote an efficient SMR reaction.

In this paper, we present new insights into the reaction mechanism of SMR using Ru as the catalyst. We performed first principles calculations based on dispersion-corrected density functional theory (DFT-D2) to analyze the structures and energetics of possible intermediate species in the SMR reaction and the thermodynamics of proposed elementary reaction pathways for the overall reaction.

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2. COMPUTATIONAL MODEL

It is by now clear that corrugated surfaces are more reactive for SMR. The B5 site on a unique step-edge-type model on Ru(0001) has now been recognized as an active site especially for the bond cleavage of π bonds of diatomic molecules. As shown in Figure 1a, a B5 site is composed of a fourfold hollow site (atoms 1–4) and a threefold hollow site (atoms 3–5). Hu and co-workers have proposed a slab model for such B5 sites, where the surface can be conveniently constructed by removing two neighboring rows on one side of the slab. Such a model for a step-edge-type site on Ru(0001) was also used for the DFT investigation of other reactions such as Fischer–Tropsch synthesis and ammonia synthesis. Our calculations have used a similar slab model, composed of four layers of (4 × 3) supercell, separated by around 14 Å of vacuum space, as shown in Figure 1b. Calculation of the density of states projected on the d band of Ru for the bulk case, clean Ru(0001) surface or terrace site, and step-edge site shows that with respect to the bulk case, the occupied states of the d band are “forward-shifted” (skewed) to the Fermi level for the case of surface Ru atom, with the greatest shift for the step site, followed by that for the terrace site. This is shown schematically in Figure 2.

Accordingly, the calculated d band centers are −2.89, −2.55, and −2.47 eV for the bulk, terrace, and step sites, respectively. These indicate that the step-edge site is more reactive than the terrace site.

The stable adsorption configuration of the molecules considered in this study was determined by exhausting a number of different orientations on the surface. The top two layers of the slab and adsorbates were fully relaxed in all directions, whereas the bottom two layers were held fixed at their bulk structure. The optimization of isolated gas-phase molecules was performed with one free molecule within a 25 × 25 Å unit cell. Adsorption energies, $E_{ads}$, were computed by taking the difference between the total energy of the adsorbate-slab system in the lowest-energy adsorption configuration and the summed energies of the optimized clean surface and the gas-phase molecule. The Gibbs free energy $G_\text{ads}$ of the adsorbed species A* (A* denotes the surface-bound species) was calculated by adding the zero-point vibrational energy and the vibrational energy change for temperature increase from 0 to $T$ K ($\Delta E_{vb,0\rightarrow T}$) and subtracting the vibrational entropy. The vibrational terms can be conveniently combined into the Helmholtz vibrational energy, denoted by $E_{vb}$.

$$G_\text{ads} = E_\text{ads} + E_{ZPVE} + \Delta E_{vb,0\rightarrow T} - S_{vb}T = E_\text{ads} + F_{vb}$$

The Gibbs free energy of gas-phase molecules (A) was computed similarly, by adding the contributions of rotational and translational degrees of freedom to entropy and the PV term

$$G_A = E_\text{ads} + E_{ZPVE} + E_{vb,0\rightarrow T} - (S_{vb} + S_{trans} + S_{rot})T + PV$$

Spin-polarized DFT calculations were carried out using the Vienna ab initio simulation package (VASP) within the generalized gradient approximation based on Perdew–Burke–Ernzerhof functional with an empirical dispersion correction of Grimme (DFT-D2). This van der Waals correction was shown to be suitable in describing the adsorption of molecules on metals. Harmonic vibrational frequencies were calculated using the finite difference method with a step size of 0.02 Å. The interaction between ions and electrons was described using the projector-augmented wave method. Wave-plane basis sets were used with an energy cutoff of 400 eV. Electric dipole correction was used to cut the dipole interactions between the repeated-image layer systems. The surface Brillouin zone integrations were performed on a grid of $4 \times 3 \times 1$ Monkhorst–Pack k-points using Methfessel–Paxton smearing of $\sigma = 0.2$ eV. A conjugate-gradient algorithm was used to relax the ions into their ground state.

