Supporting Information

Source and Existence form of CH$_x$(x=1-3) Species in Acetic Acid Synthesis from Methane-Syngas on Rh Catalyst: A Theoretical Study

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Part 1. Rate constants calculation

In this manuscript, the rate constants of three key steps involved in acetic acid synthesis at different temperatures have been calculated to further understand the effect of reaction temperature on the kinetic of CH$_x$ formation on Rh(111) surface. The three key steps selected are CH$_4$ dehydrogenation to CH$_3$, CO hydrogenation to CHO, and CO insertion into CH, respectively. Previous studies has reported that Rh-based catalysts exhibit a good catalytic activity toward C$_2$ oxygenates, where the reaction temperature ranges from 563 K to 593 K. Hence, on the basis of the Eyring’s transition state theory (TST), the rate constants of these three key steps at T=550, 575 and 600 K have been considered, respectively.

The rate constant can be described with the following formula:

$$k = \frac{k_b T}{h} \left( \frac{p^0}{RT} \right)^{1-n} \exp\left[-\frac{\Delta G^\circ}{RT}\right]$$
Here $k$ is the rate constant, $T$ is the reaction temperature, $n$ is the number of reactants, $k_b$, $h$, $p^0$ and $R$ are the Boltzmann’s constant, Planck’s constant, standard atmospheric pressure, and the fundamental gas constant, respectively. The $\Delta r G_m^\neq$ in above formula is calculated as follows:

$$\Delta r G_m^\neq = \Delta r H_m^\neq - T \Delta r S_m^\neq$$

Here, $\Delta r H_m^\neq$ and $\Delta r S_m^\neq$ are activation enthalpy and activation entropy of the corresponding reactions, respectively, and the $\Delta r H_m^\neq$ and $\Delta r S_m^\neq$ are obtained with the following formula:

$$\Delta r H_m^\neq = E(TS) + H_m^0(TS) - E(R) - H_m^0(R)$$

$$\Delta r S_m^\neq = S_m^0(TS) - S_m^0(R)$$

In these two formulas, since the VASP program can not obtain the values of the enthalpy $H_m^0$ and entropy $S_m^0$ corresponding to the reactants and transition states, the enthalpy $H_m^0$ and the entropy $S_m^0$ of the reactants and transition states are obtained by Dmol$^3$ program in Materials Studio 4.4 with the same calculation parameters as that implemented in VASP. While $E(R)$ and $E(TS)$ are the calculated energies for the reactants and transition states, respectively.

According to these formulas as described above, the rate constants for CH$_4$ dehydrogenation to CH$_3$, CO hydrogenation to CHO, and CO insertion into CH have been calculated, and the corresponding results are listed in Table 1 in the main text.

**Part 2. Microkinetic Modeling**

In this study, the microkinetic modeling technique has been employed to examine the catalytic activity and selectivity of major products in acetic acid synthesis from methane-syngas on Rh(111) surface, in which the method applied is similar to the previous studies. The adsorption process of methane, water and syngas are assumed to be in equilibrium. Besides, all reactions involved in the micro-kinetic modeling have been summarized in Table 2 in the main text.

The equilibrium constants for CH$_4$, H$_2$O and CO adsorption are estimated according to the
formula:

\[ K = \exp\left[-(\Delta E_{ads} - T\Delta S) / RT\right] \]

Here, \( \Delta E_{ads} \) is the adsorption energy of adsorbate, \( \Delta S \) is the entropy change of gas-phase adsorbate, which can be obtained from NIST Chemistry WebBook. While \( R \) is the fundamental gas constant, and \( T \) is the reaction temperature.

The rate constants for \( R1-R14 \) that listed in Table 2 have been calculated using transition state theory (TST) as described in Part 1, and the calculated results are listed in Table S1.

Table S1 Rate constants \( k \) for the major elementary reactions involved in acetic acid synthesis on \( \text{Rh(111)} \) surface at different temperatures.

