

# Microkinetic deactivation studies on nickel supported catalyst for dry reforming of methane

P R K Fu<sup>1</sup>, Twaiq F<sup>1</sup> and W L Chung<sup>1</sup>

<sup>1</sup> Faculty of Engineering, Computing and Science, Swinburne University of Technology Sarawak Campus, Jalan Simpang Tiga, 93350 Kuching, Sarawak, Malaysia

**Abstract.** In recent decades, greenhouse gases (GHG) such as CO<sub>2</sub> and CH<sub>4</sub> have been on the rise affecting climate change. Consequently, researchers have been studying on chemical reactions that are able to consume and convert GHG into useful resources. Dry reforming of methane is a heterogeneous catalytic reaction that consumes greenhouse gases such as CO<sub>2</sub> and CH<sub>4</sub> to produce syngas, CO and H<sub>2</sub>, which later becomes an essential feedstock for Fischer-Tropsch process. Various researchers due to its affordability have studied nickel-based catalyst and it exhibits excellent performance in DRM reaction. However, coke formation is a major issue concerning catalyst deactivation during the dry reforming reaction. Therefore, thermodynamic study based on Gibbs energy minimization is conducted to identify the reaction routes that favour carbon deposition. In addition, the deactivation mechanism of coke formation together with microkinetic modelling of dry reforming of methane on nickel catalyst is being developed.

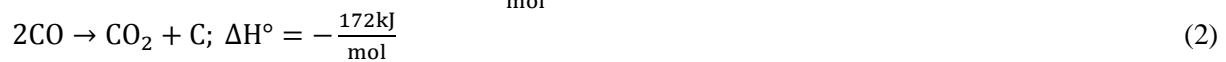
## 1. Introduction

Greenhouse gases (GHG) in the atmosphere has increased significantly since the beginning of Industrial Revolution. The main concerning issue associated with GHG is global warming which induces climate change. Dry reforming of methane (DRM) has drawn attention from researchers due to its benefit to be able to consume and convert GHG into useful resource, synthesis gas. DRM is a heterogeneous catalytic reaction that enables the production of valuable syngas, while consuming GHG such as methane and carbon dioxide as reactants for the catalytic process (1). The product from this catalytic process produces syngas or better known as synthesis gas is a mixture of hydrogen (H<sub>2</sub>) and carbon monoxide (CO) that acts as a chemical intermediate for the production of Fischer-Tropsch synthesis, methanol and fine chemicals (2).

There are various types of catalysts used in the dry reforming reaction, such as noble metals and transition metals. Noble metals such as ruthenium and rhodium are comparatively more expensive to transition metal such as nickel. Therefore, nickel-based catalyst is more favourable for DRM process even at industrial scale. The type of supports may lead to different degree of dispersion of nickel in the support's pores support, which in turns affect catalytic behaviours and performance (3). The problem of coke formation on the catalyst's surface remains a major drawback in the dry reforming reaction. Accumulation of coke deposit on the surface of nickel catalyst causes inhibition of active sites that, eventually leads to catalyst deactivation. Hence, the formulation of kinetic model for dry reforming of methane is important to analyse the reaction mechanism of coke formation in accordance with the catalyst reaction activity.



Dry reforming of methane is a highly endothermic reaction, as shown in equation (1). This indicates that the large required energy input for methane and carbon dioxide to transform into syngas. Thus, the reforming reaction is carried out at high temperatures of above 1073K in order to produce H<sub>2</sub>/CO ratio of unity.



The Boudouard reaction in equation (2) occurs at temperatures below 800K that encourages carbon deposition on the catalyst surface. Ultimately, the amount of carbon deposits on Ni catalyst covering active sites of the nickel will deactivate the catalyst. This affects the overall DRM performance. The aim of this work is to carry out thermodynamic study to understand the reaction routes that favour carbon deposition, which later a microkinetic model is proposed.

## 2. Modelling Expression

The order of elementary reaction steps in a heterogeneous catalytic gas reaction comprises of adsorption and desorption of species, surface diffusion and chemical reaction of adsorbed species. There are different models that describe the reaction mechanism steps. The frequently used models in DRM are namely power law model, Langmuir-Hinshelwood-Hougen-Watson (LHHW) model and microkinetic (MK) model. This model expression together with the kinetic data gives a best fit in accordance to the experimental data and is used to describe the rate of reaction. This correlation allows further optimization for both the design of catalyst and reactor.

