Electronic Supplementary Information

Ethanol Steam Reforming on Rh: Microkinetic Analyses on the Complex Reaction Network

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1. **Generation of reaction network**

Following the algorithm introduced in the main text, we first defined CH$_3$CH$_2$OH and H$_2$O as reactants and H$_2$ and CO/CO$_2$ as final products. The elementary step types defined for ethanol steam reforming include:

1. removal (addition) of hydrogen from (to) carbon atoms;
2. removal (addition) of OH* and O* from (to) carbon atoms;
3. removal (addition) of hydrogen from (to) oxygen atoms;
4. coupling between carbon atoms in different intermediates.

The screening boundary conditions we defined for identifying the effectiveness of the intermediates generated include:

1. no more than 4 and 2 bonds can be found on carbon and oxygen atoms, respectively;
2. no more than one OH connected to the carbon atom;
3. no more than two carbon atoms in each species;
4. at least one O when the species contains two C;
5. the number of oxygen and carbon atoms in total must be no more than 3 in each species.

Application of boundary conditions (3)–(5) will keep the generated reaction network within a reasonable complexity.

Upon identification of the reaction intermediates and elementary steps, the reaction network for ethanol steam reforming can be generated automatically with microkinetic simulation.
2. Species generated for ethanol steam reforming

2.1 Species in ethanol to CO network

Gas:
H$_2$O, CH$_3$CH$_2$OH, CO, H$_2$

Intermediates:

Transition States:
2.2 Species in ethanol to CO$_2$ network

Gas:

H$_2$O, CH$_3$CH$_2$OH, CO$_2$, H$_2$

Intermediates:


Transition States:

3. Reaction energy ($\Delta E$) and activation barrier ($E_a$) of ethanol steam reforming

Most reaction energies and activation barriers of ethanol steam reforming can be found in our previous study.\textsuperscript{1}

Newly calculated energies in this work are listed below.

**Table S1.** Reaction energy ($\Delta E$) and activation barrier ($E_a$) of surface species on Rh(111).

<table>
<thead>
<tr>
<th>Elementary steps</th>
<th>$E_a$(eV)</th>
<th>$\Delta E$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO* + O* ↔ CO-O* + * ↔ CO$_2$ + 2*</td>
<td>1.22</td>
<td>0.46</td>
</tr>
<tr>
<td>HCOO* + * ↔ H-COO* + * ↔ CO$_2$ + H* + *</td>
<td>1.03</td>
<td>0.26</td>
</tr>
<tr>
<td>COOH* + * ↔ COO-H* + * ↔ CO$_2$ + H* + *</td>
<td>1.12</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Figure S1. Structures of the transition states involved in Table S1.
4. Configurations of adsorption involved in Table 1

Figure S2. Structures of the adsorption species involved in Table 1.
4. Reaction energies and activation energies of the elementary reactions mentioned in this paper and in previous publications

**Table S2.** Reaction energy (ΔE) and activation energy (Ea) of surface reactions on Rh(111) obtained in this work and in previous publications.

<table>
<thead>
<tr>
<th>Elementary steps</th>
<th>This work</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (eV)</td>
<td>$\Delta E$ (eV)</td>
</tr>
<tr>
<td>CH$_3$CH$_2$O$^<em>$ + * $\rightarrow$ CH$_3$CHO$^</em>$ + H$^*$</td>
<td>0.63</td>
<td>-0.05</td>
</tr>
<tr>
<td>CH$_3$CH$_2$O$^<em>$ + * $\rightarrow$ CH$_2$CH$_2$O$^</em>$ + H$^*$</td>
<td>0.93</td>
<td>0.37</td>
</tr>
<tr>
<td>CH$_2$CO$^<em>$ + * $\rightarrow$ CH$_2^</em>$ + CO$^*$</td>
<td>0.59</td>
<td>-0.51</td>
</tr>
<tr>
<td>CH$_2$CO$^<em>$ + * $\rightarrow$ CHCO$^</em>$ + H$^*$</td>
<td>0.67</td>
<td>0.04</td>
</tr>
</tbody>
</table>
5. The equations and the values for each term used for the calculation of CO and 
CO₂ formation rate.

Table S3. The value of parameters involved in the equation of CO₂(a) and CO(b)
formation rate on Rh(111) with different S/E ratio at the temperature of 923 K. θ, Gₐ
and r is in the unit of ML, eV and site⁻¹s⁻¹, respectively.