3. RESULTS AND DISCUSSION

3.1. Adsorption of Molecules. We considered (CO$_2$H$_4$ + zH)$^*$-type of adsorbed molecule species, with $x = 0–2$ and $y = 0–4$, and various isomerization (e.g., COH and CHO), for the complete four H$_2$ production process. This type of molecules (AO$_2$H$_4$, where A is carbon or boron) was also used in our previous studies exploring the elementary steps of borohydride electrochemical oxidation. The optimal adsorption configurations of these molecules are shown in Figure 3. The corresponding adsorption energies, arranged in an increasing number of O and H atoms in the molecules, are plotted in Figure 4. The actual values of adsorption energies and other stable configurations of molecules can be found in Table S1 and Figure S1, respectively.

3.1.1. CH$_y$ ($y = 0–4$) Adsorption. C* has the largest adsorption energy (absolute value) among the species considered. It is adsorbed at the fourfold hollow site with an average Ru–C distance of 2.03 Å, in agreement with a previous study on Ru(1010) surface. Carbon adsorption at the fourfold hollow site was also reported on stepped Co(1124) surface. Adsorption at the near-edge hcp site is 0.17 eV less stable than that at the fourfold hollow site.
Similar to carbon, CH* is strongly bound on the surface and binds at the fourfold hollow site, in agreement with a previous study on Ru(1010) surface. The C−H bond length is 1.10 Å and the average Ru−C distance is 2.15 Å, in excellent agreement with a previous study on Ru(1010) surface. The adsorption energy of CH* is slightly smaller in magnitude than that of C*. Accordingly, it can be noted that the average Ru−C distance is greater for the case of CH* than for C*.

CH₂* adsorbs near the bridge site of two step-edge atoms. It forms a bent shape with an average C−H bond length of 1.10 Å and H−C−H angle of 113°. The average Ru−C distance of CH₂ with the two step-edge atoms is 2.06 Å, in agreement with a related study. CH₃* binds on an adsorption site similar to CH₂*. The Ru−C distances with the two Ru atoms at the step-edge are 2.14 and 2.30 Å, in excellent agreement for the case of Ru(1010). The average C−H bond length is 1.12 Å, which is also in agreement with a previous study.

CH₄* weakly adsorbs on a step-edge atom with the two H atoms pointing toward the surface. An analysis of the local density of states projected on the sp states of CH₄ and Ru atom at the step-edge site nearest to the adsorbed CH₄ shows the broadening of the sp states of CH₄ compared with the delta peaks in the isolated gas-phase CH₄, which indicates weak chemisorption. The average C−H bond length for H atoms pointing to the surface is 0.02 Å longer than that for the case of H atoms pointing away from the surface. This indicates a weak interaction between the H atoms pointing toward the surface and Ru atoms, which was also noted for the case of Ru(1010). A similar “tilted” adsorption configuration for a molecule with a
tetrahedral structure was previously noted for the case of borohydride on Au–Ni alloys, which indicates susceptibility to bond-breaking reactions.

For CH₄-type species, the adsorption energy decreases in magnitude as the number of C–H bonds in the molecule increases. However, it must be noted that this trend in adsorption energy does not necessarily imply that all dehydrogenation steps (methane decomposition) are exothermic. C* and CH* are the most stable species, as similar noted for the case of Ni catalysts.

3.1.2. COH₃ (y = 0–4) Adsorption. CO* binds on an adsorption site similar to CH₂ and CH₃. It has a much lesser adsorption energy than CH*, which binds lower into the fourfold hollow site, indicating a weaker Ru–C interaction for CO* compared with CH*. The preference of CO to bind at this site was also noted in CO dissociation on Ru(112). The C–O bond length is 1.19 Å, whereas the average Ru–C distance is 2.07 Å. These are very close to the calculated C–O bond length (1.15 Å) and Ru–C distance (1.94 Å) for CO adsorption on Ru(001).