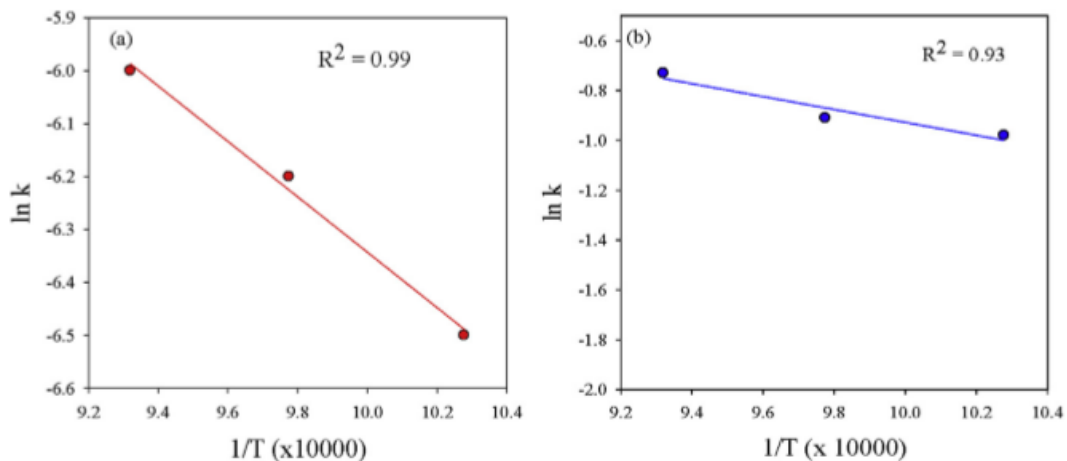
### 2.1. Power Law Model

The power law provides an evaluation of the overall rate of reaction with only consideration given to its reactants. This method of evaluation is applicable to initial guess estimates without consideration of the reaction mechanism in details (4). The power-law model as shown in equation (3), only evaluates the kinetics parameters of DRM reaction, where  $r$  represents the rate of reaction,  $m$  and  $n$  are the reaction orders with respect to the partial pressure,  $P$  of the reactant species, CH<sub>4</sub> and CO<sub>2</sub>.

$$r = k[P_{\text{CH}_4}]^m[P_{\text{CO}_2}]^n \quad (3)$$

This analytical technique provides a rough estimation in evaluating reaction parameter, which does not represent the kinetics of reaction (5). Osazuwa et al (6) studied the reaction between CO<sub>2</sub> and CH<sub>4</sub> by fitting the reaction rates and partial pressure of reactants into the power law model. The rate equation for the kinetic model as shown in equation (4) enables the determination of the reaction order and pre-exponential factor. Figure 1 shows the estimated activation energy for methane and carbon dioxide obtained from Arrhenius plot.

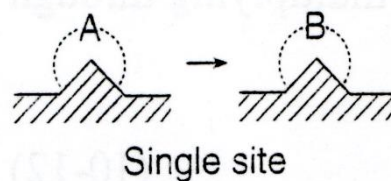
$$r = A \exp\left(-\frac{E_a}{RT}\right) [P_{\text{CH}_4}]^\alpha [P_{\text{CO}_2}]^\beta \quad (4)$$



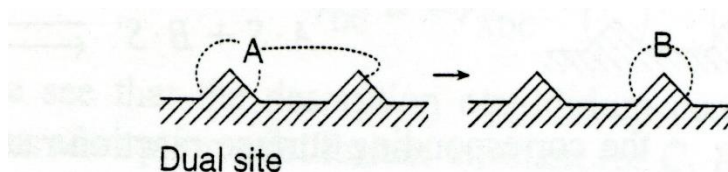
**Figure 1.** Estimation of activation energy,  $E_a$  for both methane (red line) and carbon dioxide (blue line) obtained via Arrhenius plot (6)

