Contents lists available at ScienceDirect





Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Partial oxidation of methane on a nickel catalyst: Kinetic Monte-Carlo simulation study



Sirawit Pruksawan^a, Boonyarach Kitiyanan^{a,*}, Robert M. Ziff^b

^a The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand
^b Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Partial oxidation of methane on a nickel surface is modeled by Monte-Carlo method.
- The controlling step for CO production changes when the temperature changes.
- If diagonal actions are allowed, the discontinuous transition becomes continuous.
- The selectivity of H₂ significantly lowers when the diffusion of O* is allowed.
- The results on the feed and temperature effects agree with previous experiments.

ARTICLE INFO

Article history: Received 14 January 2016 Received in revised form 11 March 2016 Accepted 12 March 2016 Available online 24 March 2016

Keywords: Kinetic Monte-Carlo simulation Partial oxidation Kinetics Diffusion Impurities



ABSTRACT

Kinetic Monte-Carlo simulation is applied to study the partial oxidation of methane over a nickel catalyst. Based on the Langmuir–Hinshelwood mechanism, the kinetic behavior of this reaction is analyzed and the results are compared with previous experiments. This system exhibits kinetic phase transitions between reactive regions with sustained reaction and poisoned regions without reaction. The fractional coverages of the adsorbed species and the production rates of H₂, CO, H₂O, and CO₂ are evaluated at steady state as functions of feed concentration of the methane and oxygen, and reaction temperature. The influence of lattice coordination number, diffusion, and impurities on the surface is also investigated. The simulation results are in good agreement with the experimental studies where such results are available. It is observed that when the lattice coordination number is increased to eight, the width of the reactive region increases significantly. Moreover, the phase transition becomes continuous. The diffusion of adsorbed O and H on the surface plays a measurable role in the reaction, increasing the maximum production rates as the diffusion rate increases. In systems with impurities, the production rates are greatly reduced and the phase transition is also changed from being abrupt to continuous. © 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The catalytic conversion of methane is one of the most attractive areas of research in both academia and industry. Steam

* Corresponding author. E-mail address: boonyarach.k@chula.ac.th (B. Kitiyanan).

http://dx.doi.org/10.1016/j.ces.2016.03.012 0009-2509/© 2016 Elsevier Ltd. All rights reserved. reforming has been used in industry to produce hydrogen or syngas from methane. Nevertheless, steam reforming is an energyintensive process. The catalytic partial oxidation (CPOx) process is an attractive alternative because it avoids the need of large amounts of energy and requires smaller reactors due to the faster oxidation reaction. Another advantage of the CPOx process is that the H₂-to-CO ratio in syngas products is 2:1, which allows a straightforward syngas utilization for methanol or Fischer-Tropsch synthesis. The CPOx of methane has been extensively studied by various researchers (Hu and Ruckenstein, 1996; Tsipouriari and Verykios, 1998; Smith and Shekhawat, 2011; Al-Sayari, 2013). Even though several catalytic systems have been reported in the literature to be active for this reaction, nickel catalysts are generally believed to be the most promising candidate owing to their moderate cost and good catalytic performance compared to that of noble metals (Al-Sayari, 2013). In spite of the large quantity of experimental studies devoted to the partial oxidation of methane on nickel catalysts, the mechanisms and kinetic studies in this system are still unclear. Theoretical studies have not clarified this issue. Moreover, the published experimental results are contradictory (Smith and Shekhawat, 2011). Therefore, further studies on the kinetic behavior are expected to provide a better understanding to the reaction mechanism.

Kinetic Monte-Carlo (KMC) is an effective tool for investigating surface reaction mechanisms and predicting complex kinetic behaviors. KMC simulation can be viewed as a numerical method to solve the Master Equation that describes the evolution of the catalyst's surface and the adsorbates. The rate constants in this equation are obtained from kinetic studies carried out on the selected catalyst. KMC simulation allows one to visualize the state of surface. One of the simplest kinetic models for the oxidation reaction of CO on a catalytic surface, introduced by Ziff, Gulari and Barshad (ZGB) (Ziff et al., 1986), has provided a source of continual investigation for studies of complex phenomena (Fichthorn et al., 1989; Fichthorn and Weinberg, 1991; Evans, 1993; Tomé and Dickman, 1993; Loscar and Albano, 2003; Machado et al., 2005). Other lattice models have been introduced to simulate different catalytic surface reaction, including CPOx of methane. The CPOx of methane was extensively studied for the oscillatory behavior of the dynamics by a model (Lashina et al., 2012; Ren et al., 2008; Ren and Guoa, 2008). The present work provides information on the kinetic behavior in which the reaction is conducted under steadystate conditions.

The purpose of this work is to develop the KMC simulation for the partial oxidation of methane on a nickel catalyst based on the Langmuir–Hinshelwood (LH) mechanism combined with the formation and removal of nickel oxide under isothermal conditions. The kinetic behavior at steady state is analyzed in different operating conditions and the results are compared with previous experiments. The effects of diffusion of adsorbed species, lattice

 Table 1

 Elementary reactions and corresponding kinetic parameters used in this work.

coordination number and inactive impurities on the surface are also evaluated.

