Ethanol Synthesis from Syngas on the Stepped Rh(211) Surface: Effect of Surface Structure and Composition

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ABSTRACT: The mechanisms of ethanol synthesis from syngas including CH₂ (x = 1 – 3) species and C₂ oxygenates on the stepped Rh(211) surface have been systematically investigated by using density functional theory together with a periodic slab model. Our results show that among all CH₂ (x = 1 – 3) species, CH₃ is the most favorable monomer, which is more favorable than CH₃OH formation; this result is quite different from that on the flat Rh(111). Beginning with CH₃ species, CH₃ + CHO → CH₃CHO dominantly contributes to the formation of C₂ oxygenates; subsequently, CH₃CHO is successively hydrogenated to ethanol via CH₂CH₂O intermediate. Meanwhile, CH₄ formation by CH₄ hydrogenation is energetically compatible with CH₃CHO formation; that is, the productivity and selectivity of ethanol is determined by the formations of CH₃CHO and CH₄. As a result, the strategy of improving the Rh-based catalyst with the help from the promoter Mn is employed to tune the relative activity of CH₂CH₂O and CH₄ formations that control the productivity and selectivity of ethanol from syngas. Our results show that the productivity and selectivity of ethanol from syngas can be improved by introducing promoter Mn into the Rh catalyst.

1. INTRODUCTION

Ethanol is a versatile feedstock applied in the synthesis of various products (e.g., chemicals, fuels, and polymers), and has also been used commercially as an additive or a potential substitute for gasoline.¹ ² Ethanol production from syngas is one of the major processes in industry;³ however, one of the major hurdles for this catalytic process is low yield and poor selectivity of ethanol because of slow kinetics of the formations of CH₂ and C₂ oxygenate intermediates.³ ⁴ Currently, Rh-based catalysts have been found to exhibit excellent catalytic performances for ethanol formation from syngas,¹ ⁵ ⁶ ⁻ ¹⁵ in which the catalytic performances of Rh-based catalysts are closely related to the corresponding surface structure and composition.¹ ⁶ ¹⁷

For the effect of surface structure on catalytic performance, it has been long believed that under realistic conditions the important properties of most metal surfaces, including surface reactivity, are closely related to the presence of surface defects.¹⁸ - ²⁴ the surface defect plays an important role in determining reaction route and affecting the reaction activity and selectivity.¹⁷ ²⁵ ²⁶ In fact, the step site is the most common defect for metal catalysts, which may play a key role in catalysis; previous studies have proven that the catalytic properties of metal catalysts are sensitive to surface structure, for example, González et al.²⁷ have reported that compared to that on the flat Rh(111) surface, NO dissociation on the stepped Rh(221) surface not only forms new adsorption sites for NO adsorption but also results in the appearance of a completely new reaction pathway; Catapan et al.²⁸ have investigated the water—gas shift reaction on the Ni(111) and Ni(211) surfaces, indicating that the generation of formate is favored on the stepped Ni(211); Behrens et al.²⁹ have revealed that methanol formation via the hydrogenation of CO and CO₂ on the stepped Cu(211) surface is more active than that on the flat Cu(111) surface; and Mavrikakis et al.³⁰ have shown that the activation barrier of CO dissociation on the stepped Rh(211) surface is 120 kJ mol⁻¹ lower than that on the flat Rh(111) surface.

For the effect of surface composition on catalytic performance, a second metal (M), like Mn,³ ³⁰ — ³³ Cu,²⁷ ³⁴ Fe,¹ ¹¹ ³⁷ V,³⁸ or Sm,³⁹ is introduced into Rh to form a MRh alloy catalyst, which combines the advantage of each of its constituents because of the cooperative effect of Rh and M. As a result, the MRh alloy catalyst exhibits higher catalytic activity and selectivity, making the catalyst more efficient. For example, Li et al.³⁴ have examined the catalytic performance of pure and Mn-modified Rh(100) surfaces for ethanol formation from syngas, indicating that the activation barrier of CO dissociation on MnRh(100) is remarkably lowered compared to that on Rh(100). Moreover, CO insertion into CH₂ on MnRh(100) is easier than CH₄ formation by CH₃ hydrogenation; that is, the role of Mn promoter can improve the selectivity of Rh to convert syngas to ethanol. Zhao et al.³⁶ have shown that the production rate of C₂ oxygenates is higher than CH₄ on the RhCu(111) surface under experimental conditions, compared to that of the Rh(111) surface that is highly selective to CH₄. Recently, Choi and Liu³ have systematically investigated ethanol formation from syngas on the flat Rh(111); their work suggested that the selectivity to ethanol from syngas largely depends on the activation barriers of CH₄ formation by CH₃ hydrogenation and C₂ oxygenate formation by CO insertion into CH₂ species and provided that introducing the promoter Fe into Rh(111) surface can suppress CH₄ formation.

