

## Modeling of Catalyst Deactivation on the Dry Reforming of Methane (DRM) Using the Generalized Power Law Expression (GPLE)

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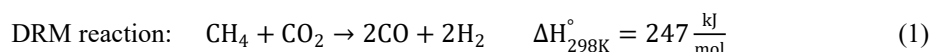
### Abstract

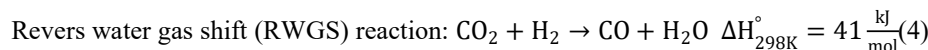
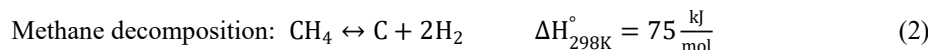
A generalized power law expression (GPLE) model was used to model the catalyst deactivation mechanism for two sets of catalytic systems used in the dry reforming reaction (DRM). The first set is the monometallic (10%Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and bimetallic (10%Ni<sub>8</sub>Cu<sub>1</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalyst, the second set is the commercial catalyst (Riogen) tested at two different temperatures (650 and 550°C). The GPLE model was able to fit the experimental data with a regression factor (R<sup>2</sup>) ranged between 0.95 and 0.99. Also, the first and second order GPLE model was used to deconvolute the activity profile based on the deactivation mechanism for all the catalyst systems. In the commercial catalyst (Riogen) the model results indicate that at 550 °C the percent of activity lost from carbon deposition is higher than the percent at 650 °C which is in agreement with literature reports. In the bimetallic and monometallic catalysts, the results indicate that the rapid deactivation of monometallic catalyst is primarily due to significant coke formation whereas, the bimetallic catalyst experienced minimal deactivation owing to both particle sintering in the initial stages followed by coke formation

**Keywords:** Dry reforming of methane, Generalized power-law expression, Catalyst deactivation.

### 1. Introduction

The DRM reaction is the process of using two of the greenhouse gases GHG (CO<sub>2</sub> and CH<sub>4</sub>) to produce the synthesis gas (a mixture of CO and H<sub>2</sub>) that can be used as a building block for different application such as Fischer-Tropsch Synthesis (FTS), methanol and other valuable liquid chemicals. The DRM is an endothermic process that consists of a main reaction to produce the synthesis gas and three side reaction (Boudouard reaction, Methane decomposition, and Revers Water Gas shift (RWGS) reaction).





The main problems related to the DRM is the low-quality syngas ( $\text{H}_2$ :  $\text{CO}=1$ ), the high endothermicity of the reaction and the catalyst deactivation.

The catalyst deactivate during the DRM reaction mainly due to coke formation, sintering of the active metal and oxidation of metallic active sites (C. Price, E. Earles, L. Pastor-Pérez, J. Liu, and T. Reina, 2018). Since the DRM reaction usually operates at high temperature ( $\geq 800$  °C) and the Ni catalyst crystals have low thermal stability, the deactivation by sintering is common in the DRM reaction. Also, in the DRM reaction two side reactions (Boudouard reaction and Methane decomposition) produce carbon which arises the deactivation by carbon deposition.

Modeling of the catalyst deactivation process is essential in providing the needed information to design efficient catalyst and to identify the suitable operating conditions that decrease the rate of deactivation. Also, success in developing accurate deactivation models will save resources compared to the experimental investigations.

Over the past several years, numerous studies focused on modeling the catalyst deactivation in DRM reaction. A recent review by Fu et al. (P. R. K. Fu, F. Twaiq, and W. L. Chung, 2018) focused on using a microkinetic model to identify the deactivation mechanism and the favorable reaction routes for carbon deposition in the DRM reaction using Ni as a catalyst. They found that carbon deposition is expected to increase in the temperature range between 700-750 °C.

Bartholomew (C. H. Bartholomew, 1993) studied the sintering kinetics using the General Power Law Expression (GPLe). He fitted the dispersion versus time-on-stream (TOS) data to first and second order GPLe. Choudhury et al. (H. A. Choudhury) used the GPLe model to predict the catalyst deactivation for FTS.

Azarpour and Wan Alwi (D. Operasi, 2017) predicted the catalyst deactivation rate of the industrial palladium supported on carbon (Pd/C) catalyst using the first principle model (FPM) and the process data. They used the GPLe to account for the catalyst deactivation by sintering. The model was able to predict the sintering deactivation rate with less than 3% error.

From the previous listed review of the catalyst deactivation on the DRM reaction, it is understandable that modeling of the catalyst deactivation is not adequately addressed and specifically in terms of quantifying its impact on the catalyst performance. This study is aiming at evaluating the catalyst deactivation mechanism of the DRM reaction using the GPLe method.

