[Article]

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甲烷部分氧化过程中强制振荡的动力学 Monte Carlo 模拟

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摘要: 为了有效控制动力学振荡行为以提高反应的转化率, 利用 Monte Carlo 方法研究了甲烷催化部分氧化过程中的强制振荡行为, 探讨了原料气周期性变化对振荡动力学和转化率的影响. 研究表明原料气周期性变化不仅可以有效调控振荡的动力学行为, 产生如短周期振荡和双峰振荡等特殊动力学过程, 而且还可以提高反应的转化率. 当强制过程的周期从 $T/3$ 增大到 $2T$ (T 为自发振荡过程的平均周期), 振荡过程从短周期振荡变化为双峰振荡. 对反应过程中 CO 的转化率进行了计算, 结果表明原料气周期性变化可以有效提高反应的转化率. 振荡动力学的改变和转化率的提高主要是因为强制振荡过程使得催化剂表面发生了从氧化态向还原态的转变.

关键词: Monte Carlo 模拟; 强制振荡; 甲烷部分氧化

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A Kinetic Monte Carlo Simulation on Forced Oscillations of Methane Partial Oxidation

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Abstract: To control the kinetic oscillations for the purpose of obtaining a high conversion rate, external forcing of methane oxidation on metal catalysts was studied with kinetic Monte Carlo simulations. The influence of composition cycling of the feed on the dynamics and conversion rate was investigated. The results showed that the composition cycling of feed cannot give rise to different kinetic behavior, such as short periods or double-peaks, but does bring about a higher conversion rate. It was shown that with forcing periods from $T/3$ to $2T$ (T is the average period of autonomous oscillations), the oscillations changed from short periods and small amplitudes to typical double-peak oscillations. The conversion rate can also be calculated, and the results showed that the mean conversion was slightly higher with forced oscillations. The changing of the kinetics can be attributed to phase transition of the metal catalysts from the oxidized surface to a partially reduced state.

Key Words: Monte Carlo simulation; Forced oscillation; Partial oxidation of methane

1 Introduction

The oxidation of methane on metal catalysts can result in partial oxidation to syngas (CO and H₂), which is mostly used for synthesis of chemical materials, for example methanol. It has been reported that the catalytic oxidation of methane exhibits kinetic oscillations in a variety of catalysts including palladium, nickel,

cobalt, and nickel/chromium alloy.¹ The analysis of oscillatory behavior can present valuable information about the intrinsic mechanisms of catalytic reactions. Besides, it is practical to use oscillations to avoid dangerous oscillatory state of reactors, or bring better catalytic performance in some cases. For instance the utilization of pressure cycling is targeted at changing kinetic

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oscillations, which results in high conversion rate.²

To interpret this complex dynamics in partial oxidation of methane under Ni catalysts, both experimental studies and simulations have been proposed. With experimental studies, the oscillations over Ni foam,³ wire and foil,^{4,5} nickel/chromium alloy,⁶⁻⁹ and supported nickel catalyst¹⁰ have been investigated. With simulations, Slinko¹¹ and Lashina¹² *et al.* developed continuous mathematical models for describing the oscillatory behavior during methane partial oxidation in isothermal and nonisothermal conditions, respectively. In our previous studies,¹³⁻¹⁷ the oscillations during partial oxidation of methane have been surveyed by Monte Carlo (MC) simulations with 12- and 18-step Langmuir-Hinshelwood (LH) mechanism and the formation and removal of nickel oxide under isothermal and nonisothermal conditions, and the formation mechanism of reaction rate oscillations has also been discussed in detail. In all the studies, it is generally suggested that the oscillations over Ni catalysts originate from the repetitive cycles of oxidation and reduction of the metal surface.

After the fact of mechanism has been clarified, the next goal is to control the kinetics on the purpose of avoiding dangerous oscillatory state or bringing about better catalytic performance and high conversion rate. Practically, a large number of researches have been focused on improving the conversion rate of methane to syngas, such as catalytic oxidation of methane on special catalysts in high pressure or high temperature.¹⁸⁻²⁰ In earlier studies, it has also been shown that forced composition cycling of the feed to catalytic reactions can lead to significant dynamic change and rate enhancement for the platinum catalyzed CO+N₂O reaction,²¹ and CO+O₂ reaction.²² How does the composition cycling of feed influence the dynamics and conversion during partial oxidation of methane on catalysts? This paper studies the impact of forced composition cycling of the feed on the dynamics and conversion in methane oxidation to CO and H₂ by using kinetic MC simulations.