## 2.2. Langmuir Hinshelwood-Hougen-Watson Model

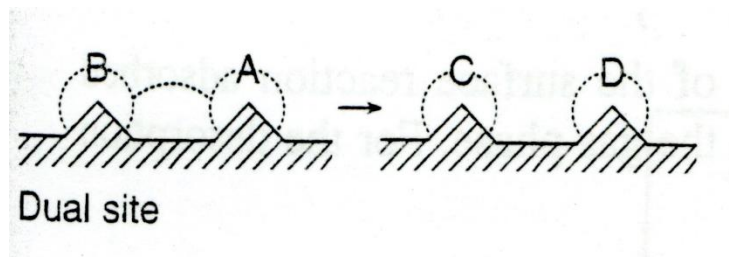
Langmuir-Hinshelwood kinetic describes the surface reaction of adsorbed species that consists of either a single-site or a dual-site mechanism (7). Single site mechanism only allows adsorbed reactants on the active site to take part in the surface reaction. A dual site mechanism happens when the adsorbed reactants interact with its adjacent site; the adjacent site can be either vacant or occupied with different reactant species. All the potential reaction pathways that accounts for adsorption, surface reaction and desorption will be included in the model. The letter  $S$  in the elementary reaction below represents species adsorbed on the active site and the letter alone indicates vacant site.



**Figure 2.** Single site mechanism



**Figure 3.** Dual site mechanism with vacant adjacent site



**Figure 4.** Dual site mechanism with occupied adjacent site

LHHW model requires a rate-determining step (RDS) in order to formulate the rate law. Sawatmongkhon et al (8) proposed a LHHW model for dry reforming of methane on Pt/Rh catalyst. The reaction mechanism consisted of five steps, which included adsorption of reactant species  $\text{CO}_2$  and  $\text{CH}_4$ , surface reaction between adsorbed species and active sites at catalyst surface, and desorption of products,  $\text{CO}$  and  $\text{H}_2$ . Their reaction mechanism model is described as below.



### 2.3. Microkinetic Model

Microkinetic modelling is an approach to study and understand the catalytic processes at a microscale level (9). The model accounts for all possible elementary steps that sum up the catalytic cycle. Microkinetic model provides quantitative information of a catalytic reaction that includes absorption, surface reactions and desorption for a catalytic cycle (10). The prerequisite for this approach is to measure the reaction rate in the absence of heat and mass-transfer limitations. Dehimi et al (11) studied the microkinetic model of dry reforming of methane over  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ . The model provides detail surface mechanism in DRM that includes the formation of carbon on the catalyst surface. The study is conducted under atmospheric pressure over a temperature range of  $450^\circ\text{C}$  to  $650^\circ\text{C}$ . The microkinetic model includes 34 irreversible elementary reactions, amounting to 12 surface species and 6 gas phase species.

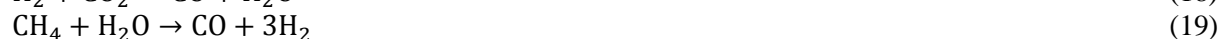
### 3. Modelling Methodology

Thermodynamic equilibrium analysis on the proposed reactions is performed with ASPEN HYSYS based on direct minimization of Gibbs free energy method. All possible reaction pathways for DRM as listed, is studied at a temperature range of  $600^\circ\text{C}$  to  $800^\circ\text{C}$ , all at 1 atmospheric pressure. The evaluation of equilibrium constant,  $K$  for a reaction is done based on the Gibbs free energy of a reaction, as shown in equation (15). The enthalpy and entropy values are obtained from HYSYS simulation for the calculation of Gibbs free energy in Equation (16).

$$\text{Equilibrium constant, } K = \exp\left(\frac{-G}{RT}\right) \quad (15)$$

$$\text{Gibbs free energy, } \Delta G = \Delta H - T\Delta S \quad (16)$$

All possible reaction pathways in DRM reaction are described as below:





The rate equation for all the proposed reactions is done based on simple collision theory. The collision rate is to provide possibility of effective collision between reactants. The rate of collision for both unimolecular and bimolecular collision is calculated with equation (22) and equation (23), where  $d_{AB}$  is the arithmetic mean of two molecular diameter (m),  $d_A$  is the kinetic diameter (m),  $c'_A$  is the concentration of molecule A ( $\text{m}^{-3}$ ),  $c'_B$  is the concentration of molecule B ( $\text{m}^{-3}$ ),  $k_B$  is Boltzmann constant and T is the operating temperature.

