

KINETIC MONTE-CARLO SIMULATION OF METHANE STEAM REFORMING TO SYNTHESIS GAS OVER NI CATALYST

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ABSTRACT

The methane steam reforming reaction over nickel surface is investigated by using kinetic monte-carlo (KMC) simulation technique. This simulation model is based on the Langmuir–Hinshelwood mechanism, and the Random Selection Method (RSM) for algorithm of KMC simulation is utilized. The kinetic rate constants of elementary reactions are used to determine the probability of each possible reaction pathway for the overall reaction. The effect of pressure and temperature on the adsorption and surface elementary step reactions are also included in the rate constants. The effect of feed concentration of methane (CH₄), steam (H₂O) and temperature are further investigated by performing the KMC simulation. The fractional coverage of the adsorbed species, selectivity of CO, and CO₂ and the production rates of H₂, CO, and CO₂ are evaluated at steady state as functions of feed concentration and reaction temperature. From the simulation results, the mole fraction of methane (y) in gas phase reveals a range of active window between y₁ and y₂, where y₁=0.3 and y₂=0.6 at 823 K. Outside of this range, the surface is mostly covered by O*, C* and CH₃*. The results from KMC study show similar trend with the experimental data reported by other research groups.

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INTRODUCTION

Methane is a main component in natural gas and can be chemically converted to synthesis gas or syngas. Syngas is the mixture of hydrogen and carbon monoxide which can subsequently reacts to form other chemicals. There are three main processes to produce syngas, which are reforming, partial oxidation and gasification. Steam reforming is one of the most common and economical way to make hydrogen. The raw materials for this process are steam (H₂O) and hydrocarbon (methane). Hydrogen atom is disassociated from steam and the hydrocarbon. The remaining oxygen from steam and the carbon from the hydrocarbon react to form carbon monoxide (CO). Noble metals have been successfully used in methane reforming catalysts, providing stable and active catalysts at low temperatures. Ni catalysts are preferred in industrial applications due to high activity and relatively low costs, but the disadvantage is the rapid carbon deposition on the catalyst. Consequently, deactivation of Ni catalysts results from coke formation at high

temperatures. This work focuses on the modelling of methane steam reforming over Ni catalysts based on the Langmuir-Hinshelwood (LH) mechanism under isothermal conditions by using kinetic Monte-Carlo (KMC) simulation. KMC is a method that utilizes the statistical approach to the kinetics study, particularly, on surface reaction. KMC is applied to investigate complex kinetic behavior for heterogeneous catalyst. The well-known Kinetic Monte-Carlo model for the oxidation reaction of carbon monoxide on the surface catalyst is by ZGB model (Ziff *et al.*, 1986). This work is based on ZGB model to study the steaming reforming reaction. The simulated results are obtained after sufficient steps of simulation (steady production rate). For the same kinetics constants, the simulated results are also compared with the results from experiments reported previously by other group (Sprung *et al.*, 2014). Subsequently, the effect of feed concentration, reaction temperature are also investigated.

SIMULATION PROCEDURE

The reaction pathways of methane steam reforming on nickel catalyst are described 34 elementary steps as following, adsorption of reactant (R1-R2, activation of methane without oxygen (R3-R10), activation of methane with oxygen (R11-R18), dissociation of water (R19-R22) and the surface reaction to form products (CO₂, CO, H₂) followed by desorption (R23-R34) as summarized in Table 1.

Table 1 Elementary step mechanism for methane steam reforming including the activation energies (Ea) and pre-exponential factors (A).