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Up to now, to the best of our knowledge, previous studies of ethanol synthesis from syngas on the Rh catalyst mainly focused on the Rh(111) and Rh(100) surfaces. Although step is the most common defect for the nanosized metal catalyst used in reality, many studies in this area are still limited. Kapur et al.25 have investigated C1 and C2 oxygenate formation by CO hydrogenation on the stepped Rh(211) surface by using density functional theory (DFT) calculations; however, the actual mechanism of ethanol formation from syngas on the stepped surface is still unclear. Many questions remain unanswered: (1) What are the most favored CH monomer and C2 oxygenates of ethanol precursor? (2) What is the most favorable reaction pathway for ethanol formation? (3) What is the key step for controlling the productivity and selectivity of ethanol? (4) How does the stepped surface influence the catalytic performance compared to that of the flat Rh(111) surface? (5) What method can be carried out to improve the catalytic performance of the Rh catalyst?

In order to tackle these puzzles, in this study, the mechanisms of ethanol formation from syngas on the stepped Rh(211) surface have been systematically investigated by using DFT calculations. Rh(211) surface, as a defect surface, has the (100)-type step, which is generally quite active in catalytic reactions. By probing into the whole reaction network, we can obtain a clear picture of ethanol formation from syngas on the stepped Rh(211) surface, and the results can provide useful information for the rational design of better Rh-based catalysts.

2. COMPUTATIONAL DETAILS

2.1. Surface Model. The stepped Rh(211) surface is modeled using a $p(2 \times 3)$ unit cell slab with eight atomic layers, and a 10 Å vacuum space is used to ensure the negligible interaction between any two successive slabs. During the calculations, the atomic positions of the upper five layers together with the adsorbed species are relaxed, whereas the bottom three layers are kept fixed at the bulk positions. According to surface morphology of Rh(211)-$(2 \times 3)$, as shown in Figure 1, nine possible adsorption sites exist on the stepped Rh(211) with the (111) terrace and (100) step. They are step edge (atop, bridge, fcc, and hcp), lower edge (fcc and hcp), terrace (atop and bridge), and (100) step (hollow site).

2.2. Calculation Methods. The Vienna Ab Initio Simulation Package (VASP), 41–43 implementing the DFT with a three-dimensional (3D) periodic boundary condition, has been employed for all calculations. The generalized gradient approximation (GGA) with Perdew–Wang formulation (PW91) is used for the exchange-correlation function. 44 The electron–ion interaction is modeled by the project-augmented wave (PAW) method. The Brillouin zone is sampled using a $4 \times 4 \times 1$ Monkhorst-Pack $k$-point grid with the Methfessel–Paxton smearing of 0.1 eV. 47 The plane-wave cutoff energy is set at 400 eV to describe the electronic wave functions. A force difference between two steps less than 0.01 eV Å$^{-1}$ is used as the criterion for convergence of ionic relaxation. The relaxation of the electronic degrees of freedom is assumed to be converged if the total energy change and the band structure energy change between two steps are both smaller than $5 \times 10^{-6}$ eV.

Reaction pathways have been investigated using the climbing-image nudged elastic band method (CI-NEB). 48,49 Transition states have been optimized using the dimer method. 50,51 The structure of a transition state is deemed converged when the forces acting on the atoms were all <0.05 eV Å$^{-1}$ for the various degrees of freedom set in the calculation. The molecules in the gas phase are calculated using a $10 \times 10 \times 10$ Å cubic unit cell.

3. RESULTS AND DISCUSSION

In this section, the adsorptions of reactants and all possible intermediates are first investigated on the stepped Rh(211) surface; then, the formation mechanisms of CH$_x$ (x = 1–3) species, C$_x$ oxygenates, and ethanol are discussed on the stepped Rh(211). The differences of ethanol formation between the stepped Rh(211) and the flat Rh(111) surfaces are then identified to obtain the effect of surface structures on reaction mechanism of ethanol formation; finally, an expanded strategy of improved catalytic performance of an Rh-based catalyst by introducing a promoter metal to change surface composition has been proposed.

3.1. Adsorption of All Possible Species in Ethanol Synthesis. For the adsorption of various reactants, intermediates, and products on the stepped Rh(211) surface, the adsorption energy is defined as $E_{\text{ads}} = E_{\text{Rh(211)}} + E_{\text{adsorbate}} - E_{\text{adsorbate/Rh(211)}}$, where the $E_{\text{adsorbate/Rh(211)}}$ is the total energy of Rh(211) slab with the adsorbate, $E_{\text{Rh(211)}}$ the energy of clean Rh(211) surface and $E_{\text{adsorbate}}$ the energy of gas-phase adsorbate. Herein, spin-polarized calculations are carried out for the gas-phase radical species involved in ethanol formation from syngas. By this definition, a negative value corresponds to exothermic adsorption.

As the starting point, the adsorption of various reactants, intermediates, and products is investigated on the stepped Rh(211), in which nine possible adsorption sites are considered. Only the most stable configurations of these species obtained by our calculations are shown in Figure 2. Table 1 summarizes the adsorption site, the corresponding adsorption energy, and the important geometric parameters of these stable configurations.

Our results show that the majority of the stable configurations for C$_1$ and C$_2$ oxygenates are adsorbed at the step edge sites, except for COH bonding to the hollow site via C atom. Our results are consistent with the available literature data from previous studies. On the other hand, when compared to the adsorption sites and adsorption energies on the flat Rh(111) surface, our results on the stepped Rh(211) surface show that the different surface structures not only result in different adsorption sites of adsorbed species but also lead to...
different adsorption strength. Compared to the surface atom on the flat Rh(111) surface, Zhang et al.\textsuperscript{17} have shown that the lower coordination number of step metal atoms on the stepped Rh(211) surface mainly contributes to the high adsorption strength of adsorbed species, in which the extra dangling bonds induced by the defect make the surface step more active in catalytic reactions.

