**BRIEF ANALYSIS OF METHANATION KINETICS**

The kinetics chosen for this work were developed by Xu & Froment 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\textsubscript{2} methanation shows that the activation energy on Ni catalyst is in the range of 70 to 100 kJ/mol. For example, Weatherbee & Bartholomew\textsuperscript{2} reported a constant $E_A = 94$ kJ/mol for Langmuir-Hinshelwood rate expression. Maatman & Hiemstra\textsuperscript{3} reported activation energies at different CO\textsubscript{2}:H\textsubscript{2} ratios, and found them to be in the range of 79 to 91.6 kJ/mol. Beierlein et al.\textsuperscript{4} studied structure-activity relationships of CO\textsubscript{2} methanation and reported that all catalysts had similar values of activation energies, between 79 and 86 kJ/mol. Garbarino et al.\textsuperscript{5} reported similar apparent activation energies for Ni/Al\textsubscript{2}O\textsubscript{3} (80 kJ/mol); the same authors\textsuperscript{6} reported activation energy of 75 kJ/mol for catalysts containing smaller particles of Ni; Lefebvre et al.\textsuperscript{7} found the apparent activation energy is 79 kJ/mol; Konishcheva et al.\textsuperscript{8} reported activation energy of 90 kJ/mol on Ni(Cl)/CeO\textsubscript{2} for CO\textsubscript{2} methanation and 140 kJ/mol for CO methanation. Tada et al.\textsuperscript{9} presented sponge Ni as a promising catalyst for CO\textsubscript{2} methanation with apparent activation energy of 70 kJ/mol to 99 kJ/mol on NiO/CeO\textsubscript{2}.

In contrast, the activation energy for Reaction-3 reported in Table 1 as 243.9 kJ/mol. Since Xu & Froment\textsuperscript{1} had written the rate expressions for reforming and WGS, this is the activation energy for methane reforming to CO\textsubscript{2}, i.e. CH\textsubscript{4} + 2H\textsubscript{2}O $\rightleftharpoons$ CO\textsubscript{2} + 4 H\textsubscript{2}. Let us consider the CO\textsubscript{2} methanation reaction:
Reaction 3:  \( \text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O} \)

\[
\begin{align*}
    r_3 &= -\frac{1}{\text{Den}^2 p_{\text{H}_2}^{3.5}} \left( k_3 \left( p_{\text{CH}_4} p_{\text{H}_2}^2 - \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_3} \right) \right) = \frac{k_3}{\text{Den}^2 p_{\text{H}_2}^{3.5}} \left( \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_3} - p_{\text{CH}_4} p_{\text{H}_2}^2 \right)
\end{align*}
\]

This can be written in a normal “reversible” form as

\[
\begin{align*}
    r_3 &= \frac{k_3 p_{\text{H}_2}^{6.5} p_{\text{CO}_2}}{\text{Den}^2 K_3} \left( 1 - \frac{K_3 p_{\text{CH}_4} p_{\text{H}_2}^2}{p_{\text{H}_2}^4 p_{\text{CO}_2}} \right) \\
    &= \frac{k_3 p_{\text{CO}_2}^{2n} p_{\text{H}_2}}{\text{Den}^2} \left( 1 - K_3 \frac{p_{\text{CH}_4} p_{\text{H}_2}^2}{p_{\text{H}_2}^4 p_{\text{CO}_2}} \right)
\end{align*}
\]

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

\[
k_3 = 4.71 \times 10^4 \exp \left( -\frac{8364.7}{T} \right)
\]

**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:

\[
\begin{align*}
    r_3 &= \frac{k_3 p_{\text{CO}_2}^{2n} p_{\text{H}_2}}{\text{Den}^2} \left( 1 - \frac{1}{K_3 \frac{p_{\text{CH}_4} p_{\text{H}_2}^2}{p_{\text{H}_2}^4 p_{\text{CO}_2}}} \right)
\end{align*}
\]
\[ k_3 = A_3 \exp \left( -\frac{E_3}{RT} \right), \quad A_3 = 4.71 \times 10^4 \frac{\text{kmol}}{\text{bar}^{1.5} \text{m}^2 \text{s}}, \quad E_3 = 69.54 \frac{\text{kJ}}{\text{mol}} \] (4-a)

\[ K_3 = 0.974 \exp \left( 33.165 + \frac{28183.2}{T^2} + \frac{17429.8}{T} - 8.254 \ln(T) + 0.0028T \right) \] (4-b)

References