	Elementary reaction step	A(cm ² /mol·s)/S ₀	b	Ea(kJ/mol)
R1	H ₂ O _(g) + * → H ₂ O*	2870 ^a	0	0
R2	CH _{4(g)} + * → CH ₄ *	2700 ^a	0	0
R3†	CH ₄ * + Ni* → CH ₃ * + H*	1.54×10 ²¹	0.087	55.8
R4†	CH ₃ * + H* → CH ₄ * + *	1.44×10 ²²	-0.087	63.4
R5†	CH ₃ * + Ni* → CH ₂ * + H*	1.54×10 ²⁴	0.087	98.1
R6†	CH ₂ * + H* → CH ₃ * + *	3.09×10 ²³	-0.087	57.2
R7†	CH ₂ * + * → CH* + H*	3.70×10 ²⁴	0.087	95.2
R8†	CH* + H* → CH ₂ * + *	9.77×10 ²⁴	0.087	81
R9†	CH* + * → C* + H*	9.88×10 ²⁰	0.5	21.9
R10	C* + H* → CH* + *	1.70×10 ²⁴	0.5	157.9
R11†	CH ₄ * + O* → CH ₃ * + OH*	5.62×10 ²⁴	0.101	92.7
R12†	CH ₃ * + OH* → CH ₄ * + O*	2.98×10 ²²	-0.101	25.8
R13	CH ₃ * + O* → CH ₂ * + OH*	1.22×10 ²⁵	0.101	134.6
R14†	CH ₂ * + OH* → CH ₃ * + O*	1.39×10 ²¹	-0.101	19
R15	CH ₂ * + O* → CH* + OH*	1.22×10 ²⁵	0.101	131.3
R16	CH* + OH* → CH ₂ * + O*	4.40×10 ²²	0.101	42.4
R17†	CH* + O* → C* + OH*	2.47×10 ²¹	0.312	57.7
R18	C* + OH* → CH* + O*	2.43×10 ²¹	0.312	118.9
R19	H ₂ O* + * → H* + OH*	3.67×10 ²¹	0.086	92.9

R20†	$H^* + OH^* \rightarrow H_2O^* + *$	1.85×10^{20}	-0.086	41.5
R21	$H^* + O^* \rightarrow OH^* + *$	3.95×10^{23}	0.188	104.3
R22†	$OH^* + * \rightarrow H^* + O^*$	2.25×10^{20}	0.188	29.6
R23	$C^* + O^* \rightarrow CO^* + *$	3.40×10^{23}	0	148.1
R24†	$C^* + OH^* \rightarrow H^* + CO^*$	3.88×10^{25}	0.188	62.5
R25†	$CO^* + O^* \rightarrow CO_2^* + *$	2.00×10^{19}	0	123.6
R26†	$CO_2^* + * \rightarrow CO^* + O^*$	4.64×10^{23}	-1	89.3
R27	$CO^* + OH^* \rightarrow COOH^* + *$	6.00×10^{21}	0.213	97.6
R28†	$COOH^* + * \rightarrow CO^* + OH^*$	1.46×10^{24}	0.213	54.3
R29	$CO_2^* + H^* \rightarrow COOH^* + *$	6.25×10^{24}	0.475	117.2
R30†	$COOH^* + * \rightarrow CO_2^* + H^*$	3.73×10^{20}	-0.475	33.6
R31†	$H^* + H^* \rightarrow * + * + H_{2(g)}$	2.54×10^{20}	0	95.2
R32	$CO_2^* \rightarrow CO_{2(g)} + *$	6.44×10^7	0	25.9
R33	$CO^* \rightarrow CO_{(g)} + *$	3.56×10^{11}	0	111.2
R34†	$H_2O^* \rightarrow H_{2O(g)} + *$	3.73×10^{12}	0	60.7

† assumed instantaneous (probability of an event = 1).

A is the pre-exponential factors for adsorption reactions ($Pa^{-1}s^{-1}$).

The surface site density of $\Gamma = 2.66 \times 10^{-9} \text{ mol.cm}^{-2}$ is calculated by assuming a site area of $6.5 \times 10^{-2} \text{ nm}^2$ as observed for nickel.

R1-R2 from Sprung *et al.* (Sprung *et al.*, 2014).

R3-R34 from Delgado *et al.* (Delgado *et al.*, 2015).

The model was initially defined surface catalyst as a two-dimensional square lattice of $L \times L$ sites with periodic boundary conditions. The surface is in contact with an infinite reservoir of methane (CH_4) and steam (H_2O) gas molecules at a fixed pressure. After reactants adsorption, the reaction is initiated and the intermediate species are formed. The KMC algorithm consists of the following steps:

1. Set the lattice site and initial configuration for the simulation.
2. Select one of the lattice sites randomly and random number (n) uniformly distributed in the range of (0,1).
3. Perform the instantaneous events. (R3, R4, R5, R6, R7, R8, R9, R11, R12, R14, R17, R20, R22, R24, R25, R26, R28, R30, R31 and R34). If the conditions for the selected site and its neighboring are satisfied, the surface reaction will spontaneously take place.
4. Calculate the probability of an event i (p_i) as defined by Eq. 1. An event i is chosen from the all the possible events in the possible mechanism, except the instantaneous events (for this case, $i = R1, R2, R10, R13, R15, R16, R18, R19, R21, R23, R27, R29, R32, R33$)

$$p_i = \frac{k_i}{\sum k_i} \quad (1)$$

Where k_i corresponds to the rate constant of step i of the mechanism. In the case of adsorption, k_i can be calculated from the Eq. 2, where k_i^0 is adsorption coefficient, y_i is

mole fraction in the gas phase and P is the total pressure of reactant. In the case of surface reaction (Eq. 3), A_i is the pre-exponential factor, E_{ai} is the activation energy, R is the gas constant and T is the reaction temperature.