COH* and CHO* are important intermediates in the formation of C–O bonds. COH* binds on the step-edge corner with C at the fourfold hollow site. Only C binds with Ru atoms, with an average Ru–C distance of 2.16 Å. In the case of CHO*, both C and O atoms directly interact with Ru atoms. The average Ru–O and Ru–C distances are 2.16 and 2.09 Å, respectively.

CH₂O* binds on the step-edge atoms via the Ru–O bond with a length of 1.93 Å. The C–O bond is approximately parallel to the surface, with a length of 1.38 Å. CHOH* binds at the step-edge with a Ru–C distance of 2.10 Å. Contrary to that of CH₂O*, the C–O bond of CHOH* is perpendicular to the surface, with a length of 1.38 Å.

CH₃O* is a proposed reaction intermediate for the decomposition of methanol. It adsorbs at the step-edge, bridging two Ru atoms with an average Ru–O distance of 2.06 Å. The C–O bond length is stretched to 1.44 Å from 1.36 Å in the gas phase, indicating a weakened C–O bond. The hydrogen atoms are pointing away from the surface.

CH₂OH* is highly unstable on the surface as its optimization at different sites leads to dissociated structures containing either CO*, COH*, or CHOH*. A molecular structure that is relatively far from the surface was found with the shortest Ru–C distance of 2.13 Å. The C–O bond is elongated by 0.04 Å from its gas-phase structure, making it easy to break into OH* and CH₂O on the surface.

CH₂OH* binds at the step-edge with two H atoms pointing toward the surface. Optimization at the other sites leads to dissociated structures. The C–O bond length is 1.41 Å. The C–H bond length for the H atom close to the surface is longer than that for the other H atoms, indicating a weak interaction between Ru and H, as noted for CH₂O in the previous section.

3.1.3. CO₂H₃ (y = 0–3) Adsorption. CO₂* adsorbs at the step-edge with a bent configuration, in contrast to its linear structure in the gas phase. This adsorption structure was also found for other surfaces such as γ-Al₂O₃ and Cu₂O and is attributed to surface defects and corrugation. The average C–O distance is 1.29 Å, whereas the O–C–O angle is 122°.

CH(OH)₂* binds at the step-edge via Ru–C and Ru–O bonds. The initial C=O bond in the gas phase was stretched from 1.19 to 1.28 Å in the adsorbed state, indicating the weakening of this bond as C and O bind with Ru. The other C–O bond that points away from the surface was shortened by only 0.01 Å, suggesting that it has not been significantly affected by the adsorption process.

CH(OH)₂* binds at the step-edge with a Ru–C bond length of 1.99 Å. One O–H bond points away from the surface, whereas the other one points toward the surface. The O–H bond that points toward the surface is 0.03 Å longer than the other one, indicating a weak Ru–H interaction as similarly noted for other molecules. The surface parallel and perpendicular C–O bonds are 1.33 and 1.34 Å, respectively.

CH(OH)₂* binds on the step-edge atoms through Ru–C and Ru–O bonds with lengths of 2.10 and 2.22 Å, respectively. The two O–H bonds point toward the surface, whereas the C–H bond points away from the surface.

3.2. Thermodynamics of Elementary Steps. There are a number of proposed reaction mechanisms for the complete steam reforming of methane. These involve elementary reactions such as methane activation, COH formation, water–gas shift reaction, and water activation. In the current study, the following reaction coordinate is proposed

\[
\text{CH}_4 + x\text{H}_2\text{O} + \gamma \rightarrow (\text{CO}_2\text{H}_y + z\text{H})^* + \frac{y}{2}\text{H}_2
\]
where $x = 0–2$; $z, y = 0–4$; and $\alpha = 4 + 2x - y - z$. The free energy change of this reaction, $\Delta G_f$, gives the relative free energy of adsorbed species (CO$_x$H$_y$ + zH)$^*$ that corresponds to a particular $\alpha$-step.