3.2. CH\textsubscript{x}(x = 1−3) Formation. Starting from the adsorbed CO species, two possibilities exist for the formation of CH\textsubscript{x}(x = 1−3) species; one is the direct C−O bond scission of CO to C and O atoms followed by C hydrogenation to CH\textsubscript{x}(x = 1−3) species, and the other is CO hydrogenation to CH\textsubscript{2}O oxigenates followed by its C−O bond scission to form CH\textsubscript{x}(x = 1−3) species in the presence or absence of hydrogen. First, we investigate CO dissociation and hydrogenation. As shown in Table 2, three reactions (R1−R3) may occur.

Figure 3 presents the relative energy profile of these reactions together with the structures of initial states (ISs), transition states (TSs), and final states (FSs). It can be seen that the activation barriers of COH and CHO formation are 196.3 and 121.9 kJ mol\textsuperscript{−1}, respectively, which are more favorable than direct CO dissociation. CHO formation is more preferred. Therefore, the adsorbed CO species on the stepped Rh(211) is dominantly hydrogenated to form CHO (R2); similarly, Choi and Liu\textsuperscript{4} have shown that CHO species exist in the reaction of CO hydrogenation on the flat Rh(111). Furthermore, previous experiments using the chemical trapping approach proposed the significance of CHO species for alcohol synthesis on Rh/SiO\textsubscript{2} catalysts.\textsuperscript{52}

3.2.1. CH Formation. Above results show that CHO is the dominant product for the adsorbed CO species on the stepped Rh(211); thus, starting from the initial state CHO and CHO + H, four possible pathways with five elementary reactions (R4−R8) are responsible for CH formation, as shown in Table 2. Meanwhile, CHO hydrogenation to CH\textsubscript{2}O (R9) is also considered. Figure 4 provides the relative energy profiles of these reactions together with the structures of ISs, TSs, and FSs.

As illustrated in Figure 4, starting with CHO or CHO + H, among the four reaction pathways of CH formation, the pathway of CHO + H → CHOH → CH + OH (R6, R7) is dominantly responsible for CH formation via CHOH intermediate, which has the highest barrier of 134.9 kJ mol\textsuperscript{−1} with the reaction energy of −36.4 kJ mol\textsuperscript{−1}. However, the pathway of CHO + H → CH\textsubscript{2}O (R9) has the highest barrier and reaction energy of 68.6 and 46.5 kJ mol\textsuperscript{−1}, respectively. These results demonstrate that CH\textsubscript{2}O is the dominant product by CHO hydrogenation rather than CH species by direct CHOH dissociation.

3.2.2. CH\textsubscript{2} Formation. As mentioned above, CH\textsubscript{2}O is preferred to be formed by CHO hydrogenation. Thus, starting from CH\textsubscript{2}O and CH\textsubscript{2}O + H, as listed in Table 2, four possible pathways with five elementary reactions (R11−R15) are responsible for CH\textsubscript{2} formation; meanwhile, CH\textsubscript{3}O formation by CH\textsubscript{2}O hydrogenation to (R16) is also considered. In addition, H-assisted CHO dissociation can also produce CH\textsubscript{2} species (R10). The relative energy profile of these reactions together with the structures of ISs, TSs, and FSs are presented in Figure 5.

As presented in Figure 5, starting with CH\textsubscript{2}O or CH\textsubscript{2}O + H, among five reaction pathways of CH\textsubscript{2} formation, the pathway of CHO + 2H → CH\textsubscript{2}O + H → CH\textsubscript{2} + OH (R9, R12) is dominantly responsible for CH\textsubscript{2} formation, which has the highest barrier of 127.9 kJ mol\textsuperscript{−1} with the reaction energy of −0.6 kJ mol\textsuperscript{−1}. However, the pathway of CH\textsubscript{2}O + H → CH\textsubscript{3}O (R16) has the highest barrier and reaction energy of 104.6 and 47.1 kJ mol\textsuperscript{−1}, respectively. These results demonstrate that CH\textsubscript{3}O rather than CH\textsubscript{2} species is the dominant product of CH\textsubscript{2}O hydrogenation.