2. Model and simulation procedure

2.1. Model

Our kinetic model was developed for the CPOx on a nickel catalyst based on the reaction mechanism of Lashina et al. (2012). According to these authors, the mechanism of CPOx can be described by an 18-step elementary reaction (Table 1). The steps 1–14 describe the CPOx of methane on the surface of nickel metal (denoted by *) with the formation of CO, H_2 , CO_2 and H_2O . The formation of nickel oxide (Ox) in step 15 leads directly or indirectly to the formation of CO, CO_2 and H_2O with the participation of the oxidized form of nickel in steps 16–18 (Shen et al., 1998).

The estimation of the kinetic parameters of elementary reactions was obtained from the literature as summarized in Table 1. Here, steps 3, 4, 5, 6, 11 and 14 are assumed to be instantaneous (probability of an event=1) since the experiments suggested that they are not kinetically significant (Hei et al., 1998; Chen et al., 2001a, 2001b). The diffusion of adsorbed species is also considered. However, only the diffusion of adsorbed CH₄, O, CO and H is included because of their relatively rapid diffusion rates (Ren et al., 2008; Chen et al., 2001b).

The adsorption constants (k_i) for methane and oxygen in steps 1 and 7 depend on the reactant pressures in the gas phase estimated by Eq. (1), where k_i° is adsorption coefficient and y_i is the feed concentration and P is the pressure of the reactants.

$$k_i = k_i^0 y_i P \tag{1}$$

The reaction constant (k_i) in steps 2, 8, 9, 10, 12, 13, 15, 16, 17 and 18 can be calculated by the Arrhenius equation (Eq. (2)), where A_i is the pre-exponential factor, Ea_i is the activation energy, R is the gas constant and T is the absolute temperature.

$$k_i = A_i \exp(-Ea_i/RT) \tag{2}$$

The diffusion constant (k_{diff}) of adsorbed CH₄, O, CO and H can be calculated by Eq. (3), where D_{0i} is the pre-exponential factor for the diffusion process, *a* is the cell parameter of the nickel surface with a value of 2.48×10^{-8} cm (Ren and Guoa, 2008) and Q_i is the

Steps (i)	Elementary reactions	A_i or k_i° (s ⁻¹ or s ⁻¹ Pa ⁻¹)	Ea _i (kcal/mol)	References
1	$CH_4(g)+[*] \rightarrow [CH_4^*]$	0.0045 (k ⁰ _i)	0	Ren et al. (2008)
2	$[CH_4^*] \rightarrow CH_4(g) + [*]$	$1.0 imes 10^4$	7.9	Ren et al. (2008)
3 ^a	$[CH_4^*] + [*] \rightarrow [CH_3^*] + [H^*]$	1.3×10^{8}	13.8	Hei et al. (1998)
4 ^a	$[CH_3^*] + [*] \rightarrow [CH_2^*] + [H^*]$	1.0×10^{13}	27.6	Chen et al. (2001a)
5 ^a	$[CH_2^*] + [*] \rightarrow [CH^*] + [H^*]$	1.0×10^{13}	23.2	Chen et al. (2001a)
6 ^a	$[CH^*] + [*] \rightarrow [C^*] + [H^*]$	$1.0 imes 10^{13}$	4.5	Chen et al. (2001b)
7	$O_2(g) + 2[*] \rightarrow 2[O^*]$	$0.011 \ (k_{i}^{0})$	0	Ren et al. (2008)
8	$2[O^*] \rightarrow O_2(g) + 2[^*]$	1.0×10^{11}	44.6	Ren et al. (2008)
9	$[C^*] + [O^*] \rightarrow [CO^*] + [^*]$	1.0×10^{12}	35	Ren et al. (2008)
10	$[CO^*] \rightarrow CO(g) + [*]$	1.0×10^{10}	27.85	Ren et al. (2008)
11 ^a	$2[H^*] \rightarrow H_2(g) + 2[^*]$	3.1×10^{12}	23.3	Chen et al. (2001b)
12	$[CO^*] + [O^*] \rightarrow CO_2(g) + 2[*]$	$5.0 imes 10^6$	15.2	Ren et al. (2008)
13	$[H^*] + [O^*] \rightarrow [OH^*] + [^*]$	$1.0 imes 10^7$	19.6	Li and Xiang (2000)
14 ^a	$[H^*] + [OH^*] \rightarrow H_2O(g) + 2[^*]$	3.1×10^{11}	7.7	Chen et al. (2001a)
15	$[O^*] \rightarrow [Ox]$	$1.0 imes 10^5$	15.7	Ren et al. (2008)
16	$[C^*] + [Ox] \rightarrow [CO^*] + [^*]$	$1.0 imes 10^7$	26.24	Ren et al. (2008)
17	$[CO^*] + [Ox] \rightarrow CO_2(g) + 2[*]$	$1.0 imes 10^5$	17	Ren et al. (2008)
18	$[H^*] + [Ox] \rightarrow [OH^*] + [*]$	5.2×10^3	11	Ren et al. (2008)

Note : [X*] = adsorbed X species.

^a Assumed instantaneous.

Download English Version:

https://daneshyari.com/en/article/154479

Download Persian Version:

https://daneshyari.com/article/154479

Daneshyari.com