$$k_i = k_i^0 y_i P \quad (2)$$

$$k_i = AT^b \exp(-E_a/RT) \quad (3)$$

5. Update time from t to $t + \Delta t$ by using Eq. 4, where r is a uniformly distributed random number between 0 and 1, L is lattice length and $\sum k_i$ is the sum of all reaction constants (excluding the instantaneous events).

$$\Delta t = \frac{-\ln(r)}{L^2 \sum k_i} \quad (4)$$

6. Repeat from 2, and perform the calculation until all the lattice sites are checked. After all sites are calculated, then a step of Monte Carlo is completed. All procedure is started again for the next Monte Carlo Step (MCS) until the steady state is obtained.

In this study, up to 120,000 MCS was carried out to ensure that the steady state is reached. To avoid non-steady state behavior, the first 10,000 MCS were omitted. The fractional coverages and production rate were then known by averaging after 100,000 MCS. The production rates of H_2 , CO , and CO_2 , are shown in the unit of molecules per lattice site per a unit time.

RESULTS AND DISCUSSION

A. Effect of reaction temperature

In this simulation, the reaction temperature was varied in the range of 600 – 1000 K. The fractional coverages and the production rate are shown in Figure 1a and 1b respectively. At the temperature below 700 K, it is obviously seen that the surface of catalyst is mostly covered by O^* , CH_3^* and C^* . Because the reaction is preferable at high temperature, therefore, the step R23 reaction does not effectively take place leading to remaining of oxygen and carbon atoms on the surface. If reaction is in a range of higher temperature (700 – 900 K), the oxygen and carbon atoms on the surface are lower. The appropriate reaction temperature was found to be at 800 - 850 K as indicated by high production rate of H_2 and CO (Figure 1b). When the temperature is higher than 900 K, it is found that the production rate is considerably reduced due to less methane and steam adsorption as shown in Figure 1a.

B. Effect of feed concentration

The effects of feed concentration at 823 K on fractional coverages and production rate are shown in Figure 2a and 2b respectively. It can be noticed that the reaction considerably occurs in a range of $y_{CH_4} = 0.3-0.6$. However, when the methane mole fraction is outside of

this range, the catalyst surface is mostly covered by O*, C* or CH₃*. As shown in Figures 2b, the production rates of H₂, CO₂ and CO continuously increase with increasing y_{CH₄} toward 0.5. However, the surface of catalyst is mainly covered by C* and CH₃* resulting in decreasing of the production rates when y_{CH₄} is higher than 0.6 as shown in Figure 3c.

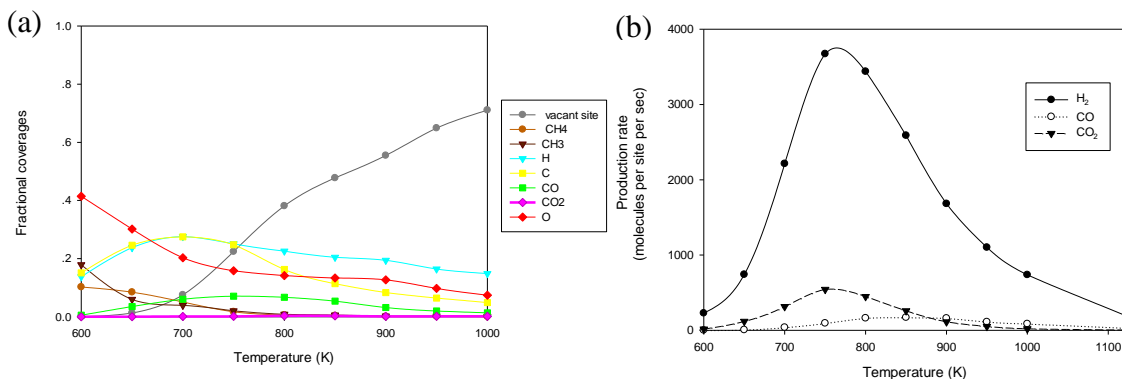


Figure 1. (a) Fractional coverages and (b) Production rates of H₂, CO and CO₂ as functions of temperature 600 – 1000 K; L= 64, y_{CH₄}= 0.5, P= 1 atm, Z= 4, I= 0 (steady state).