3.2.3. CH\textsubscript{3} Formation. As mentioned above, CH\textsubscript{3}O hydrogenation prefers to form CH\textsubscript{3}O; thus, we further investigate CH\textsubscript{3} formation, starting from CH\textsubscript{3}O and CH\textsubscript{3}O + H. H-assisted CH\textsubscript{3}O dissociation can also produce CH\textsubscript{3} species.
species | \(E_{\text{ads}}\) (kJ mol\(^{-1}\)) | configuration | \(d_{\text{Rh-C}}\) (Å) | \(d_{\text{Rh-O}}\) (Å) |
---|---|---|---|
C | 760.4 | hollow | 1.984, 1.984, 2.001, 2.001 |
H | 272.3 | bridge-SE | Rh−H: 1.770, 1.770 |
O | 547.4 | bridge-SE | 1.899, 1.899 |
OH | 369.1 | bridge-SE via O | 2.097, 2.097 |
H₂O | 47.4 | away from surface | |
CO | 201.4 | atop-SE via C | 1.857 |
CHO | 283.7 | bridge-SE via C and O | 1.935, 2.146 |
COH | 452.9 | bcp-SE via C | 1.995, 2.007, 2.011 |
CH | 674.9 | hollow | 2.105, 2.106, 2.107, 2.107 |
CH₂ | 430.6 | bridge-SE via C | 2.024, 2.024 |
CH₃ | 229.3 | atop-SE via C | 2.111 |
CH₄ | 15.1 | away from surface | 2.602 |
CH₃H₂ | 125.7 | atop-SE via C1 and C2 | 2.134, 2.128 |
CH₃H₆ | 22.2 | away from surface | 2.743, 2.940 |
CHOH | 341.2 | bridge-SE via C | 2.051, 2.052 |
CH₂O | 122.6 | bridge-SE via C and O | 2.101, 1.992 |
CH₂OH | 231.4 | bridge-SE via C and O | 2.058, 2.231 |
CH₃O | 281.8 | bridge-SE via O | 2.090, 2.091 |
CH₃OH | 63.9 | atop-SE via O | 2.225 |
CH₂CO | 163.0 | bridge via α-C and β-C | α: 2.240, 2.244; β: 1.937 |
CH₂CHO | 282.8 | bridge via β-C and O | 2.216, 2.028 |
CH₂CO | 276.5 | bridge via α-C and O | 2.195, 2.134 |
CH₃CHO | 99.3 | bridge via α-C and O | 2.186, 2.021 |
CH₂CHOH | 221.5 | bridge via α-C and O | 2.076, 2.219 |
CH₃CH₂O | 279.9 | bridge via O | 2.089, 2.088 |
C₃H₄OH | 63.4 | atop-SE via O | 2.222 |

(R17). In addition, CH₂O hydrogenation to CH₃OH (R20) is also considered. The corresponding potential energy diagram for these processes together with the structures of ISs, TSs, and FSs are shown in Figure 6.

We can obtain from Figure 6 that the pathway of CHO + 2H → CH₂O + H → CH₃ + O is the most favorable pathway for CH₃ formation, which has the highest barrier of 81.8 kJ mol\(^{-1}\); the rate-controlling step (R9) has the activation barrier of 68.6 kJ mol\(^{-1}\). Meanwhile, CH₂OH formation has the highest barrier of 170.4 kJ mol\(^{-1}\); the rate-controlling step (R20) has the activation barrier of 123.3 kJ mol\(^{-1}\). More importantly, starting with CH₂O + H, the reaction of CH₂O + H → CH₃ + O (R17) with the activation barrier of 35.3 kJ mol\(^{-1}\) is more favorable than the reaction of CH₂O + H → CH₃O (R16); thus, the CH₃ species is the dominant product by hydrogen-assisted CH₂O dissociation rather than CH₃O by CH₃O hydrogenation, as well as CH₃OH by CH₂O hydrogenation.

3.2.4. Brief Summary about CHₙ (x = 1–3) and CH₂OH Formation. With respect to CHO + H, Figure 7 presents the potential energy profile for the most favorable pathway of CH₃ (x = 1–3) species and CH₂OH formations. CH formation (black line) has the highest barrier of 134.9 kJ mol\(^{-1}\); CH₂ formation (red line) has the highest barrier of 127.9 kJ mol\(^{-1}\); CH₃ formation (blue line) has the highest barrier of 81.8 kJ mol\(^{-1}\). CH₂OH formation (green line) has the highest barrier of 170.4 kJ mol\(^{-1}\). The above results show that among all CHₙ (x = 1–3) species, CH₃ is the most favorable monomer via the reaction process of CO + 3H → CHO + 2H → CH₂O + H → CH₃ + O (R2, R9, R17). CH₃ formation is energetically more favorable than CH₂OH formation. Our results on the stepped Rh(211) are quite different from those obtained on the flat Rh(111).4 Thus, the stepped Rh(211) surface can catalyze the conversion reaction of syngas to form the important intermediate CH₃ with high selectivity rather than forming CH₂OH.

3.3. Formation of C₂ Oxygenates and Ethanol. For C₂ oxygenate formation, Zhao et al.53 have shown that CHO insertion into CH₃ (x = 1–3) is superior or competitive to CO insertion; thus, CO/CHO insertion into CH₃ to C₂ oxygenates has been considered. Meanwhile, CH₃ species will undergo the reaction of hydrogenation, dissociation, and coupling. Figure 8 presents the potential energy profile of these reactions related to CH₃ species together with the structures of ISs, TSs, and FSs.

As shown in Figure 8, among all reactions related to CH₃ species, CH₃ coupling (R25) and CO insertion into CH₃ (R21) are more difficult to realize because of the high activation barrier, whereas CH₃ dissociation into CH₂ and H (R24) is the most favorable with activation barrier and reaction energy of 48.5 and 5.6 kJ mol\(^{-1}\), respectively. The second is CHO insertion into CH₃ to CH₂CHO (R22). This elementary reaction has an activation barrier and reaction energy of 74.1 and −1.3 kJ mol\(^{-1}\), respectively. The third is CH₃ hydrogenation to CH₄ (R23). This elementary reaction has an activation barrier and reaction energy of 77.2 and 22.9 kJ mol\(^{-1}\), respectively.