$$\text{Rate of collision for bimolecular, } Z_{AB} = d_{AB}^2 c'_A c'_B \left( 8\pi k_B \frac{T}{\mu} \right)^{\frac{1}{2}} \quad (22)$$

$$\text{Rate of collision for unimolecular, } Z_{AA} = 2d_A^2 (c'_A)^2 \left( \pi k_B \frac{T}{m_A} \right)^{\frac{1}{2}} \quad (23)$$

$$\text{Reduced molecular mass, } \mu = \frac{m_A m_B}{m_A + m_B} \quad (24)$$

## 4. Results and Discussion

### 4.1. Dry Reforming Reaction

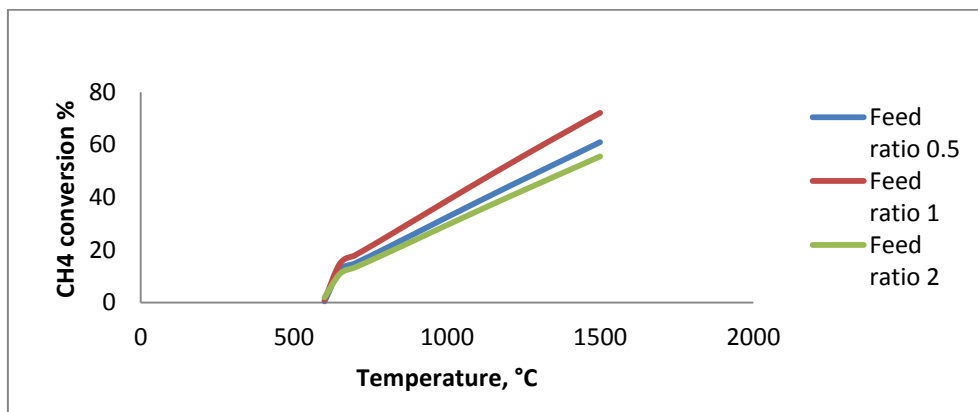
Table 1 shows the equilibrium constant for dry reforming of methane. According to Le Chatelier's principle, as the K value decreases, the reaction is found to shift to the left. This indicates that more reactants are formed. Based on the result in Table 1, it is found that as the temperature increases, there is a slight decrease in equilibrium constant and rate of collision.

Reaction: $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$		
Temperature (°C)	Equilibrium constant, K	$Z_{AB} (\text{m}^{-3}\text{s}^{-1})$
600	-2.85804	1.91E+31
650	-3.38482	1.81E+31
700	-3.90839	1.72E+31
750	-4.42375	1.63E+31
800	-4.92819	1.56E+31

**Table 1.** Equilibrium constant and rate of collision for the DRM reaction at various temperatures

#### 4.1.1. $\text{CH}_4$ Conversion

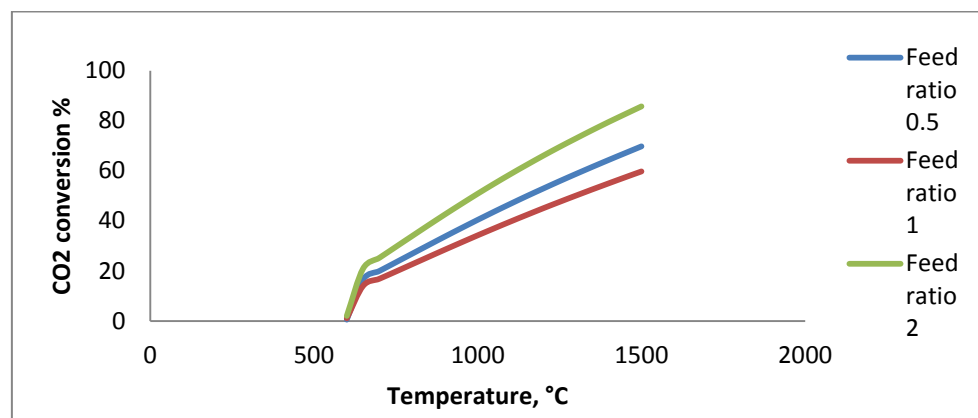
Several feed ratio of  $\text{CH}_4:\text{CO}_2$  is used to study the conversion of  $\text{CH}_4$  in dry reforming of methane in a R-GIBBS reactor over a temperature range of 600°C to 1500°C at atmospheric pressure 1 atm. Figure 5 shows the  $\text{CH}_4$  conversion against temperature. The highest  $\text{CH}_4$  conversion is observed at  $\text{CH}_4:\text{CO}_2$  feed ratio of 1 over the entire temperature range, whereas the lowest  $\text{CH}_4$  conversion is observed at  $\text{CH}_4:\text{CO}_2$  feed ratio of 2.