$$\Delta G_f = G(\text{CO}_x\text{H}_y + \text{zH})^* + \frac{\alpha}{2}G_\text{H}_2 - G_\text{CH}_4 - xG_\text{H}_2\text{O} - G_\text{g}$$

This was used to construct a free energy diagram that facilitates the comparison of reaction pathways. Figure 5 shows the free energy diagram for this reaction, evaluated at $T = 600$ °C and $P = 10$ bar, which are the typical values in experiments. Each process to the right corresponds to one $\alpha$-step. In each $\alpha$-step, the number of atoms from the initial CH$_4$ gas state is conserved. For example, in $\alpha = 2$ step, a possible reaction is CH$_4$ + H$_2$O $\rightarrow$ CH$_3$OH$^*$ + H$_2$.

3.2.1. Methane Activation. Methane activation is the C–H bond cleavage reaction of a highly stable CH$_2$. Results have shown that its adsorption on the Ru surface is highly exothermic and dissociative, as shown by the $\alpha = 0$ step reaction in the energy diagram. Molecular adsorption is less exothermic compared with dissociative adsorption that results in (CH$_4$ + zH)$^*$ (with $y + z = 4$) species. The adsorption configuration of CH$_\alpha^*$ species in (CH$_{\alpha+1}$ + H)$^*$ follows the case of no zH$^*$ coadsorption. The formation of C$^*$ and CH$^*$ with coadsorbed H$^*$ is highly exothermic, and their conversions to other species are largely endothermic. These radicals are strongly adsorbed on the surface, as shown in Figure 4. This indicates that C$^*$ and CH$^*$ are the most stable surface-bound species, as similarly noted for the case of Ni catalysts. This supports the experimental finding that Ru is active for carbon formation on the surface.

The reaction energy diagram shows that at low adsorbate coverage used in this calculation, the subsequent elementary steps that would desorb H$^*$ from (C + 4H)$^*$ are highly endothermic. However, because this complete dissociation of methane produces four H$^*$ for every C$^*$, increasing the rate of methane dissociation would result in a much higher coverage of H$^*$ on the surface than C$^*$. Previous studies have shown that the associative desorption of H$^*$ into H$_2$ gas (hydrogen evolution) becomes more favorable as the surface coverage of H$^*$ increases.

The production of methanol (CH$_3$OH) from methane has been reported in the literature for various applications. On the basis of the free energy diagram, CH$_3$OH$^*$ can be produced on the surface by the C–O bond formation of CH$_4$ with OH$^*$, as shown by the blue path. However, it can easily be dehydrogenated into CH$_3$OH$^*$ or CH$_3$O$^*$, which agrees with an experiment that detected CH$_3$O as an intermediate species for methanol decomposition. The dehydrogenation of CH$_3$OH$^*$ and CH$_3$O$^*$ into coadsorbed CO$^*$ and H$^*$ proceeds downhill in energy.

3.2.2. Carbon Conversion. As shown in the free energy diagram, at $\alpha = 4$ step, an isolated C$^*$ (i.e., no H$^*$ coadsorption) is thermodynamically unstable in relative energy compared with the other species in the same $\alpha$-step. This corresponds to the low C$^*$ adsorbate coverage limit. Its conversion via the CO$^*$ formation pathway to the final CO$_2$ product is exothermic, as shown by the red dashed line. CO$^*$ formation can proceed via COH$^*$ or CHO$^*$ intermediate. The conversion of COH$^*$ or CHO$^*$ to CO$_2$ proceeds uphill in energy, whereas CO$_2$ can be converted to COOH$^*$ exothermically. These results support the experimental finding that the rate-determining steps in SMR produce CO and CO$_2$ from CHO intermediate species.