As mentioned above, because of easy formation of CH₃ by CH₂ dissociation, we further investigate the hydrogenation, dissociation, and coupling of CH₂ (R28–R30), as well as CO/CHO insertion into CH₂ (R26, R27), as shown in Figure 9. Our results show that CH₄ prefers to be hydrogenated to CH₃; thus, once the CH₃ species is formed, among all reactions related to the CH₂ species, CH₃ is the dominant product. On the other hand, the above results also show that CHO insertion into CH₂ and CH₃ are responsible for the formation of C₂ oxygenates; thus, starting from the CH₃ species, C₂ oxygenate formation via CH₃ + CHO → CH₃ + CHO → CH₂CHO (R24, R27) has the highest barrier of 67.4 kJ mol\(^{-1}\), which is energetically compatible with the reaction of CH₃ + CHO → CH₂CHO (R22) with the activation barrier of 74.1 kJ mol\(^{-1}\). Furthermore, CH₂CHO undergoes hydrogenation to ethanol. However, it is noted that when CHO insertion into CH₂ occurs, most of the CH₂ species mainly participate in hydrogenation to CH₃; that is, a small quantity of CH₂ species is involved in CHO insertion into CH₂CHO, suggesting that C₂ oxygenate formation mainly depends on the CHO insertion into CH₃ to CH₂CHO.
Thus, starting from the dominant CH$_3$ species, CHO insertion into CH$_3$ to CH$_3$CHO is the most favorable pathway leading to the formation of C$_2$ oxygenates. Meanwhile, beginning with CHO species, CHO hydrogenation to CH$_2$O has an activation barrier and reaction energy of 68.6 and 46.5 kJ mol$^{-1}$, respectively, which are energetically compatible with CHO insertion into CH$_3$ to CH$_3$CHO; thus, when CHO insertion into CH$_3$ occurs, partial CHO can also participate in hydrogenation to CH$_2$O, and the rest is involved in insertion to CH$_3$CHO. On the other hand, for the formation of C$_2$ oxygenates, CO insertion into CH$_3$ has an activation barrier higher than that of CHO insertion, and CO hydrogenation to CHO has an activation barrier of 121.9 kJ mol$^{-1}$, which is lower than CO insertion into CH$_3$ with the activation barrier of 141.8 kJ mol$^{-1}$. As a result, CO prefers to be hydrogenated to CHO rather than CO insertion into CH$_3$ to CH$_3$CO, suggesting that C$_2$ oxygenates are dominantly formed by CHO insertion into CH$_3$ rather than CO insertion into CH$_3$.

Furthermore, one can see that for the dominant CH$_3$ species, CH$_4$ formation by CH$_3$ hydrogenation and CH$_3$CHO formation by CHO insertion into CH$_3$ can energetically compete because of the very small difference of the activation barrier by 3.1 kJ mol$^{-1}$, suggesting that on the stepped Rh(211) CH$_3$CHO formation is energetically compatible with CH$_4$ formation, which reduces the productivity and selectivity of ethanol from syngas.

Finally, starting from CH$_3$CHO species, there are two possibilities for CH$_3$CHO hydrogenation, as seen in Figure 10. One is the formation of CH$_3$CH$_2$O by adding H to the $\alpha$-C atom (R31), which needs to overcome an activation barrier of 51.5 kJ mol$^{-1}$ with the reaction energy of $-0.9$ kJ mol$^{-1}$. The other is the formation of CH$_3$CHOH by adding H to the O