**Figure 5.** CH<sub>4</sub> conversion at temperature range of 600°C to 1500°C

#### 4.1.2. CO<sub>2</sub> Conversion

Figure 6 shows that at CH<sub>4</sub>:CO<sub>2</sub> feed ratio of 2, the CO<sub>2</sub> conversion reached 88%, whereas at CH<sub>4</sub>:CO<sub>2</sub> feed ratio of 1 shows the lowest conversion. Based on the result obtained, the CO<sub>2</sub> conversion is found to be higher than the CH<sub>4</sub> conversion. As more CO<sub>2</sub> is consumed in the reverse water gas shift (RWGS) reaction, this will inevitably result in higher conversion of CO<sub>2</sub> as compared to CH<sub>4</sub>.



**Figure 6.** CO<sub>2</sub> conversion at temperature range of 600°C to 1500°C

#### 4.2. Reverse Water Gas Shift (RWGS) Reaction

Table 2 shows the equilibrium constant and rate of collision for reverse water gas reaction (RWGS). Based on the result obtained, the K values decreased gradually and fewer products are expected to form.

Reaction: $H_2 + CO_2 \rightarrow CO + H_2O$		
Temperature (°C)	Equilibrium constant, K	$Z_{AB} (m^{-3}s^{-1})$
600	2.730183	9.07E+31
650	2.148473	8.58E+31
700	1.633966	8.14E+31
750	1.195031	7.74E+31
800	0.846437	7.38E+31

**Table 2.** Equilibrium constant and rate of collision for the reaction,  $H_2 + CO_2 \rightarrow CO + H_2O$  at various temperatures

#### 4.3. Steam Reforming of Methane

Table 3 displays the equilibrium constant and collision rate for reaction between  $\text{CH}_4$  and  $\text{H}_2\text{O}$ . As K value is found to decrease at elevated temperatures, very limited or no production of CO and  $\text{H}_2$  can be obtained. The result in table 3 below shows that the overall collision rate is decreasing over this temperature range.

Reaction: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$		
Temperature (°C)	Equilibrium constant, K	$Z_{AB} (\text{m}^{-3}\text{s}^{-1})$
600	-3.50283	1.93E+31
650	-3.9552	1.82E+31
700	-4.39927	1.73E+31
750	-4.83291	1.65E+31
800	-5.25372	1.57E+31

**Table 3.** Equilibrium constant and rate of collision for the reaction,  $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$  at various temperatures

#### 4.4. Methane Decomposition Reaction

Table 4 shows the equilibrium constant and rate of collision for methane decomposition reaction. The equilibrium constant, K is relatively constant over the range of temperatures. The K value for this reaction is considered insignificant as compared to the K value of other reactions.

Reaction: $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$		
Temperature (°C)	Equilibrium constant, K	Rate of collision, $Z_{AA} (\text{m}^{-3}\text{s}^{-1})$
600	-26.6627	1.42E+37
650	-25.1647	1.34E+37
700	-25.1493	1.27E+37
750	-25.1544	1.21E+37
800	-25.1735	1.15E+37

**Table 4.** Equilibrium constant and rate of collision for methane decomposition,  $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$  at various temperatures

#### 4.5. Boudouard Reaction

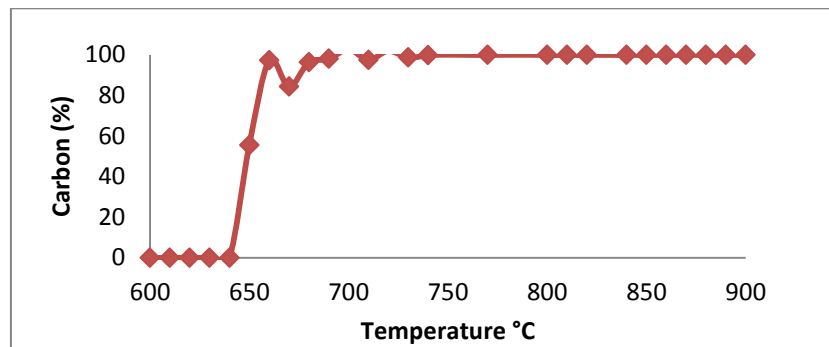
Table 5 shows the equilibrium constant and rate of collision for Boudouard reaction. The highest K value is observed between 700°C and 750°C. Thus, carbon formation is expected between the temperatures of 700°C to 750°C. There is a slight decrement in rate of collision as the temperature increases.