## **2. Material and Methods**

The General Power Law Expression (GPLe) is a model to predict the catalyst deactivation rate assuming a non-zero steady-state activity (SSA) after a long time on stream. The GPLe modeled the catalyst deactivation rate as follow:

$$-\frac{da}{dt} = k_d P(c)_d a^d + constant \quad (5)$$

where  $a$  is the normalized activity,  $k_d$  is deactivation rate constant,  $P(c)_d$  represent the kinetic function that depends on the concentration,  $d$  is the deactivation order, and  $a_{ss}$  is the SSA The linearized solution for the GPLE equation for the first order deactivation process is:

$$a(t) = (1 - a_{ss}) \exp(-k_1 t) + a_{ss} \quad (6)$$

While for the second deactivation rate:

$$a(t) = (k_2 t + (1 - a_{ss})^{-1})^{-1} + a_{ss} \quad (7)$$

In this research the GPLE model used to predict the catalyst deactivation mechanism during two deactivation regimes: (1) fast deactivation regime by sintering and carbon deposition, and (2) slow deactivation regime by carbon deposition.

### Ni-based catalysts selected for the DRM deactivation model development

Four catalytic systems were chosen to study the catalyst deactivation on the DRM reaction, as shown in Table 1. The DRM was examined in the bench-scale reactor using a vertical quartz reactor at atmospheric pressure. The catalyst bed was prepared by mixing 5.5 mg of catalyst and 100mg of SiO<sub>2</sub> as a diluent. The reaction mixture mainly consisted of 10% CH<sub>4</sub>/10% CO<sub>2</sub>/80% He.

Table 1 Catalytic systems used in the catalyst deactivation study.

Catalyst	Test length (hr)	T (°C)	P (bar)	CH <sub>4</sub> /CO <sub>2</sub>	X <sub>CH<sub>4o</sub></sub> (%)
10% Ni/Al <sub>2</sub> O <sub>3</sub>	70	650	1	1	0.47
10% Ni <sub>8</sub> -Cu <sub>1</sub> /Al <sub>2</sub> O <sub>3</sub>	70	650	1	1	0.76
Riogen <sup>1</sup> 1	40	650	1	1	0.52
Riogen 2	40	550	1	1	0.31

### 3. Results and Discussion

All the catalytic systems were fitted to the first and second order GPLE to ensure that the model can predict the catalyst activity with a high degree of accuracy. The fitting results given in Table 2 indicate that the model is perfectly fitted to the experimental data with R<sup>2</sup> value ranged between 0.96 and 0.99.

For the mono-metallic and bimetallic catalysts, both the first and second order GPLEs fit the experimental deactivation data quite well with R<sup>2</sup> values of 0.96 and 0.98, respectively. As depicted in Table 2, the predicted SSA for the monometallic catalyst is almost reached zero given an infinite amount of TOS for both first and second order

<sup>1</sup> Industrial catalyst that used in methane reforming

GPLe models. In this specific scenario,  $a_{ss}$  tends to zero most probably due to the high rate of the carbon deposition, which eventually covers the catalyst surface, preventing accessibility of the reactants to the active site.

Table 2 The fitting results of the deactivation study.

Catalyst	First order			Second order		
	$K_d(1/h)$	$a_{ss}$	$R^2$	$K_d(1/h)$	$a_{ss}$	$R^2$
<b>Ni<sub>8</sub>Cu<sub>1</sub>/γ-Al<sub>2</sub>O<sub>3</sub></b>	0.029	0.725	0.965	0.061	0.615	0.965
<b>Ni/γ-Al<sub>2</sub>O<sub>3</sub></b>	0.036	0	0.981	0.066	0	0.955
<b>Riogen (650 °C)</b>	0.146	0.237	0.985	0.189	0.092	0.995
<b>Riogen (550 °C)</b>	0.101	0.254	0.961	0.111	0.060	0.972

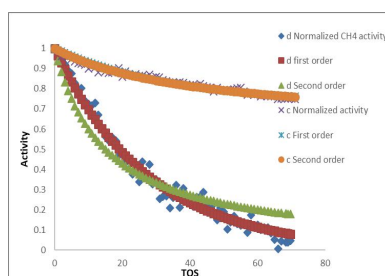


Fig. 1 Deactivation fitting results of (c) bimetallic catalyst and (d) monometallic catalyst.

