

# MULTISCALE MODELING FOR NON-OXIDATIVE METHANE COUPLING OVER EARTH ABUNDANT CATALYSTS

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## *Abstract*

Direct methane conversion routes to liquids and light alkanes have received considerable interest. In this study, we develop a first-principles-based microkinetic model on a Fe@SiO<sub>2</sub> catalyst for non-oxidative methane conversion that combines catalytic and gas-phase reaction mechanisms. The simulations are performed using the state-of-the-art multiscale kinetic modeling software, OpenCK. Based on the microkinetic simulations, ethylene is shown as the only primary species among the major products. The kinetic models combined with reactor scale simulations and detailed analysis provide process optimization guidelines for enhanced selectivity towards desired products.

## *Keywords*

Non-oxidative methane coupling, Multiscale modeling, Process optimization.

## **Introduction**

The production of large amounts of shale gas, lower overall costs, and sustainability concerns have generated interest for the production of fuels and chemicals directly from methane (Olivos-Suarez et al., 2016). One of the grand challenges is the activation of methane, which is the most stable and unreactive alkane (Schwach et al., 2017). Currently, methane is converted into fuels and chemicals through syngas, an energy intensive and large capital investment process (Aasberg-Petersen et al., 2011). The latter prevents methane utilization at remote locations resulting in flaring methane.

Recently, single atom catalysts (SAC) specifically, isolated iron atoms embedded in a non-acidic silica matrix (Fe@SiO<sub>2</sub>), has enabled the direct non-oxidative conversion of methane (NOCM) to olefins, aromatics, and hydrogen at high temperatures (1223 – 1363 K) (Guo et al., 2014). In addition to the unprecedented carbon utilization efficiency without coke formation and the high stability of Fe@SiO<sub>2</sub>, high methane one-pass conversion of 48%

indicates opportunities for an economically viable process. It has been proposed that methane conversion is initiated by catalytic generation of methyl radicals followed by subsequent gas-phase reactions to produce products such as ethylene, benzene, and naphthalene. This mechanism suggests that the product distribution from methane pyrolysis and NOCM over Fe@SiO<sub>2</sub> should be similar to each other due to the gas-phase chain propagation reactions. Methane pyrolysis mainly produces light hydrocarbons, such as acetylene and coke, whereas NOCM over Fe@SiO<sub>2</sub> mainly produces ethylene and higher hydrocarbons, such as benzene and naphthalene without any coke formation. This results strongly point out that further research is necessary for fundamental understanding of the reaction mechanism and the role of Fe@SiO<sub>2</sub> catalyst. In this study, we develop a first-principles-based microkinetic model on a Fe@SiO<sub>2</sub> catalyst for non-oxidative methane conversion that combines detailed catalytic and gas-phase reaction mechanisms. The results provide insights into the reaction

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mechanisms, the role of Fe@SiO<sub>2</sub> catalyst, and process optimization.

## Methodology

An isolated Fe atom in its proper thermodynamic state was placed on an amorphous silica model. Spin-polarized periodic density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) and the projector-augmented wave (PAW) method. The exchange-correlation energies were calculated on the basis of the generalized gradient approximation (GGA) according to Perdew and Wang (PW91). The plane-wave energy cutoff was set to 400 eV, while the Brillouin zone was sampled using a  $3 \times 3 \times 1$   $\Gamma$ -centered k-point mesh. A maximum force convergence criterion of 0.05 eV  $\text{\AA}^{-1}$  was used and each self-consistency loop was iterated until a convergence level of  $10^{-6}$  eV was achieved. Thermodynamic and kinetic parameters of all elementary steps were computed using statistical thermodynamics and incorporated into a mean-field microkinetic model.

The microkinetic model was solved in a plug flow reactor using the in-house reactor code, OpenCK. The NOCM was modeled using a combination of catalytic reactions developed here and gas-phase reaction mechanisms (Figure 1). For the former, we investigate the C-H activation of methane and C-C coupling reactions using DFT calculations, as described above.

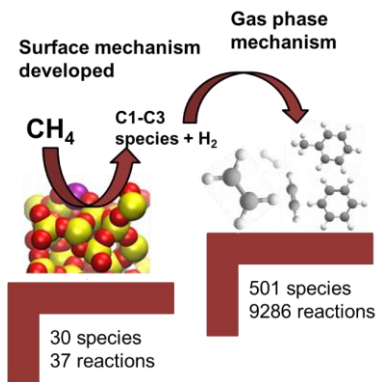


Figure 1. Schematic representation of catalytic and gas-phase reactions used for microkinetic simulations.

## Results and Discussion

Microkinetic simulations show that ethylene is a primary product. Figure 2 shows an increase in selectivity towards acetylene and higher molecular weight cyclic species (benzene, toluene, and naphthalene) at the expense of ethylene and ethane with increasing temperature. The complex interplay between catalytic and gas-phase reactions lead to higher hydrocarbons and acetylene whereas consumption of ethylene proceeds via gas-phase reactions. Simulation results are compared to experimental data and good agreement is found. Reaction path and

sensitivity analyses are carried out to delineate the dominant paths, the contribution of each phase on conversion and selectivity, and how to optimize the process.

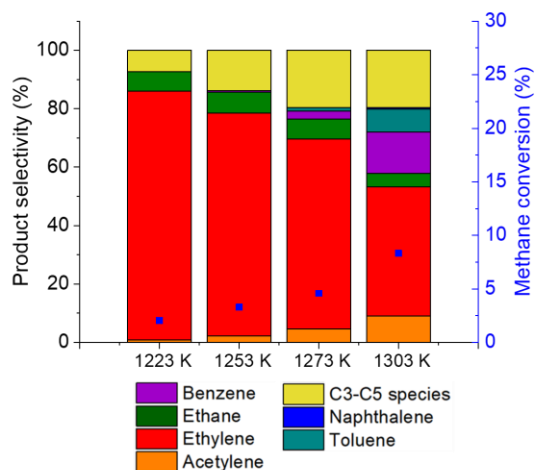


Figure 2. Effect of temperature on catalytic performance of Fe@SiO<sub>2</sub> catalyst in NOCM.

## Conclusions

A coupled surface and gas-phase microkinetic model was developed for NOCM, assessed against experimental data, and analyzed. It was found that gas-phase reactions should be minimized to increase selectivity towards ethylene. The kinetic models combined with reactor scale simulations and detailed analysis, such as reaction pathway analysis, provide guidelines for enhanced selectivity towards desired products.

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