<table>
<thead>
<tr>
<th>Elementary reactions</th>
<th>Rate constant ( k/s^{-1} )</th>
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<tbody>
<tr>
<td></td>
<td>550K</td>
</tr>
<tr>
<td>R1 ( \text{CH}_4 \rightarrow \text{CH}_3+H )</td>
<td>1.52×10^5</td>
</tr>
<tr>
<td>R2 ( \text{CH}_3 \rightarrow \text{CH}_2+H )</td>
<td>3.37×10^9</td>
</tr>
<tr>
<td>R3 ( \text{CH}_2 \rightarrow \text{CH}+H )</td>
<td>1.08×10^10</td>
</tr>
<tr>
<td>R4 ( \text{CH}+\text{CO} \rightarrow \text{CHCO} )</td>
<td>3.37</td>
</tr>
<tr>
<td>R5 ( \text{CHCO}+\text{OH} \rightarrow \text{CHCOOH} )</td>
<td>9.24×10^4</td>
</tr>
<tr>
<td>R6 ( \text{CHCOOH}+\text{H} \rightarrow \text{CH}_2\text{COOH} )</td>
<td>2.62×10^5</td>
</tr>
<tr>
<td>R7 ( \text{CH}_2\text{COOH}+\text{H} \rightarrow \text{CH}_3\text{COOH} )</td>
<td>3.53×10^6</td>
</tr>
<tr>
<td>R8 ( \text{H}_2\text{O} \rightarrow \text{OH}+\text{H} )</td>
<td>1.88×10^4</td>
</tr>
<tr>
<td>R9 ( \text{CO}+\text{H} \rightarrow \text{CHO} )</td>
<td>6.55×10^{-3}</td>
</tr>
<tr>
<td>R10 ( \text{CHO}+\text{H} \rightarrow \text{CHOH} )</td>
<td>3.26×10^5</td>
</tr>
<tr>
<td>R11 ( \text{CHOH}+\text{H} \rightarrow \text{CH}_2\text{OH} )</td>
<td>1.60×10^5</td>
</tr>
<tr>
<td>R12 ( \text{CH}_2\text{OH}+\text{H} \rightarrow \text{CH}_3\text{OH} )</td>
<td>3.91×10^5</td>
</tr>
<tr>
<td>R13 ( \text{CHO}+\text{H} \rightarrow \text{CH}_2\text{O} )</td>
<td>1.69×10^5</td>
</tr>
<tr>
<td>R14 ( \text{CH}_2\text{O}+\text{H} \rightarrow \text{CH}_2\text{OH} )</td>
<td>6.24×10^4</td>
</tr>
</tbody>
</table>

The site balance of all intermediate species involved in the reaction mechanism can be described in terms of coverage (\( \theta_x, x=\text{surface species} \)), as presented in Equation (1):
\[ \begin{align*}
\theta_{\text{CH}_4} & + \theta_{\text{CH}_3} + \theta_{\text{CH}_2} + \theta_{\text{CHO}} + \theta_{\text{CHCOOH}} + \theta_{\text{CH}_2\text{COOH}} + \theta_{\text{CO}} + \theta_{\text{H}} + \\
\theta_{\text{CHO}} & + \theta_{\text{CH}_2\text{O}} + \theta_{\text{CH}_3\text{OH}} + \theta_{\text{H}_2\text{O}} + \theta_{\text{OH}} + \theta_\ast = 1
\end{align*} \]  

The coverages of \( \text{CH}_4, \text{H}_2\text{O} \) and \( \text{CO} \) are \( \theta_{\text{CH}_4} = P_{\text{CH}_4} K_{\ast} \theta_\ast \), \( \theta_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}} K_{\ast} \theta_\ast \) and \( \theta_{\text{CO}} = P_{\text{CO}} K_{\ast} \theta_\ast \), respectively. Other involved surface species can be described according to the steady-state approximation as summarized below, where the rates for the production and the consumption are considered to be the same.

\( \text{CH}_4: \ \theta_{\text{CH}_4} = P_{\text{CH}_4} K_{\ast} \theta_\ast \)

\( \text{CH}_3: \ \frac{d\theta_{\text{CH}_3}}{dt} = k_1 \theta_{\text{CH}_4} \theta_\ast - k_2 \theta_{\text{CH}_2} \theta_\ast = 0 \)

\( \theta_{\text{CH}_3} = \frac{k_1}{k_2} \theta_{\text{CH}_4} = \frac{k_1}{k_2} P_{\text{CH}_4} K_{\ast} \theta_\ast \)

\( \text{CH}_2: \ \frac{d\theta_{\text{CH}_2}}{dt} = k_2 \theta_{\text{CH}_3} \theta_\ast - k_3 \theta_{\text{CH}_2} \theta_\ast = 0 \)

\( \theta_{\text{CH}_2} = \frac{k_2}{k_3} \theta_{\text{CH}_3} = \frac{k_1}{k_3} P_{\text{CH}_4} K_{\ast} \theta_\ast \)

\( \text{CH}: \ \frac{d\theta_{\text{CH}}}{dt} = k_3 \theta_{\text{CH}_2} \theta_\ast - k_4 \theta_{\text{CO}} \theta_{\text{CH}} = 0 \)

\( \theta_{\text{CH}} = \frac{k_1 P_{\text{CH}_4} K_{\ast}}{k_4 P_{\text{CO}} K_{\ast}} \theta_\ast \)

\( \text{CHCO}: \ \frac{d\theta_{\text{CHCO}}}{dt} = k_4 \theta_{\text{CH}} \theta_{\text{CO}} - k_5 \theta_{\text{CHCO}} \theta_{\text{OH}} = 0 \)

