**ELECTRONIC SUPPLEMENTARY INFORMATION**

# Analysis of autothermal operability of Sabatier reaction in a heat recirculating microreactor using CFD

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**BRIEF ANALYSIS OF METHANATION KINETICS**

The kinetics chosen for this work were developed by Xu & Froment[1] for both reforming and methanation, which are reverse of each other. The authors ensured that thermodynamic consistency of the rate expressions. In this ESI document, we analyze Reaction-3, although the same arguments are valid for the other three reactions as well.

A brief literature review on $CO_2$ methanation shows that the activation energy on Ni catalyst is in the range of 70 to 100 kJ/mol. For example, Weatherbee & Bartholomew[2] reported a constant $E_A$ = 94 kJ/mol for Langmuir-Hinshelwood rate expression. Maatman & Hiemstra[3] reported activation energies at different $CO_2$:$H_2$ ratios, and found them to be in the range of 79 to 91.6 kJ/mol. Beierlein et al.[4] studied structure-activity relationships of $CO_2$ methanation and reported that all catalysts had similar values of activation energies, between 79 and 86 kJ/mol. Garbarino et al.[5] reported similar apparent activation energies for Ni/$Al_2O_3$ (80 kJ/mol); the same authors[6] reported activation energy of 75 kJ/mol for catalysts containing smaller particles of Ni; Lefebevre et al.[7] found the apparent activation energy is 79 kJ/mol; Konishcheva et al.[8] reported activation energy of 90 kJ/mol on Ni(Cl)/$CeO_2$ for $CO_2$ methanation and 140 kJ/mol for CO methanation. Tada et al.[9] presented sponge Ni as a promising catalyst for $CO_2$ methanation with apparent activation energy of 70 kJ/mol to 99 kJ/mol on NiO/$CeO_2$.

In contrast, the activation energy for Reaction-3 reported in Table 1 as 243.9 kJ/mol. Since Xu & Froment[1] had written the rate expressions for reforming and WGS, this is the activation energy for methane reforming to $CO_2$, i.e. $CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$. Let us consider the $CO_2$ methanation reaction:

$$\text{Reaction-3:} \quad CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2H_2O$$
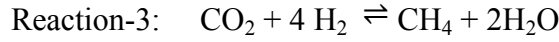
$$r_3 = -\frac{1}{Den^2 p_{H_2}^{3.5}} k_3 \left( p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_3} \right) \quad = \frac{k_3}{Den^2 \cdot p_{H_2}^{3.5}} \left( \frac{p_{H_2}^4 p_{CO_2}}{K_3} - p_{CH_4} p_{H_2O}^2 \right) \tag{3}$$

This can be written in a normal "reversible" form as

$$r_3 = \frac{k_3}{Den^2} \frac{p_{H_2}^{0.5} p_{CO_2}}{K_3} \left( 1 - \frac{K_3 p_{CH_4} p_{H_2O}^2}{p_{H_2}^4 p_{CO_2}} \right)$$

$$= \frac{\bar{k}_3 p_{CO_2} \sqrt{p_{H_2}}}{Den^2} \left( 1 - K_3 \frac{p_{CH_4} p_{H_2O}^2}{p_{H_2}^4 p_{CO_2}} \right)$$

where, $\bar{k}_3 = k_3/K_3$. Using the expressions given in Tables 1 and 2 of the manuscript, we computed $\bar{k}_3$ for temperatures in the range of 300 to 900 K. Figure S1 shows that $\ln(\bar{k}_3)$ vs. 1/T is linear, with the Arrhenius equation for $\bar{k}_3$ showing an excellent fit:

$$\bar{k}_3 = 4.71e4\exp\left( -\frac{8364.7}{T} \right)$$
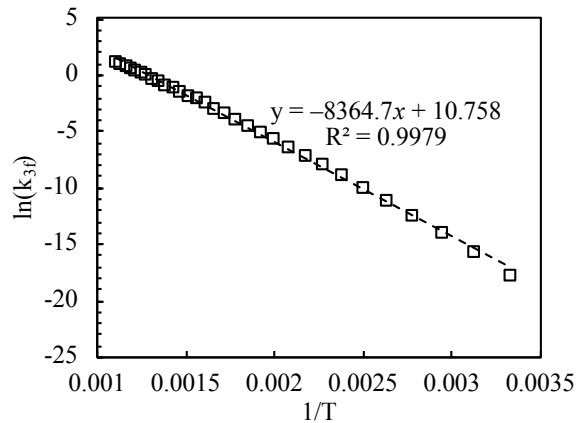


**Figure S1:** Numerical calculation of activation energy for the forward reaction for $CO_2$ methanation. Symbols represent the value obtained by substituting rate constants from Table 1 and Table 2, whereas the line represents a linear fit.

With this expression, the activation energy for CO2 methanation is 69.54 kJ/mol, which falls in the range of what is reported in the literature. In summary, it could be argued that the rate of Reaction-3 would be mathematically equivalent to:

$$r_3 = \frac{\bar{k}_3 p_{CO_2} \sqrt{p_{H_2}}}{Den^2} \left( 1 - \frac{1}{K_3} \frac{p_{CH_4} p_{H_2O}^2}{p_{H_2}^4 p_{CO_2}} \right) \tag{4}$$

$$k_3 = \bar{A}_3 \exp\left(-\frac{E_3}{RT}\right), \quad \bar{A}_3 = 4.71 \times 10^4 \frac{kmol}{bar^{1.5}.m^2.s}, \quad E_3 = 69.54 \frac{kJ}{mol}, \qquad \text{(4-a)}$$

$$\bar{K}_3 = 0.974 \exp\left(33.165 + \frac{28183.2}{T^2} + \frac{17429.8}{T} - 8.254\ln(T) + 0.0028T\right) \qquad \text{(4-b)}$$

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