Reaction: $2\text{CO} \rightarrow \text{C} + \text{CO}_2$		
Temperature (°C)	Equilibrium constant, K	Rate of collision, $Z_{AA} (\text{m}^{-3}\text{s}^{-1})$
600	47.78895	7.93E+36
650	30.90787	7.50E+36
700	50.68433	7.11E+36
750	50.68945	6.77E+36
800	44.11203	6.45E+36

**Table 5.** Equilibrium constant and rate of collision for Boudouard reaction,  $2CO \rightarrow C + CO_2$  at various temperatures

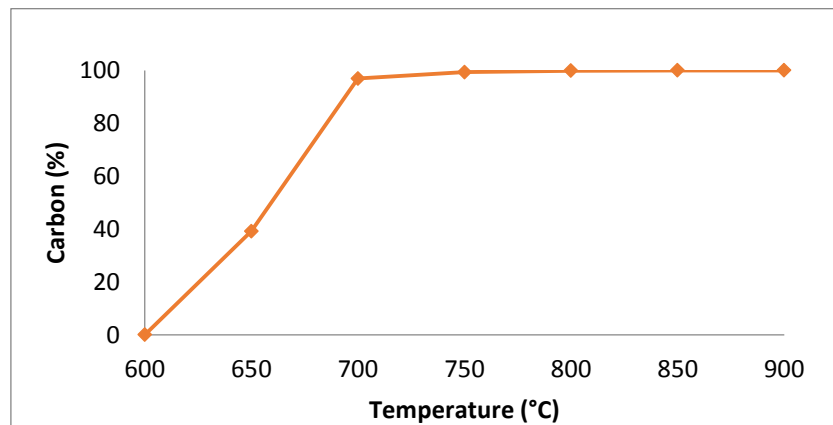
#### 4.6 Mechanism for Coke Formation

The simulation is carried out for every possible reaction concerning both DRM's reactants,  $CO_2$  and  $CH_4$ . The possible products from both reactants of DRM are;  $CO_2$ ,  $CH_4$ ,  $C$ ,  $H_2O$ ,  $CO$  and  $H_2$ . Methane decomposition is one of the major reaction pathways to coke formation. This endothermic reaction requires +74.87 kJ/mol of energy to initiate reaction (1). Figure 7 shows the result generated by HYSYS simulation. The carbon formation occurs rapidly as the temperature increases from 650°C onwards.



**Figure 7.** Conversion of carbon from methane decomposition reaction

Boudouard reaction is an exothermic reaction that requires -172 kJ/mol of energy to transform  $CO$  to  $CO_2$  and  $C$ . Figure 8 shows the formation of carbon via Boudouard reaction. As the temperature rises from 600°C, carbon formation occurs drastically.



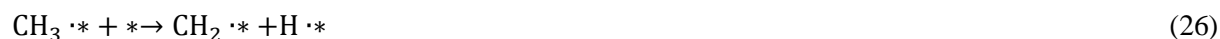
**Figure 8.** Conversion of carbon from Boudouard reaction

#### 4.7 Proposed Reaction Mechanism

Considering the results from the thermodynamic equilibrium analysis, it is assumed that both  $CH_4$  and  $CO_2$  undergo dissociative adsorption and attachment onto the active site of nickel catalyst. Both  $CH_4$  and  $CO_2$  go through surface reaction, where other components such as  $C$  and  $H_2O$  are produced along with syngas. There are four reactions steps, which are required to complete the process of  $CH_4$  dissociative adsorption.







The reaction steps below describe the dissociative adsorption undergone by  $\text{CO}_2$ .



Both the dissociative adsorption steps for  $\text{CH}_4$  and  $\text{CO}_2$  has the possibilities to form C on the nickel surface. Another possible component that will form is  $\text{H}_2\text{O}$ . Dissociated O from  $\text{CO}_2$  often reacts with H from  $\text{CH}_4$  to form  $\text{H}_2\text{O}$ . The produced  $\text{H}_2\text{O}$  is then able to react with CO, which produces both  $\text{CO}_2$  and  $\text{H}_2$ . The last step in the catalytic cycle of DRM is desorption, where products including  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , CO and  $\text{CO}_2$  will be detached from the nickel surface.



## 5. Conclusion

Based on direct minimization of Gibbs free energy method, the thermodynamic equilibrium analysis on the proposed reactions has been performed. All possible reaction pathways for DRM are studied at a temperature range of 600°C to 800°C and a microkinetic model has been proposed.

## 6. References

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