Moreover, when y_{CH₄} is less than 0.3, the surface of catalyst is largely covered by O* resulting in the oxidation of Ni surface as shown in Figure 3a. Furthermore, it is interesting to note that the maximum of H₂ and CO production rates is obtained when y_{CH₄} approaching 0.5. The surface of catalyst is therefore covered by C*, H*, O*, CO* and CO₂* in accordance with this condition as shown in Figure 3b. From these results, it also exhibits the CO* formation (R23, R24, R26 and R28) on the surface when C* reacts with a neighboring site of O* or OH* to form CO* during desorption of CO*. Consequently, vacant sites is again obtained on the surface where subsequently the new incoming reactants can be adsorbed.

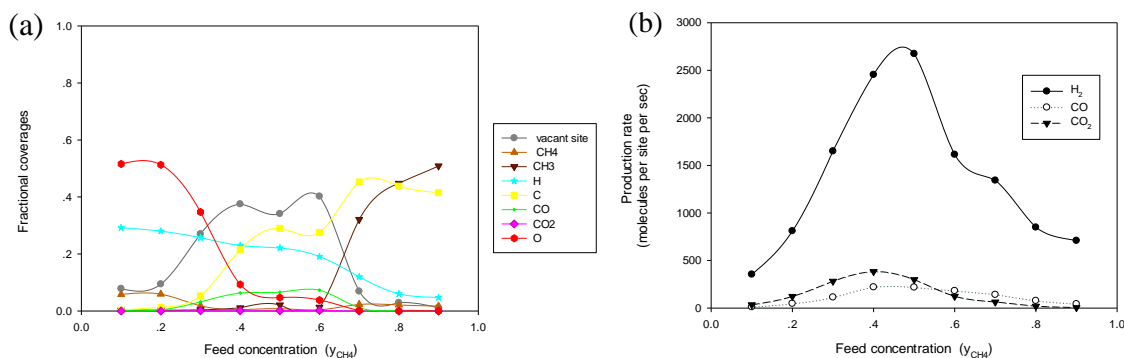


Figure 2. (a) Fractional coverages and (b) Production rates of H₂, CO and CO₂ as functions of y_{CH₄}; L= 64, T = 823 K, P= 1 atm, Z= 4, I= 0 (steady state).

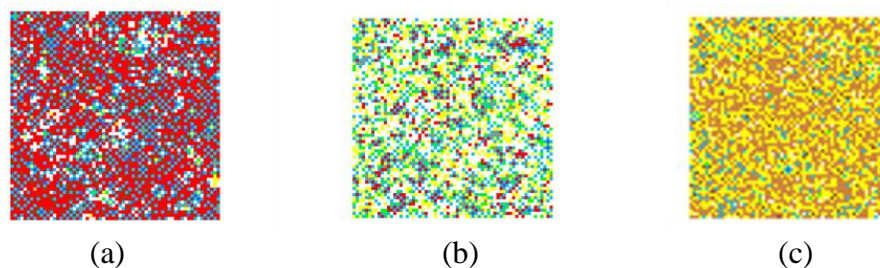


Figure 3. Snapshots of the substrate's surface (steady state conditions) for (a) $y_{\text{CH}_4}= 0.20$ (b) $y_{\text{CH}_4}= 0.50$ (c) $y_{\text{CH}_4}= 0.70$; $L= 64$, $T= 823$ K , $P= 1$ atm, $Z= 4$, $I= 0$. \square = Empty, \blacksquare = H, \blacksquare = C, \blacksquare = O, \blacksquare = CH_4 , \blacksquare = CH_3 , \blacksquare = CH_2 , \blacksquare = C, \blacksquare = CO, \blacksquare = OH.

CONCLUSIONS

Kinetic Monte-Carlo model is applied to investigate the mechanism of methane steam reforming over Ni catalyst. According to the simulation results, the reaction appropriately occurs in a range of methane feed concentration at 0.3 to 0.6 and reaction temperature from 800 to 850 K. Outside of this range, the surface of catalyst is mainly covered by O^* , C^* or CH_3^* . When the mole fraction of methane (y_{CH_4}) is lower than 0.3, the surface of catalyst is covered by O^* resulting in prohibiting the new incoming reactants on the surface. If y_{CH_4} is higher than 0.6, deposition of carbon on the catalyst surface is observed. Another notable result is that the maximum of H_2 and CO production rates is obtained when y_{CH_4} approaching 0.5.

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