2 MC model

The partial oxidation of methane on Ni catalysts follows the Langmuir-Hinshelwood mechanism. Because the formation of CO₂ and H₂O may be ruled out in some circumstances, in the simulation the main products (CO and H₂) are only considered. The detailed 12 step elementary reactions have been given and summarized in Table 1.

In the MC model, the catalyst surface is represented by a two-dimensional square lattice of $L \times L$ sites with periodic boundary conditions. CH₄ adsorption occurs on an empty site while O₂ adsorption on a pair of nearest-neighbor (nn) empty sites. CH₄ desorption and nickel oxide formation are treated as first-order processes. The sum of rate constants for O desorption, LH step (reaction between adsorbed C and O), and oxide formation are taken as a normalized constant. Probability (p_i) for each reaction step i is drawn from the ratio of the reaction rate constant (k_i) to the sum of above three rate constants. That is, the probability p_i for each event is,

Table 1 Elementary steps

Step No.	Elementary reaction	Probability
1	CH ₄ (g)+*→CH ₄ *	p_1
2	CH ₄ *→CH ₄ (g)+*	p_2
3	CH ₄ *+*→CH ₃ *+H*	1
4	CH ₃ *+*→CH ₂ *+H*	1
5	CH ₂ *+*→CH*+H*	1
6	CH*+*→C*+H*	1
7	O ₂ (g)+2*→2O*	p_7
8	2O*→O ₂ (g)+2*	p_8
9	C*+O*→CO(g)+2*	$1-p_8-p_{11}$
10	2H*→H ₂ (g)+2*	1
11	O*→Ox	p_{11}
12	C*+Ox→CO(g)+2*	p_{12}

The asterisks stand for active sites and Ox for nickel oxide.

$$p_i = \frac{k_i}{k_8 + k_9 + k_{11}} \quad (1)$$

Especially, the p_i for steps 3, 4, 5, 6, 10, is considered as being equal to 1 because those steps can proceed completely. Adsorbed CH₄, O, and H species are allowed to diffuse to an empty nn site.

A dimensionless parameter p_{rea} is used to characterize the relative rates of reaction and diffusion, and the rates of the reaction and diffusion processes are considered to be proportional to p_{rea} and $1-p_{\text{rea}}$, respectively. The MC algorithm is shown in the following:

(1) A random number χ ($0 < \chi < 1$) is firstly generated. The reaction trial is executed with $\chi < p_{\text{rea}}$, and the diffusion trial is performed with $\chi > p_{\text{rea}}$.

(2) For a diffusion trial, if the randomly selected site is occupied by adsorbed CH₄, O, or H, and a randomly selected nn site is empty, the particle jumps to the selected nn site.

(3) For a reaction trial, a lattice site is randomly selected and a random number χ_1 ($0 < \chi_1 < 1$) is used to determine a reaction event.

(i) If the selected site is empty, CH₄ or O₂ adsorption can occur for $\chi_1 < p_1$ or $p_1 \leq \chi_1 < p_1 + p_7$, respectively. For O₂ adsorption, one of the nn sites is chosen at random and the O₂ adsorption succeeds when the latter site is also empty.

(ii) If the selected site is occupied by adsorbed CH₄, CH₄ desorption or dissociation can occur when $\chi_1 < p_2$ or $\chi_1 \geq p_2$, respectively. For CH₄ dissociation, one of the nn sites is chosen at random, and the trial succeeds when the latter site is empty.

(iii) If the selected site is occupied by CH_x ($x=1-3$), the trial of CH_x dissociation is considered to be successful if the randomly selected nn site is empty.

(iv) If the selected site is occupied by C, one of the nn sites is chosen at random. If the nn site is occupied by nickel oxide (Ox), the reaction can occur with the probability p_{12} .

(v) If the selected site is occupied by O, O₂ desorption, formation of NiO or reaction with C can occur for $\chi_1 < p_8$, $p_8 \leq \chi_1 < p_8 + p_{11}$, or $\chi_1 \geq p_8 + p_{11}$, respectively. For O₂ desorption, one of the nn sites is chosen at random, and the trial is accepted provided that the nn site is also occupied by O. LH step succeeds provided that the randomly selected nn site is occupied by C.

