Improved microkinetic models for oxidative coupling of methane (OCM) using sensitivity analysis based (SAB) method and high throughput experiments

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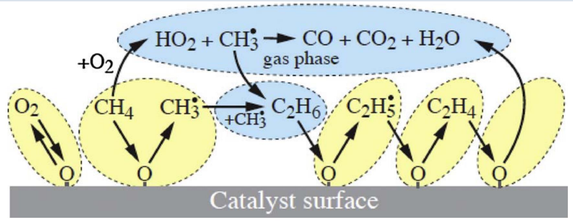
Introduction

Increased production of natural gas has motivated interests to develop advanced chemical technologies that valorise methane. Oxidative coupling of methane (OCM) to produce C_2 paraffins and olefins is a promising route for producing value-added chemical feedstocks. However, this chemical process has not been commercialized yet, and it still relies on fundamentals development. Improvements can be made through advancing micro-kinetic models describing the surface and gas-phase reactions. In this work, high throughput catalytic reactor experiments with a high fidelity statistical approach like sensitivity analysis based (SAB) method are applied to study the OCM catalysis micro-kinetics.

Objective

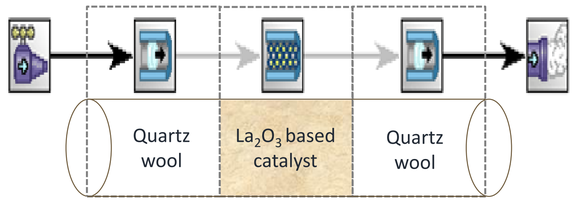
This work aims to investigate the OCM surface-phase reactions and improve a published mechanism to match our experimental data. To reflect the effect of the catalyst composition in the microkinetic models, different weight percent of metals, such as Sr, Ce, and Ca, are doped. Other process variables are also experimented such as bed temperature, gas hour space velocity, and methane to oxygen ratio. Then, CHEMKIN PRO was used to simulate a packed bed reactor using Karakaya, C., et al. [2] surface-phase reactions and a reduced version of AramcoMech 3.0 for gas-phase reactions. The reduced mechanism was developed and validated for OCM. It consists of 971 reactions between 129 species. The parameters for each reaction were written in the form of Arrhenius' equation, given as $k = A * T^{\beta} * e^{-E_a/RT}$. The most sensitive surface reactions were first identified, then the SAB method was applied to them to find which kinetic parameters need to be modified, so the simulation results agree with the experimental data under the studied operating conditions.

Methodology



Proposed OCM reaction pathway [1]

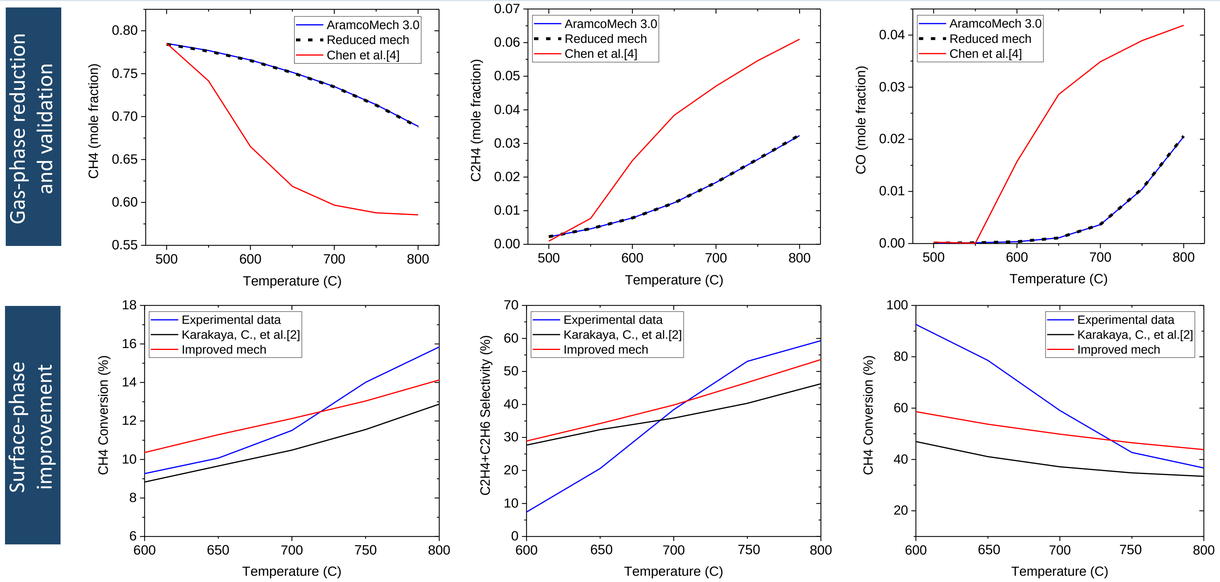
A brief description of the contribution of the homogeneous (blue) and heterogeneous (yellow) reactions to the OCM. The catalytic reactions are improved in this work.



CHEMKIN PRO reactor configuration

The catalyst bed was modeled in CHEMKIN PRO to utilize both homogeneous and heterogeneous reactions. Plug flow reactors were also added to match the experimental setup.

Results



The reduced gas-phase mechanism graphs show a perfect match with AramcoMech 3.0 and reveal deviations with a previously published OCM gas-phase mechanism at various operating conditions. The improved surface-phase mechanism did not successfully match the experimental results, and this work is still under further investigation and improvement.

SAB Method

$$x_i = \frac{\ln(k_i/k_{i,0})}{\ln f_i} \qquad \ln \eta = a_0 + \sum_i^L a_i x_i + \sum_i^L \sum_{j \geq i}^L a_{ij} x_i x_j$$

$$a_0 = \ln \eta_0$$

$$a_i = \frac{\ln \eta[\mathbf{x}(\alpha)_i] - \ln \eta[\mathbf{x}(-\alpha)_i]}{2\alpha} \qquad (i = 1, 2 \ldots, L)$$

$$a_{ii} = \frac{s_{i,i} - s_{-i,i}}{4\alpha} \ln f_i$$

$$a_{ij} = \frac{[(s_{i,j} - s_{-i,j}) \ln f_j + (s_{j,i} - s_{-j,i}) \ln f_i]}{4\alpha} \qquad (i \neq j)$$

SAB method equations and parameters are explained by Davis, Scott G., et al. [3].

Conclusion

The SAB method demonstrated some improvements were made on the Karakaya, C., et al.[2] surface-phase mechanism. The most improvement was presented on the methane conversion compared to the ethane and ethylene (C_2), and carbon monoxide and carbon dioxide (CO_x) selectivities. However, the developed mechanism still needs additional improvements to match our high throughput experimental results. Species sensitivity and reaction path analysis, among other techniques, are under investigation currently to further optimizing the surface reactions rates.

References

[1] Karakaya, C. and R.J. Kee, Progress in the direct catalytic conversion of methane to fuels and chemicals. Progress in Energy and Combustion Science, 2016. 55: p. 60-97.
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