| Table 2. Possible Elementary Reactions Involved in Ethanol Synthesis from Syngas Together with the Activation Energies ($E_a$) and Reaction Energies ($\Delta H$) |
|-----------------|----------------|----------------|----------------|
| elementary reactions | transition state | $E_a$(kJ mol$^{-1}$) | $\Delta H$(kJ mol$^{-1}$) |
| R1 | CO $\rightarrow$ C + O | TS1 | 396.3 | 64.5 |
| R2 | CO + H $\rightarrow$ CHO | TS2 | 121.9 | 85.0 |
| R3 | CO + H $\rightarrow$ COH | TS3 | 196.3 | 95.5 |
| R4 | CHO $\rightarrow$ CH + O | TS4 | 251.4 | 0.6 |
| R5 | CHO + H $\rightarrow$ CH + OH | TS5 | 152.8 | $-36.4$ |
| R6 | CHO + H $\rightarrow$ CHOH | TS6 | 120.9 | 31.4 |
| R7 | CHOH $\rightarrow$ CH + OH | TS7 | 103.5 | $-67.8$ |
| R8 | CHOH + H $\rightarrow$ CH + H$_2$O | TS8 | 179.2 | $-5.7$ |
| R9 | CHO + H $\rightarrow$ CH$_2$O | TS9 | 68.6 | 46.5 |
| R10 | CHO + H $\rightarrow$ CH$_2$ + O | TS10 | 205.9 | 44.0 |
| R11 | CH$_3$O $\rightarrow$ CH$_2$ + O | TS11 | 159.4 | $-2.5$ |
| R12 | CH$_3$O + H $\rightarrow$ CH$_2$ + OH | TS12 | 81.4 | $-47.1$ |
| R13 | CH$_3$O + H $\rightarrow$ CH$_2$OH | TS13 | 101.4 | $-3.3$ |
| R14 | CH$_2$OH $\rightarrow$ CH$_2$ + OH | TS14 | 83.9 | $-43.8$ |
| R15 | CH$_2$OH + H $\rightarrow$ CH$_2$ + H$_2$O | TS15 | 94.0 | $-25.1$ |
| R16 | CH$_2$O + H $\rightarrow$ CH$_2$O | TS16 | 58.1 | 0.6 |
| R17 | CH$_2$O + H $\rightarrow$ CH$_2$ + O | TS17 | 35.3 | $-0.5$ |
| R18 | CH$_3$O $\rightarrow$ CH$_2$ + O | TS18 | 175.3 | $-1.1$ |
| R19 | CH$_3$O + H $\rightarrow$ CH$_2$ + OH | TS19 | 153.7 | $-30.0$ |
| R20 | CH$_3$O + H $\rightarrow$ CH$_2$OH | TS20 | 123.3 | 38.1 |
| R21 | CH$_3$ + CO $\rightarrow$ CH$_3$CO | TS21 | 141.8 | 44.9 |
| R22 | CH$_3$ + CHO $\rightarrow$ CH$_3$CHO | TS22 | 74.1 | $-1.3$ |
| R23 | CH$_3$ + H $\rightarrow$ CH$_3$ | TS23 | 77.2 | 22.9 |
| R24 | CH$_3$ $\rightarrow$ CH$_2$ + H | TS24 | 48.5 | 5.6 |
| R25 | CH$_3$ + CH$_2$ $\rightarrow$ C$_2$H$_4$ | TS25 | 220.8 | $-10.4$ |
| R26 | CH$_3$ + CO $\rightarrow$ CH$_2$CO | TS26 | 85.7 | 66.0 |
| R27 | CH$_3$ + CHO $\rightarrow$ CH$_3$CHO | TS27 | 61.8 | $-51.6$ |
| R28 | CH$_3$ + H $\rightarrow$ CH$_3$ | TS28 | 42.9 | $-5.6$ |
| R29 | CH$_3$ + CH + H | TS29 | 56.6 | $-42.8$ |
| R30 | CH$_3$ + CH$_2$ $\rightarrow$ C$_2$H$_4$ | TS30 | 68.7 | $-47.6$ |
| R31 | CH$_3$CHO + H $\rightarrow$ CH$_3$CH$_2$O | TS31 | 51.5 | $-0.9$ |
| R32 | CH$_3$CHO + H $\rightarrow$ CH$_3$CHOH | TS32 | 101.8 | $-1.7$ |
| R33 | CH$_3$CHO + H $\rightarrow$ C$_2$H$_4$OH | TS33 | 131.1 | 38.4 |
atom (R32). This elementary reaction has an activation barrier of 101.8 kJ mol$^{-1}$, which is higher by 50.3 kJ mol$^{-1}$ than that of CH$_3$CHO formation; thus, CH$_3$CHO prefers to be hydrogenated to CH$_3$CH$_2$O rather than forming CH$_3$CHOH, in which CH$_3$CHO desorption cannot compete with CH$_3$CHO hydrogenation to CH$_3$CH$_2$O. Finally, CH$_3$CH$_2$O hydrogenation can form C$_2$H$_5$OH (R33). This elementary reaction needs to overcome an activation barrier of 131.1 kJ mol$^{-1}$ with the reaction energy of 38.4 kJ mol$^{-1}$.

3.4. Comparisons of C$_2$H$_5$OH Formation between Rh(211) and Rh(111) Surfaces. Previous DFT studies about ethanol formation from syngas on the flat Rh(111) have been obtained by Choi and Liu, which suggest that CH$_3$ is the most favorable monomer among all CH$_x$ species and that the selectivity to ethanol on Rh(111) is controlled by CH$_4$ formation by CH$_3$ hydrogenation and C$_2$ oxygenate formation by CO insertion into CH$_3$ species. Thus, it is interesting to carry out the qualitative comparisons about the key reaction steps on the flat Rh(111) by Choi and Liu with our present results on the stepped Rh(211).

3.4.1. CH$_3$ and CH$_3$OH Formation. Figure 11 presents the potential energy profile for the optimal pathway of CH$_3$ and CH$_3$OH formations on both Rh(211) and Rh(111) surfaces. We can obtain that methanol formation goes through the same favorable route of CO + 4H $\rightarrow$ CHO + 3H $\rightarrow$ CH$_2$O + 2H $\rightarrow$ CH$_3$O + H $\rightarrow$ CH$_3$OH. More importantly, on the Rh(111) surface, CH$_3$OH formation is more favorable than CH$_3$ formation; however, on the Rh(211) surface, CH$_3$ formation is more favorable than CH$_3$OH formation. Thus, for syngas conversion, the stepped Rh(211) surface exhibits high activity and selectivity to CH$_3$ species formation rather than CH$_3$OH. As a result, the CH$_3$ source is increased. Because CH$_3$ is proposed to be a prerequisite for C$_2$ oxygenate formation from syngas, the stepped Rh(211) surface may boost ethanol formation compared to that of the flat Rh(111).

