

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

Xiaojun Zhao,^{a,b} Riguang Zhang,^{a,*} Qiang Wang,^b Debao Li,^b Baojun Wang,^{a,*} Lixia Ling,^a

^a Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, P.R. China

^b State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, PR China

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 CH₄ dehydrogenation to CH₃, CO hydrogenation to CHO, and CO insertion into CH, respectively. Previous studies has reported that Rh-based catalysts exhibit a good catalytic activity toward C₂ oxygenates, where the reaction temperature ranges from 563 K to 593 K.¹⁻³ Hence, on the basis of the Eyring's transition state theory (TST),⁴ 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:

$$k = \frac{k_b T}{h} \left(\frac{P^0}{RT} \right)^{1-n} \exp\left[-\frac{\Delta_r G_m^\ddagger}{RT}\right]$$

* Corresponding author at: No. 79 Yingze West Street, Taiyuan 030024, China. Tel.: +86 351 6018239; Fax: +86 351 6041237 E-mail address: zhangriguang@tyut.edu.cn (Riguang Zhang); wangbaojun@tyut.edu.cn (Baojun Wang)

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 $\Delta_r G_m^\ddagger$ in above formula is calculated as follows:

$$\Delta_r G_m^\ddagger = \Delta_r H_m^\ddagger - T \Delta_r S_m^\ddagger$$

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

$$\Delta_r H_m^\ddagger = E(TS) + H_m^0(TS) - E(R) - H_m^0(R)$$

$$\Delta_r S_m^\ddagger = S_m^0(TS) - S_m^0(R)$$

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 Dmol³ 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 CH₄ dehydrogenation to CH₃, 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.⁵⁻⁷ 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 CH₄, H₂O and CO adsorption are estimated according to the

formula:

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

Here, ΔE_{ads} is the adsorption energy of adsorbate, ΔS is the entropy change of gas-phase adsorbate, which can be obtained from NIST Chemistry WebBook.⁸ 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)⁴ 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 Rh(111) surface at different temperatures.

Elementary reactions		Rate constant k/s^{-1}		
		550K	575K	600K
R1	$CH_4 \rightarrow CH_3 + H$	1.52×10^5	2.87×10^5	5.14×10^5
R2	$CH_3 \rightarrow CH_2 + H$	3.37×10^9	4.82×10^9	6.70×10^9
R3	$CH_2 \rightarrow CH + H$	1.08×10^{10}	1.33×10^{10}	1.61×10^{10}
R4	$CH + CO \rightarrow CHCO$	3.37	11.08	32.98
R5	$CHCO + OH \rightarrow CHCOOH$	9.24×10^4	1.81×10^5	3.36×10^5
R6	$CHCOOH + H \rightarrow CH_2COOH$	2.62×10^5	5.35×10^5	1.03×10^6
R7	$CH_2COOH + H \rightarrow CH_3COOH$	3.53×10^6	6.11×10^6	1.01×10^7
R8	$H_2O \rightarrow OH + H$	1.88×10^4	3.65×10^4	6.70×10^4
R9	$CO + H \rightarrow CHO$	6.55×10^{-3}	2.49×10^{-2}	8.52×10^{-2}
R10	$CHO + H \rightarrow CHOH$	3.26×10^5	8.62×10^5	2.10×10^6
R11	$CHOH + H \rightarrow CH_2OH$	1.60×10^5	3.03×10^5	5.45×10^5
R12	$CH_2OH + H \rightarrow CH_3OH$	3.91×10^5	8.37×10^5	1.69×10^6
R13	$CHO + H \rightarrow CH_2O$	1.69×10^5	3.61×10^5	7.26×10^5
R14	$CH_2O + H \rightarrow CH_2OH$	6.24×10^4	1.31×10^5	2.59×10^5

The site balance of all intermediate species involved in the reaction mechanism can be described in terms of coverage (θ_x , x =surface species), as presented in [Equation \(1\)](#):

$$\begin{aligned} &\theta_{CH_4} + \theta_{CH_3} + \theta_{CH_2} + \theta_{CH} + \theta_{CHCO} + \theta_{CHCOOH} + \theta_{CH_2COOH} + \theta_{CO} + \theta_H + \\ &\theta_{CHO} + \theta_{CHOH} + \theta_{CH_2O} + \theta_{CH_2OH} + \theta_{H_2O} + \theta_{OH} + \theta_* = 1 \end{aligned} \quad (1)$$