(vi) If the selected site is occupied by H, one of the nn sites is chosen at random. If the nn site is also occupied by H, a gaseous H_2 molecule is released.

(4) CH_4 and O_2 adsorption probabilities (p_i and p_7) have been changed to zero in a fixed period and width periodically.

The MC simulation starts from a clean surface, and the MC step (MCS) is employed to represent the reaction time. One MCS is defined as $L \times L$ attempts of the adsorption-reaction events.^{23,24} The reaction rate is determined by the number of produced CO or H_2 molecules per lattice site in a MCS. The average of produced CO or H_2 molecules over 50 MCS is used to calculate the reaction rate.

3 Results and discussion

It should be mentioned that the simulations are also carried out in the lattice sizes of 100 and 400 to understand the effect of lattice size on the results. The results show that when the lattice size is larger than or equal to 200×200 , the oscillatory kinetics has no obvious change. Therefore, all simulations are performed on a square lattice of 200×200 sites. The simulation parameters are executed for $p_{\text{rea}}=0.01$, $p_1=0.009$, $p_2=0.01$, $p_7=0.01$, $p_8=0.001$, $p_{11}=0.002$, and $p_{12}=0.001$.¹⁴

Autonomous oscillations are shown in Fig.1. From the figure, the coverage of empty sites, C, O, Ox and formation rates of CO and H_2 all exhibit well-developed oscillations. It is found that the transformation of the dominant reaction (from reaction of C and O to the reaction of C and Ox) results in the periodic oscillations of the reaction kinetics, while the oxidation and reduction of nickel surface play an important role in the transformation.¹³ It can also be seen that those self-sustained oscillations have a relatively fixed period. Therefore, the average period T has been calculated.

Composition cycling of feed is used for external forcing of the system. In our previous studies, the reaction rate constant for CH_4 and O_2 can be estimated by

$$k_i = J_i P_i S_i \quad (2)$$

Fig.1 Autonomous oscillations of coverages of C, O, Ox, empty sites and formation rates of CO and H_2

$p_{\text{rea}}=0.01$, $p_1=0.009$, $p_2=0.01$, $p_7=0.01$, $p_8=0.001$, $p_{11}=0.002$, and $p_{12}=0.001$.

ML: monolayer

where J_i stands for the impinging constant, P_i the partial pressure, and S_i the sticking coefficient. Then, the probabilities for CH_4 and O_2 adsorption (p_i and p_7) are taken by calculating the ratio of the reaction rate constants to normalized constant. Therefore, we can easily see that the parameters of p_i and p_7 are proportional to the concentration (partial pressure) of CH_4 and O_2 , respectively. The paper proposes that composition cycling of feed can be easily achieved by changing the adsorption probabilities of p_i and p_7 periodically. In the simulation, the forcing width is selected as $T/5$, where T is the average period of autonomous oscillations, and the results of forced oscillations for different forcing period ($T/3$, $T/2$, T , $1.3T$, $1.5T$, and $2T$) have been shown from Fig.2 to Fig.7.

In order to determine whether the forced oscillations are random, chaotic or periodic, the chaotic attractor is firstly calculated by using time delay method and the correlation dimension algorithm.^{25,26} The one-dimensional time series $u(t_k)$ ($k=0, 1, \dots, M$) measured from surface coverage is extended to m -dimensional phase space $V(t_n)$ ($n=0, 1, \dots, N$), where M and N are the number of data points, m is the dimension of phase space. Then the correlation dimension $D(m)$ can be calculated by correlation integral $C(r, m)$.

$$V(t_n) = \{u(t_n), u(t_n + \tau), \dots, u(t_n + \tau(m-1))\} \quad (3)$$

$$C(r, m) = \frac{1}{N(N-1)} \sum_{\substack{i,j=1 \\ i \neq j}}^N \theta(r - \|V_i - V_j\|) \quad (4)$$

$$D(m) = \left| \frac{\lg C(r, m)}{\lg r} \right| \quad (5)$$

where τ is the delay time, r is the scaling length, θ is the Heviside function. The correlation dimension $D(m)$ is not increased until m is up to m_c , then $D(m_c)$ is the chaotic attractor, where m_c is saturation dimension of phase space.²⁷ The calculations are performed utilizing FORTRAN software and the chaotic attractors for forced oscillations are given in Table 2.