(a) \( r_{\text{CO}_2,\text{eq}} = A \theta_{\text{CO}} \theta_{\text{O}} e^{G_{a,\text{CO-O}}/k_B T} - A P_{\text{CO}_2} \theta_{\text{e}}^2 e^{G_{a,\text{CO-O}}/k_B T} \), \( P_{\text{CO}_2} = 0.001 \), \( A = 1.92 \times 10^{13} \)

<table>
<thead>
<tr>
<th>S/E</th>
<th>( \theta_{\text{CO}} )</th>
<th>( \theta_{\text{O}} )</th>
<th>( G_{a,\text{CO-O}} )</th>
<th>( \theta_{\text{e}} )</th>
<th>( G_{a,\text{CO-O}} )</th>
<th>Log(( r_{\text{eq}} ))</th>
<th>Log(( r_{\text{CatMap}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.81×10⁻⁴</td>
<td>2.61×10⁻⁴</td>
<td>1.23</td>
<td>0.945</td>
<td>2.13</td>
<td>-0.343</td>
<td>-0.343</td>
</tr>
<tr>
<td>3</td>
<td>4.88×10⁻⁴</td>
<td>4.22×10⁻⁴</td>
<td>1.23</td>
<td>0.960</td>
<td>2.13</td>
<td>-0.115</td>
<td>-0.114</td>
</tr>
<tr>
<td>4</td>
<td>4.90×10⁻⁴</td>
<td>5.83×10⁻⁴</td>
<td>1.23</td>
<td>0.967</td>
<td>2.13</td>
<td>0.034</td>
<td>0.034</td>
</tr>
<tr>
<td>5</td>
<td>4.91×10⁻⁴</td>
<td>7.44×10⁻⁴</td>
<td>1.23</td>
<td>0.971</td>
<td>2.13</td>
<td>0.145</td>
<td>0.145</td>
</tr>
<tr>
<td>6</td>
<td>4.91×10⁻⁴</td>
<td>9.05×10⁻⁴</td>
<td>1.23</td>
<td>0.973</td>
<td>2.13</td>
<td>0.232</td>
<td>0.232</td>
</tr>
</tbody>
</table>

(b) \( r_{\text{CO},\text{eq}} = A \theta_{\text{CO}} e^{G_{a,\text{CO}}/k_B T} - A P_{\text{CO}} \theta_{\text{e}} e^{G_{a,\text{CO}}/k_B T} \), \( P_{\text{CO}} = 0.001 \), \( A = 1.92 \times 10^{13} \)

<table>
<thead>
<tr>
<th>S/E</th>
<th>( \theta_{\text{CO}} )</th>
<th>( G_{a,\text{CO}} )</th>
<th>( \theta_{\text{e}} )</th>
<th>( G_{a,\text{CO}} )</th>
<th>Log(( r_{\text{eq}} ))</th>
<th>Log(( r_{\text{CatMap}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.81×10⁻⁴</td>
<td>1.44</td>
<td>0.945</td>
<td>1.50</td>
<td>0.379</td>
<td>0.379</td>
</tr>
<tr>
<td>3</td>
<td>4.88×10⁻⁴</td>
<td>1.44</td>
<td>0.960</td>
<td>1.50</td>
<td>0.337</td>
<td>0.337</td>
</tr>
<tr>
<td>4</td>
<td>4.90×10⁻⁴</td>
<td>1.44</td>
<td>0.967</td>
<td>1.50</td>
<td>0.279</td>
<td>0.279</td>
</tr>
<tr>
<td>5</td>
<td>4.91×10⁻⁴</td>
<td>1.44</td>
<td>0.971</td>
<td>1.50</td>
<td>0.207</td>
<td>0.207</td>
</tr>
<tr>
<td>6</td>
<td>4.91×10⁻⁴</td>
<td>1.44</td>
<td>0.973</td>
<td>1.50</td>
<td>0.119</td>
<td>0.119</td>
</tr>
</tbody>
</table>
6. Microkinetic simulation test using mobile model

Figure S3. Influence of temperatures on (a) production rate and (b) DRC at constant reactant ratio (S/E = 3:1).
7. Rate of CO$_2$ and CO formation in different conditions

Figure S4. Log(rate) of CO$_2$ and CO formation at different temperatures and S/E ratios.
8. Reaction network of CH₄ generation from ethanol and hydrogen

We considered the reaction path of ethanol and hydrogen to generate CH₄ and water (C₂H₅OH + 2H₂ → 2CH₄ + H₂O). In Figure S5, one can find that most of the elementary steps in this pathway are identical to those presented in Figure 2 in the main text. In addition, methane is produced mainly through the hydrogenation of several intermediates in CO and CO₂ formation pathways, e.g. CH₂* and CO*.

Figure S5: Reaction network of ethanol and hydrogen to generate CH₄ and water on Rh(111).

References