The coverages of CH₄, H₂O and CO are $\theta_{CH_4}=P_{CH_4}K_1\theta_*$, $\theta_{H_2O}=P_{H_2O}K_2\theta_*$ and $\theta_{CO}=P_{CO}K_3\theta_*$, respectively. Other involved surface species can be described according to the steady-state approximation as summarized below,⁷ where the rates for the production and the consumption are considered to be the same.

$$\text{CH}_4: \theta_{CH_4} = P_{CH_4}K_1\theta_*$$

$$\text{CH}_3: \frac{d\theta_{CH_3}}{dt} = k_1\theta_{CH_4}\theta_* - k_2\theta_{CH_3}\theta_* = 0$$

$$\theta_{CH_3} = \frac{k_1}{k_2}\theta_{CH_4} = \frac{k_1}{k_2}P_{CH_4}K_1\theta_*$$

$$\text{CH}_2: \frac{d\theta_{CH_2}}{dt} = k_2\theta_{CH_3}\theta_* - k_3\theta_{CH_2}\theta_* = 0$$

$$\theta_{CH_2} = \frac{k_2}{k_3}\theta_{CH_3} = \frac{k_1}{k_3}P_{CH_4}K_1\theta_*$$

$$\text{CH}: \frac{d\theta_{CH}}{dt} = k_3\theta_{CH_2}\theta_* - k_4\theta_{CO}\theta_{CH} = 0$$

$$\theta_{CH} = \frac{k_1P_{CH_4}K_1}{k_4P_{CO}K_3}\theta_*$$

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

$$\theta_{CHCO} = \frac{k_1\theta_{CH_4}}{k_5k_8\theta_{H_2O}}\theta_* = \frac{k_1P_{CH_4}K_1}{k_5k_8P_{H_2O}K_2}\theta_*$$

$$\text{CHCOOH}: \frac{d\theta_{CHCOOH}}{dt} = k_5\theta_{CHCO}\theta_{OH} - k_6\theta_{CHCOOH}\theta_H = 0$$

$$\theta_{CHCOOH} = \frac{k_1\theta_{CH_4}}{k_6\theta_H}\theta_*$$

$$\text{CH}_2\text{COOH}: \frac{d\theta_{CH_2COOH}}{dt} = k_6\theta_{CHCOOH}\theta_H - k_7\theta_{CH_2COOH}\theta_H = 0$$

$$\theta_{CH_2COOH} = \frac{k_1\theta_{CH_4}}{k_7\theta_H}\theta_*$$

$$\text{H}_2\text{O}: \theta_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}} K_2 \theta_*$$

$$\text{OH}: \theta_{\text{OH}} = k_8 \theta_{\text{H}_2\text{O}}$$

$$\text{CO}: \theta_{\text{CO}} = P_{\text{CO}} K_3 \theta_*$$

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

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

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

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

$$\text{CH}_2\text{O}: \frac{d\theta_{\text{CH}_2\text{O}}}{dt} = k_{13} \theta_{\text{CHO}} \theta_H - k_{14} \theta_{\text{CH}_2\text{O}} \theta_H = 0$$

$$\theta_{\text{CH}_2\text{O}} = \frac{k_{13}}{k_{14}} \theta_{\text{CHO}} = \frac{k_9 k_{13}}{k_{14} (k_{10} + k_{13})} P_{\text{CO}} K_3 \theta_*$$

$$\text{CH}_2\text{OH}: \frac{d\theta_{\text{CH}_2\text{OH}}}{dt} = k_{11} \theta_{\text{CHOH}} \theta_H + k_{14} \theta_{\text{CH}_2\text{O}} \theta_H - k_{12} \theta_{\text{CH}_2\text{OH}} \theta_H = 0$$

$$\theta_{\text{CH}_2\text{OH}} = \frac{k_9}{k_{12}} P_{\text{CO}} K_3 \theta_*$$

$$\text{H}: \frac{d\theta_H}{dt} = \theta_{\text{H}_2} \theta_* + k_1 \theta_{\text{CH}_4} \theta_* + k_2 \theta_{\text{CH}_3} \theta_* + k_3 \theta_{\text{CH}_2} \theta_* + k_8 \theta_{\text{H}_2\text{O}} \theta_* - k_6 \theta_{\text{CHCOOH}} \theta_H - k_7 \theta_{\text{CH}_2\text{COOH}} \theta_H - k_9 \theta_{\text{CO}} \theta_H - k_{10} \theta_{\text{CHO}} \theta_H - k_{11} \theta_{\text{CHOH}} \theta_H - k_{12} \theta_{\text{CH}_2\text{OH}} \theta_H - k_{13} \theta_{\text{CHO}} \theta_H - k_{14} \theta_{\text{CH}_2\text{O}} \theta_H = 0$$

$$\theta_H = \frac{P_{\text{H}_2}^{1/2} K_4^{1/2} + k_1 P_{\text{CH}_4} K_1 + k_8 P_{\text{H}_2\text{O}} K_2}{4k_9 P_{\text{CO}} K_3} \theta_*$$