The same instability of isolated C$^*$ compared with other species in the $\alpha = 4$ step is also noted for (C + 2H)$^*$ and (C + H)$^*$ in the $\alpha = 2$ and $\alpha = 3$ steps, respectively. This indicates that C$^*$ with fewer coadsorbed H$^*$ is less thermodynamically stable in relative energy than that with more H$^*$ such as in (C + 3H)$^*$ and (C + 4H)$^*$.

3.3. Activation Barriers. It can be noted that although the use of reaction energies to determine the catalytic activity of a catalyst is computationally convenient, it is a very simple approximation as the overall SMR reaction can be dictated by elementary reaction kinetics that involves the breaking of C–H and O–H bonds and the formation of C–O bonds. Hence, it is imperative to calculate the activation barriers for these bond formation/claveage processes for elementary steps. These calculations were implemented utilizing the climbing-image nudge elastic band method within VASP using four images between the initial and the final states, as previously performed in our previous studies.

3.3.1. C–H Bond Cleavage. Methane activation (i.e., C–H bond cleavage of methane) together with the CO formation step was found to be kinetically relevant for SMR on transition.
The breaking of one C–H bond of methane was calculated via a molecularly adsorbed methane precursor

$$\text{CH}_4^* \rightarrow (\text{CH}_3 + \text{H})^*$$

The initial, transition, and final states for this reaction are shown in Figure 6a. The calculated activation barrier is 1.02 eV. It can be noted that this reaction pathway involves the translation of the molecule’s central atom at the step-edge site.

3.3.2. C–O Bond Formation. The thermodynamics of elementary reactions presented in the previous section has shown the possibility of converting C* into O-containing species. The activation barrier for this reaction was calculated via the C–O bond formation pathway in the following reaction

$$(\text{C} + \text{OH}^*) \rightarrow \text{COH}^*$$

The initial, transition, and final states for this reaction are shown in Figure 6b. The calculated activation barrier for this reaction is 1.24 eV. This is very close to the calculated activation barrier for the same reaction on Rh(211). This relatively high barrier suggests that this process is kinetically slower than methane activation. This supports a previous model determining step. However, in this model, Ni/MgAl2O4 was used as a catalyst, and the models were based on postulated kinetics fitted to the experimental data.

3.3.3. O–H Bond Cleavage. The O–H bond cleavage was considered for the following cases of C-containing species and H2O molecules (water activation)

$$\text{COH}^* \rightarrow (\text{CO} + \text{H})^*$$

$$\text{H}_2\text{O}^* \rightarrow (\text{OH} + \text{H})^*$$

The first reaction is important because one suggested pathway for SMR is through the CO formation reaction pathway. On the other hand, the second reaction would determine whether the formation of OH and H on the surface is kinetically relevant or not.

The initial, transition, and final states for the first reaction are shown in Figure 6c. This reaction requires an activation barrier of 0.94 eV. This is lower than the case of C–O bond formation, indicating that for this molecule, it is easier for O to dissociate from H than to form a bond with C.

For the second reaction, the initial, transition, and final states are shown in Figure 6d. It was found that O–H bond cleavage for H2O requires an activation barrier of 0.48 eV.

4. CONCLUSIONS

The reaction mechanism of SMR on Ru is investigated using first principles calculations based on DFT-D2. We found that methane activation (i.e., C–H bond cleavage) proceeds in a thermodynamically exothermic dissociative adsorption resulting in CH$_2$-species. C* and CH* are the most stable surface-bound intermediates, making the surface vulnerable to carbon formation that can lead to experimentally reported catalyst deactivation. The conversion of C into O-containing species is found to require a relatively high activation barrier, suggesting a slow kinetics for C–O bond formation. The overall reaction is determined by whether carbon forms stable structures on the surface that deactivates the catalyst or undergoes activated conversion into O-containing species. These findings pose significant insights into the design of catalysts for SMR.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00462.

Adsorption energies and other stable adsorption configurations of molecules and their adsorption energies (PDF)

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Notes

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