The Cu bimetallic catalyst shows better stability and higher SSA than the monometallic catalyst. Comparing both first and second-order fitting trends, it is apparent that the second-order model is more realistic in predicting  $a_{ss}$  value as previously reported for other catalytic systems (M. D. Argyle, T. S. Frost, and C. H. Bartholomew, 2014). Next, deconvolution was performed to determine the total deactivation caused by sintering and coking, following the method described by Argyle et al. (M. D. Argyle, T. S. Frost, and C. H. Bartholomew, 2014). The deconvolution results of all the catalysts are given in Table 3. For the Riogen tested at 550 °C, the model results revealed that 37 % of total activity loss is due to sintering, while 63% of the total deactivation is due to carbon deposition.

For the mono-metallic Ni/ γ-Al<sub>2</sub>O<sub>3</sub> catalyst, the model results suggest that the sintering contribution in the total deactivation is negligible (<1%) while most of the deactivation is from carbon deposition. Therefore, to corroborate these results, TPO analysis of the spent catalyst is performed to determine the coke deposition.

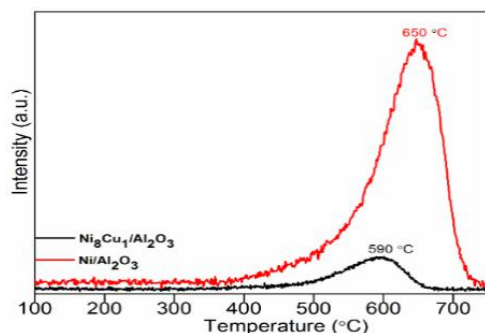


Fig. 2 O<sub>2</sub>-TPO profile of spent catalysts after DRM performance at 650 °C for 70h TOS.

The TPO results shows that for the monometallic catalyst, graphitic type of carbon is produced from the intense CO<sub>2</sub> peak at 650 °C, while for bimetallic catalyst, amorphous kind of carbon is produced at 590 °C. Also, the rate of carbon produced in the monometallic catalyst is much higher than the carbon produced in the bimetallic catalyst, which is in agreement with the model results.

In contrast to the monometallic catalyst, deconvolution of the bi-metallic Ni<sub>8</sub>Cu<sub>1</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst data revealed that the ~77% of total deactivation loss is due to carbon deposition while 23% of activity loss due to sintering of the catalyst. One has to remember that these numbers correspond to a fraction of the total deactivation, which is still far lesser for the bimetallic catalyst.

Table 3 The mechanism deconvolution results.

Catalyst	Rapid deactivation (Sintering)			Slow deactivation (C deposit)			Mechanism contribution
	TOS (h)	K <sub>d</sub> (1/h)	a <sub>ss,fast</sub>	TOS (h)	K <sub>d</sub> (1/h)	a <sub>ss,slow</sub>	
Ni <sub>8</sub> Cu <sub>1</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	0-30	6.95	0.94	30-72	0.005	0.36	Sintering (23%) C deposit (77%)
Ni/γ-Al <sub>2</sub> O <sub>3</sub>	0-30	0.13	0.99	30-70	0.01	0.01	Sintering (1%) C deposit (99%)
Riogen (650 °C)	0-15	1.23	0.595	15-39	0.06	0.548	Sintering (47%) C deposit (53%)
Riogen (550 °C)	0-20	1.05	0.683	20-39	0.05	0.461	Sintering (37%) C deposit (63%)

Examining the literature, Wu. et al. (Z. BIAN, S. Das, M. H. Wai, P. Hongmanorom, and S. Kawi, 2017) observes that the addition of Cu promotes the sintering resistance of a bimetallic Ni-Cu catalyst supported on silica nano-sheets. This is in contrast to the current study, wherein the modeling results are suggestive of a higher sintering contribution to the deactivation of the Ni-Cu bimetallic catalyst. However, the sintering occurs to a relatively lesser degree and, from experimental testing, does not appear to impact the overall catalyst activity significantly.

#### **4. Conclusion**

This study provides a quantitative framework to model the catalyst deactivation mechanism on the DRM process. The GPLE model was able to predict the deactivation mechanism and the activity profile for all the catalytic systems used. Almost all the experimental data in this study fitted well to the first and second GPLE models, and the review was able to predict the fraction loss of the activity from sintering and carbon deposition for all the catalytic systems. In the bimetallic and monometallic catalysts, the results indicate that the rapid deactivation of monometallic catalyst is primarily due to significant coke formation whereas, the bimetallic catalyst experienced minimal deactivation owing to both particle sintering in the initial phases followed by coke formation. In the commercial catalyst (Riogen) the model results indicate that at 550 °C the percent of activity lost due to carbon deposition is higher than the case for the catalyst tested for DRM at 650 °C, which agree well with the literature.

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