Putting all of the coverage expressions into Equation (1), the coverage of surface free sites θ_* can be calculated as follows. Subsequently, the coverage of adsorbates can be obtained.

$$\begin{aligned}
& P_{CH_4} K_1 \theta_* + \frac{k_1}{k_2} P_{CH_4} K_1 \theta_* + \frac{k_1}{k_3} P_{CH_4} K_1 \theta_* + \frac{k_1 P_{CH_4} K_1}{k_4 P_{CO} K_3} \theta_* + \frac{k_1 P_{CH_4} K_1}{k_5 k_8 P_{H_2O} K_2} \theta_* + \\
& \frac{4k_1 k_9 P_{CH_4} K_1 P_{CO} K_3}{k_6 (P_{H_2}^{1/2} K_4^{1/2} + k_1 P_{CH_4} K_1 + k_8 P_{H_2O} K_2)} \theta_* + \frac{4k_1 k_9 P_{CH_4} K_1 P_{CO} K_3}{k_7 (P_{H_2}^{1/2} K_4^{1/2} + k_1 P_{CH_4} K_1 + k_8 P_{H_2O} K_2)} \theta_* \\
& + P_{CO} K_3 \theta_* + \frac{P_{H_2}^{1/2} K_4^{1/2} + k_1 P_{CH_4} K_1 + k_8 P_{H_2O} K_2}{4k_9 P_{CO} K_3} \theta_* + \frac{k_9}{k_{10} + k_{13}} P_{CO} K_3 \theta_* + \frac{k_9 k_{10}}{k_{11} (k_{10} + k_{13})} P_{CO} K_3 \theta_* \\
& + \frac{k_9 k_{13}}{k_{14} (k_{10} + k_{13})} P_{CO} K_3 \theta_* + \frac{k_9}{k_{12}} P_{CO} K_3 \theta_* + P_{H_2O} K_2 \theta_* + k_8 P_{H_2O} K_2 \theta_* + \theta_* = 1
\end{aligned}$$

The rates for the major products CH₃OH and CH₃COOH are:

$$r_{CH_3OH} = k_{12} \theta_{CH_2OH} \theta_H, \quad r_{CH_3COOH} = k_7 \theta_{CH_2COOH} \theta_H$$

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

- (1) Lin, P. Z.; Liang, D. B.; Luo, H. Y.; Xu, C. H.; Zhou, H. W.; Huang, S. Y.; Lin, L. W. Synthesis of C₂₊-oxygenated Compounds Directly From Syngas. *Appl. Catal. A: Gen.* **1995**, *131*, 207–214.
- (2) Luo, H. Y.; Lin, P. Z.; Xie, S. B.; Zhou, H. W.; Xu, C. H.; Huang, S. Y.; Lin, L. W.; Liang, D. B.; Yin, P. L.; Xin, Q. The role of Mn and Li promoters in supported rhodium catalysts in the formation of acetic acid and acetaldehyde. *J. Mol. Catal. A: Chem.* **1997**, *122*, 115–123.
- (3) Chen, W. M.; Ding, Y. J.; Jiang, D. H.; Wang, T.; Luo, H. Y. A selective synthesis of acetic acid from syngas over a novel Rh nanoparticles/nanosized SiO₂ catalysts. *Catal. Commun.* **2006**, *7*, 559–562.
- (4) Zhang, R. G.; Wang, G. R.; Wang, B. J. Insights into the mechanism of ethanol formation from syngas on Cu and an expanded prediction of improved Cu-based catalyst. *J. Catal.* **2013**, *305*, 238–255.
- (5) Liu, P.; Rodriguez, J. A. Water-gas-shift reaction on metal nanoparticles and surfaces. *J. Chem. Phys.* **2007**, *126*, 164705.
- (6) Choi, Y. M.; Liu, P. Mechanism of Ethanol Synthesis from Syngas on Rh(111). *J. Am. Chem. Soc.* **2009**, *131*, 13054–13061.
- (7) Liu, P.; Logadottir, A.; Nørskov, J. K. Modeling the electro-oxidation of CO and H₂/CO on Pt, Ru, PtRu and Pt₃Sn. *Electrochimica Acta* **2003**, *48*, 3731–3742.
- (8) <http://webbook.nist.gov/chemistry/>.