3.4.2. C$_2$ Oxygenates and CH$_4$ Formation. As mentioned above, among all CH$_x$ (x = 1–3) species, CH$_3$ is the most favorable monomer on both Rh(211) and Rh(111) surfaces. Figure 12 presents the potential energy profile for the optimal pathway of CH$_4$ and C$_2$ oxygenate formations on both Rh(211) and Rh(111) surfaces starting from CH$_3$ species. The results show that on the flat Rh(111), C$_2$ oxygenates are dominantly formed by CO insertion into CH$_3$ to CH$_3$CO; meanwhile, CH$_4$ formation by CH$_3$ hydrogenation is much more favorable than CH$_3$CO, suggesting that the flat Rh(111) surface exhibits a better selectivity to hydrocarbons rather than C$_2$ oxygenates; however, on the stepped Rh(211), C$_2$ oxygenates are dominantly formed by CHO insertion into CH$_3$ to CH$_3$CHO, which is quite different from that on the flat Rh(111). CH$_3$CHO formation is energetically compatible with CH$_4$ formation by CH$_3$ hydrogenation because of the very small difference of activation barrier (3.1 kJ mol$^{-1}$), indicating that compared to that of the flat Rh(111) surface, the stepped Rh(211) surface exhibits a better selectivity to C$_2$ oxygenates.

On the basis of the above qualitative comparisons about the key reaction steps between the flat Rh(111) and the stepped Rh(211) surfaces, our results indicate that Rh(211) not only leads to the new formation pathway of CH$_3$ species and C$_2$ oxygenates but also boosts the formations of CH$_3$ species and C$_2$ oxygenates. As a result, the productivity and selectivity of ethanol from syngas on the stepped Rh(211) surface can be...
improved compared to that of the flat Rh(111) surface. In addition, starting from C₂ oxygenates, on Rh(111), ethanol is formed via the route \( \text{CH}_3\text{CO} + 3\text{H} \rightarrow \text{CH}_3\text{CHOH} + 2\text{H} \rightarrow \text{C}_2\text{H}_5\text{OH} \); however, on Rh(211), ethanol is formed via the route \( \text{CH}_3\text{CHO} + 2\text{H} \rightarrow \text{CH}_3\text{CH}_2\text{O} + \text{H} \rightarrow \text{C}_2\text{H}_5\text{OH} \).

### 3.5. General Discussion

As shown in Figure 13, the optimal pathway of ethanol formation from syngas on the stepped Rh(211) first goes through the process of \( \text{CO} + 3\text{H} \rightarrow \text{CHO} + 2\text{H} \rightarrow \text{CH}_3\text{O} + \text{H} \rightarrow \text{CH}_3 + \text{O} \) to produce \( \text{CH}_3 \) species, which is the most favored \( \text{CH} \) monomer; then, CHO insertion into \( \text{CH}_3 \) can form \( \text{CH}_3\text{CHO} \), followed by successive hydrogenation via \( \text{CH}_3\text{CH}_2\text{O} \) intermediate to ethanol. Meanwhile, \( \text{CH}_3 \) formation is much easier than \( \text{CH}_3\text{OH} \) formation; that is, the stepped Rh(211) surface can boost \( \text{CH}_3 \) source contributing to the formation of C₂ oxygenates. However, starting from \( \text{CH}_3 \) species, \( \text{CH}_3\text{CHO} \) formation is energetically compatible with \( \text{CH}_4 \) formation, which reduces the productivity and selectivity of C₂ oxygenates. As a result, Rh(211) has relatively low selectivity for \( \text{C}_2\text{H}_5\text{OH} \) from syngas because of the easy formation of \( \text{CH}_4 \).

According to our above analysis, starting from \( \text{CH}_3 \) species, by suppressing the formation of \( \text{CH}_4 \) more \( \text{CH}_3 \) species can participate in the formation of \( \text{CH}_3\text{CHO} \) by CHO insertion into \( \text{CH}_3 \); thus, the production of \( \text{C}_2\text{H}_5\text{OH} \) increases. On the other hand, high production of \( \text{C}_2\text{H}_5\text{OH} \) can also be obtained by lowering the activation barrier of \( \text{CH}_3\text{CHO} \) formation. In this way, \( \text{CH}_4 \) formation also cannot compete with \( \text{CH}_3\text{CHO} \); as a result, more \( \text{C}_2\text{H}_5\text{OH} \) is produced compared to \( \text{CH}_4 \). Therefore, only two variables significantly affect the productivity and selectivity of \( \text{C}_2\text{H}_5\text{OH} \). One is the activation barrier of \( \text{CH}_4 \) formation by \( \text{CH}_3 \) hydrogenation; the other is the activation barrier of CHO insertion into \( \text{CH}_3 \). To achieve high productivity and selectivity of ethanol, the Rh catalyst has to get help from other promoters and/or supports, by which \( \text{CH}_4 \) formation should be minimized and/or C₂ oxygenate formation from \( \text{C}_1 \) oxygenates should be maximized. Up to now, previous studies have shown that the catalytic activity and/or selectivity of the Rh catalyst can be improved by introducing promoters into Rh catalysts.\(^8\)–\(^{11},54\) for example, the promoter Mn can increase the activity and selectivity of \( \text{C}_2 \) oxygenate formation;\(^30\)–\(^34\) meanwhile, the experimental study by Luo et al. further found that the addition of Mn is essential for the
formation of acetic acid and acetaldehyde with high selectivity.\textsuperscript{55}