\( \theta_{\text{CHCO}} = \frac{k_1 \theta_{\text{CH}_4}}{k_5 k_8 \theta_{\text{H}_2\text{O}}} \theta_\ast = \frac{k_1 P_{\text{CH}_4} K_{\ast}}{k_5 k_8 P_{\text{H}_2\text{O}} K_{\ast}} \theta_\ast \)

\( \text{CHCOOH}: \ \frac{d\theta_{\text{CHCOOH}}}{dt} = k_3 \theta_{\text{CHCO}} \theta_{\text{OH}} - k_6 \theta_{\text{CHCOOH}} \theta_{\text{H}} = 0 \)

\( \theta_{\text{CHCOOH}} = \frac{k_1 \theta_{\text{CH}_4}}{k_6 \theta_{\text{H}}} \theta_\ast \)

\( \text{CH}_2\text{COOH}: \ \frac{d\theta_{\text{CH}_2\text{COOH}}}{dt} = k_6 \theta_{\text{CHCOOH}} \theta_{\text{H}} - k_7 \theta_{\text{CH}_2\text{COOH}} \theta_{\text{H}} = 0 \)

\( \theta_{\text{CH}_2\text{COOH}} = \frac{k_1 \theta_{\text{CH}_4}}{k_7 \theta_{\text{H}}} \theta_\ast \)
H₂O: \( \theta_{H,O} = P_{H,O} K_2 \theta_* \)

OH: \( \theta_{OH} = k_8 \theta_{H,O} \)

CO: \( \theta_{CO} = P_{CO} K_3 \theta_* \)

CHO: \( \frac{d\theta_{CHO}}{dt} = k_9 \theta_{CO} \theta_H - k_{10} \theta_{CHO} \theta_H - k_{13} \theta_{CHO} \theta_H = 0 \)

\[ \theta_{CHO} = \frac{k_9}{k_{10} + k_{13}} \theta_{CO} = \frac{k_9}{k_{10} + k_{13}} P_{CO} K_3 \theta_* \]

CHOH: \( \frac{d\theta_{CHOH}}{dt} = k_{10} \theta_{CHO} \theta_H - k_{11} \theta_{CHOH} \theta_H = 0 \)

\[ \theta_{CHOH} = \frac{k_{10}}{k_{11}} \theta_{CHO} = \frac{k_9 k_{10}}{k_{11} (k_{10} + k_{13})} P_{CO} K_3 \theta_* \]

CH₂O: \( \frac{d\theta_{CH₂O}}{dt} = k_{13} \theta_{CHO} \theta_H - k_{14} \theta_{CH₂O} \theta_H = 0 \)

\[ \theta_{CH₂O} = \frac{k_{13}}{k_{14}} \theta_{CHO} = \frac{k_9 k_{13}}{k_{14} (k_{10} + k_{13})} P_{CO} K_3 \theta_* \]

CH₂OH: \( \frac{d\theta_{CH₂OH}}{dt} = k_{11} \theta_{CHOH} \theta_H + k_{14} \theta_{CH₂O} \theta_H - k_{12} \theta_{CH₂OH} \theta_H = 0 \)

\[ \theta_{CH₂OH} = \frac{k_9}{k_{12}} P_{CO} K_3 \theta_* \]

\[ \frac{d\theta_H}{dt} = \theta_{H_2} \theta_H + k_3 \theta_{CH₄} \theta_H + k_5 \theta_{CH₂} \theta_H + k_7 \theta_{H₂O} \theta_H - k_8 \theta_{CH₂OH} \theta_H - k_{13} \theta_{COH} \theta_H \]

\[ -k_9 \theta_{CO} \theta_H - k_{10} \theta_{CHO} \theta_H - k_{11} \theta_{CHOH} \theta_H - k_{12} \theta_{CH₂OH} \theta_H - k_{13} \theta_{COH} \theta_H - k_{14} \theta_{CH₂O} \theta_H = 0 \]

\[ \theta_H = \frac{P_{H_2} K_4^{1/2} + k_1 P_{CH₄} K_1 + k_4 P_{H₂O} K_2}{4k_9 P_{CO} K_3} \theta_* \]

Putting all of the coverage expressions into Equation (1), the coverage of surface free sites \( \theta_* \) can be calculated as follows. Subsequently, the coverage of adsorbates can be obtained.
The rates for the major products CH₃OH and CH₃COOH are:

\[ r_{CH_3OH} = k_{12} \theta_{CH_3OH} \theta_H, \quad r_{CH_3COOH} = k_{17} \theta_{CH_3COOH} \theta_H \]

The relative selectivity is defined by the relative rate for each product, in which \( i \) is CH₃COOH or CH₃OH:

\[ s_i = r_i / (r_{CH_3OH} + r_{CH_3COOH}) \]
References


(8) http://webbook.nist.gov/chemistry/.