It is reported that if the chaotic attractor $D(m_c)$ is equal to 1, it is periodic oscillation, and if the chaotic attractor $D(m_c)$ is equal

Fig.2 Forced oscillations with the forcing period of $T/3$ and forcing width of $T/5$

T is autonomous oscillatory period in the parameters for $p_{\text{rea}}=0.01$, $p_1=0.009$, $p_2=0.01$, $p_7=0.01$, $p_8=0.001$, $p_{11}=0.002$, and $p_{12}=0.001$.

to 2, it is quasi-periodic oscillation.²⁸ When $D(m_c)$ is greater than 2, and is the fraction, the oscillation is chaotic. From Table 2 it can be seen that the chaotic attractors of forced oscillations are 1–2, which means that the oscillations with forcing periods of $T/3$, $T/2$, T , and $2T$ are periodic oscillations, and the oscillations with forcing periods of $1.3T$ and $2T$ are quasi-periodic oscillations.

In Fig.2, with the forcing period of $T/3$, though the chaotic attractor calculation demonstrates it is periodic oscillations, the obtained oscillations are complicated, which is mainly due to system noise. With the forcing period of $T/2$ (Fig.3), the oscillations show a little complicated state and the period and amplitude have changed. Compared with autonomous oscillations (Fig.1), the period of forced oscillations has reduced by half, which attributes to the transformation of nickel surface between oxidation and reduction. When the reaction begins, the surface is in the reduced state. Then the oxide formation results in the surface changing to oxidized state. Once the breakdown of feed happens, due to the main reaction of C and Ox, the surface again turns to reduced state. It is the period of changing between reduced state and oxidized state that determines the period of forced oscillations. The coverage amplitude of empty sites is slightly increasing while the coverages of C, O, and Ox are reduced by half. This can be interpreted in this way: when the reaction begins there are maximum empty sites on the surface. Methane and oxygen can be easily adsorbed and dissociated, and these processes result in the decrease of empty sites. When the breakdown of feed happens, there is no adsorption of CH_4 and O_2 . The increase of C and Ox coverages and decrease of empty sites stop, and C and Ox coverages reach their maximum or minimum respectively. Due to the main reaction of C and Ox, the coverages of C and Ox decrease. Because the reaction rate between C and Ox is very small, the

extent of C and Ox decreasing is restricted, which leads to small amplitudes of C and Ox. The consumptions of adsorbed species and oxide could also bring about a larger burst of empty sites.

With the forcing period of T (Fig.4), it is found that the period and amplitude have not changed obviously. Although any particular information has not been acquired from the coverages of C, O, and Ox, it can be seen from the figure that the double-peak oscillations are found in the coverage of empty sites. For the coverage of empty sites, the first peak is originated from external forcing and the second peak from the autonomous oscillations. When the breakdown of feed happens, the empty sites increase and firstly reach their maximum mainly due to the main surface reaction of adsorbed C and Ox. When the reactant concentration resumes, the adsorption of methane and oxygen becomes easier due to the large empty sites, and these processes result in the decrease of empty sites. With the adsorption of methane and oxygen, the quick reaction between adsorbed C and O leads to the empty sites increasing and again reaching its maximum.

With the forcing periods of $1.3T$ (Fig.5) and $1.5T$ (Fig.6), the period of forced oscillations is decreased remarkably. Besides, double-peak oscillations can be found in the coverages of empty sites, C, O, and Ox. When the forcing period comes to $2T$ (Fig.7), it can be seen from the coverage of empty sites that in one period the breakout is single-peak, but in the next period the breakout is double-peak.

The above results show that with composition cycling of feed, not only the oscillatory behavior such as the period and amplitude could be changed, but also some complex dynamics such as double-peak oscillations can be obtained. The changing of oscillatory dynamics is considered to be related with the transition of metal from oxidized to reduced state. When the forcing of feed happens, the oxidized surface changes to partially reduced surface due to the main reaction between C and Ox. When the reactant concentration resumes, the oxide formation changes reduced surface to the partially oxidized surface. If the forcing period is

Table 2 Chaotic attractors ($D(m_c)$) for different forcing conditions

	a	$T/3$	$T/2$	T	$1.3T$	$1.5T$	$2T$
$D(m_c)$	1.08	1.30	1.21	1.01	1.42	1.51	1.00

The a stands for autonomous oscillations.

Fig.3 Forced oscillations with the forcing period of $T/2$ and forcing width of $T/5$

The conditions are the same as Fig.2.