To validate our predictions about the role of promoter metal and further probe the effect of surface composition on catalytic performance, as mentioned above, we examined the role of promoter Mn and its effect on the catalytic activity and selectivity. For the MnRh(211) surface, two types of models exist: one replaces a Rh atom by a Mn atom, and the other adsorbs a surface Mn atom onto the Rh surface. Up to now, a large number of studies about the effect of the promoter on C\textsubscript{2} oxygenate formation from syngas mainly focused on the first type of model.\textsuperscript{3,4,34,36} Thus, in our study, only the first model with a Rh atom replaced by a Mn atom is employed as the promoter Mn-doped Rh(211) model. Of course, the surface Mn adatom on the Rh surface is also important for investigating the effect of the promoter on ethanol synthesis from syngas.
which will be carried out in our next work. For the promoter Mn-doped MnRh(211) surface, there are three choices for the Mn atom on Rh(211) surface: a step edge, a terrace, and a step base site. Our results show that the MnRh(211) surface with one Mn atom at the step edge is found to be the most easily formed.

Figure 14 presents the comparison of potential energy diagrams for CH3CHO and CH4 formation on Rh(211) and MnRh(211) surfaces. These results show that on the Rh(211) surface, CH3CHO formation is energetically compatible with CH4 formation by CH3 hydrogenation because of the very small difference of activation barrier and reaction energy by 3.1 and 24.2 kJ mol\(^{-1}\), respectively, indicating that the Rh(211) surface exhibits a poor selectivity to C2 oxygenates. However, on MnRh(211), CH3CHO formation by CHO insertion into CH3 requires an activation barrier of 59.3 kJ mol\(^{-1}\) with the reaction energy of −45.5 kJ mol\(^{-1}\), while CH4 formation by CH3 hydrogenation has an activation barrier of 71.8 kJ mol\(^{-1}\) with the reaction energy of 28.8 kJ mol\(^{-1}\). Thus, compared to Rh(211), Mn-promoted MnRh(211) reduces the activation barrier of CH4 and CH3CHO formations; that is, the activity of Mn-promoted MnRh(211) increases. More importantly, CH3CHO formation is much more favorable than CH4 formation, both kinetically and thermodynamically, because of the relatively large difference of activation barrier and reaction energy by 12.5 and 74.3 kJ mol\(^{-1}\), respectively, indicating that the Mn-promoted MnRh(211) surface exhibits a good selectivity to C2 oxygenates rather than CH4. This result

Figure 12. Comparison of potential energy diagram for C2 oxygenates and CH4 formation on Rh(211) and Rh(111) surfaces.

Figure 13. Optimal reaction pathway of ethanol formation from syngas on the stepped Rh(211) with the reaction energies and activation barriers of elementary reactions CH4, CH3OH, and C2H5OH formations. The data unit is kilojoules per mole. See Figure 2 for color coding.

Figure 14. Comparison of potential energy diagrams for CH3CHO and CH4 formation on Rh(211) and MnRh(211) surfaces.
4. CONCLUSIONS

In this study, we investigate the mechanism of ethanol synthesis from syngas on the stepped Rh(211) surface by means of density functional theory method together with a periodic slab model. In addition, the differences of ethanol formation from syngas between the stepped Rh(211) and the flat Rh(111) surfaces have been compared to examine the effect of surface structure on catalytic performance. Furthermore, the promoter Mn-promoted MnRh(211) surface is employed to investigate the effect of surface composition on catalytic performance. Our results show that on the Rh(211) surface, the most favorable route of ethanol formation is CO + 3H → CH3 + O + H → CH3OH, and this route is much easier than CH3 formation via CH3CHO. Finally, ethanol is formed from CH3CHO + 2H → CH3CH2O + H → C2H5OH, where the overall conversion process, CH3 formation is much easier than CH3OH formation; that is, Rh(211) can boost the CH3 source contributing to the formation of C2 oxygenates. However, starting from CH3 species, CH3CHO formation is thermodynamically the most favorable mechanism of ethanol formation from syngas on the stepped Rh(211) surface.

When the promoter Mn is introduced into the Rh(211) surface, Mn can facilitate CHO insertion into CH3, and CH3CHO formation with a lower activation barrier compared to the pure Rh(211) surface; that is, the promoter Mn can increase the catalytic activity of MnRh(211). Meanwhile, CH3CHO formation is much more favorable than CH3 formation, both kinetically and thermodynamically, indicating that the Mn-promoted MnRh(211) surface exhibits a good selectivity to C2 oxygenates rather than CH3. As a result, the promoter Mn can significantly increase the activity and selectivity of C2 oxygenate formation on the Rh catalyst, which agrees well with the reported experimental results.

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Notes
The authors declare no competing financial interest.

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