Fig.4 Forced oscillations with the forcing period of T and forcing width of $T/5$

The conditions are the same as Fig.2.

Fig.5 Forced oscillations with the forcing period of $1.3T$ and forcing width of $T/5$

The conditions are the same as Fig.2.

less than that of autonomous oscillations, the recovery of the system after the forcing of feed is not completed up to the time when the new forcing begins, the smaller oscillatory periods and amplitudes are found. If the forcing period is longer than that of autonomous oscillations and the recovery of system is achieved adequately, the complex dynamics such as double-peak oscillations can be found.

It has been reported that high conversion rate can be obtained in some forcing conditions. We will now concentrate on the conversion rates of forced oscillations. In the simulation, the conversion rate in different forcing conditions has been calculated. The conversion rate is defined as the ratio between CO production and amount of CH_4 feed. It is assumed that the amount of CH_4 feed in one MCS is proportional to the probability of CH_4 adsorption (p_1) and the value is C . Then, the relative average conversion rates of forced oscillations (X_{force}) and autonomous oscillations (X_{auto}) can be calculated as follows.

Fig.6 Forced oscillations with the forcing period of $1.5T$ and forcing width of $T/5$

The conditions are the same as Fig.2.

Fig.7 Forced oscillations with the forcing period of $2T$ and forcing width of $T/5$

The conditions are the same as Fig.2.

$$\frac{X_{\text{force}}}{X_{\text{auto}}} = \frac{\frac{r_{\text{CO}}^{\text{force}} L^2 t_{\text{MCS}}}{C p_1 (t_{\text{MCS}} - t_{\text{force}})}}{\frac{r_{\text{CO}}^{\text{auto}} L^2 t_{\text{MCS}}}{C p_1 t_{\text{MCS}}}} = \frac{r_{\text{CO}}^{\text{force}}}{r_{\text{CO}}^{\text{auto}}} \times \frac{t_{\text{MCS}}}{(t_{\text{MCS}} - t_{\text{force}})} \quad (6)$$

In the formula, $r_{\text{CO}}^{\text{force}}$ stands for CO formation rate of forced oscillations per lattice site per MCS, L the lattice size, t_{MCS} the total reaction time measured by MCS, $p_1=0.009$, t_{force} the total forcing width, $r_{\text{CO}}^{\text{auto}}$ the CO formation rate of autonomous oscillations per lattice site per MCS.

Fig.8 shows conversion rate as a function of forcing period. From Fig.8 it can be seen that the mean conversion rate of forced oscillations is higher than that of the autonomously oscillating state. When the forcing periods are T and $2T$, the average conversion rates drop to almost the same value the autonomous system shows.

Effects of forced processes on the conversion rates can be realized by changing the oxidation and reduction state of catalysts. When the surface is oxidized, the operations of composition cycling of feed (with forcing periods of $1.3T$ and $1.5T$) make the surface be reduced mainly due to the reaction between C and Ox, which results in an obvious increasing of empty sites. On this basis, CH_4 and O_2 adsorption become much easier, and much higher conversion rate of CO can be found. When the surface is

Fig.8 Relative conversion rate as a function of the forcing period

reduced, the operations of composition cycling of feed (with forcing periods of T and $2T$) result in further reduction of catalysts due to the reaction between C and Ox. Because the reaction rate of C and Ox is small, the increasing of empty sites is limited, and relative lower conversion rate of CO can be found. With the forcing periods of $T/2$, both the above effects make the conversion rate reach its maximum.

4 Conclusions

The kinetics of external forced oscillations during partial oxidation of methane over Ni surface was simulated by the MC method. Based on 12-step Langmuir-Hinshelwood mechanism and composition cycling of feed, kinetic oscillations in both products and coverage of surface species have been observed. The results indicate that with fixed forcing amplitude of $T/5$ (T is the average period of autonomous oscillations) and alterable forcing period from $T/3$ to $2T$, not only the period and amplitude change obviously, but also the kinetic oscillations show double-peak behavior. The mean conversion rates have also been calculated in both autonomous oscillations and forced oscillations. The results demonstrate that the forced oscillations show an increase in conversion rate. The changes of kinetics and conversion rate could attribute to the surface transition from oxidized to reduced states due to the operation of composition cycling of the feed. The results show that the kinetic oscillations could be effectively controlled by composition cycling of feed.

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