Kinetic fingerprints – diving into mechanistic peculiarities

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Highlights

- Normalized formation rates reveal high information density and kinetic sensitivity.
- Unique kinetic fingerprints through 3D-representation of sensitive kinetic parameters.
- Rigorous plausibility testing of kinetic models.
- Model-free stochastic and statistic approaches appear most plausible.

1. Introduction

Kinetics in catalytic reactions are traditionally approached through mathematical models of various degrees of complexity. Data fit was a goal, which could be achieved to different levels of accuracy and quality acceptance.

For a number of use cases a suitable description of the change of quantities as a function of time and space is sufficient. When it comes to the elucidation of plausibility of mechanistic features in catalytic reactions, a more sensitive choice of parameters is necessary. One approach could be the evaluation of kinetic orders for various product formation kinetics, which enables a kinetic distinction of various active sites. [1] Ratio of rates and yield ratios support the elucidation of reaction mechanisms assessing their plausibility in a rational way. [2] Rational kinetic approaches therefore provide a direct link to mechanistic features of catalytic reactions and allow for the construction of plausible reaction mechanisms.

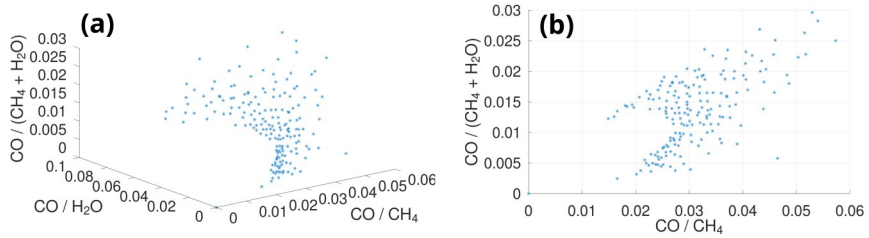

Figure 1. Experimental data of normalized CO-formation rates: (a) 3-D plot of R(CO) normalized on ($(CH_4)+(H_2O)$), (H_2O), and (CH_4), and (b) the extract of the R(CO)/($(CH_4)+(H_2O)$) | R(CO)/(CH_4) plane.

Normalized formation rates (yield ratios), and especially their combination (see Fig. 1), form a unique data trend, which can be considered as a *kinetic fingerprint* of a specific product. The scope of this contribution is to elucidate to which extend kinetic approaches are able to resemble kinetic fingerprint data trends, and provide plausibility for the underlying kinetic and mechanistic assumptions.

2. Methods

The experimental data comprises 179 data points of methane steam reforming over a nickel catalyst at 873 K, 1 bar (total pressure), < 0.1 bar reactant partial pressure, and steam-to-carbon ratios between 0.2 and 7.2.[3] Normalized formation rates (shown for CO in Fig. 1) were derived and taken as a benchmark due to their individual trend and high information content. The presented models in Fig. 2 were determined within at least a steam-to-carbon range between 0.1 and 10.

3. Results and discussion

Fig. 2 shows the CO formation rate normalized with respect to the CH_4 partial pressure and the sum of reactant partial pressures (in the feed) plotted on the x- and y-axis, respectively, for various kinetic approaches and the thermodynamic calculation.

The kinetic fingerprint of the normalized CO formation rate in Fig. 1(b) is observed with a loop-like data trend. Data trends for Graph Theory models [4] for a coupled mechanism on one active-site, presented in Fig. 2(a). Also a de-coupled mechanism was tested, however, only the one-site mechanism appears to have some hint of a loop-like characteristic. Yet this is far from the observation of the experimental trend.

Similarly, steady-state kinetics, although a common kinetic approach fails to resemble the experimental data trend. Even a sophisticated microkinetic approach [5] that was developed with a good fit of this experimental data, is observed with a completely different data trend, see Fig. 2(b).

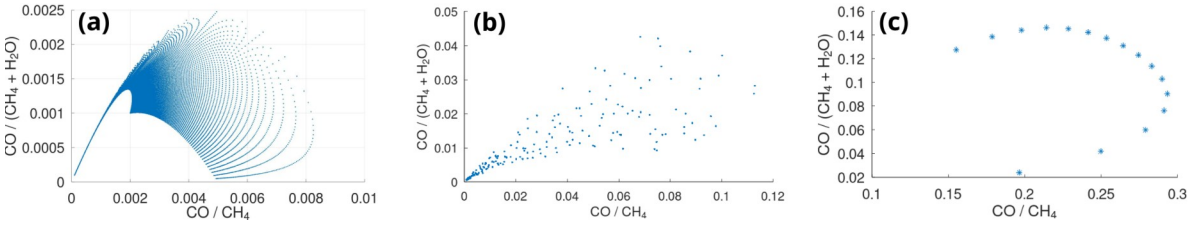

Figure 2. Normalize CO-formation rates with focus on the R(CO)/((CH$_4$)+(H$_2$O)) | R(CO)/(CH$_4$) plane: (a) Graph Theory model for a coupled mechanism on one site, (b) Microkinetic modeling [4], and (c) Thermodynamic calculations.

It is interesting to observe, that the only approaches that do resemble the loop-like data trend of the kinetic fingerprint, are the model-free approaches like stochastic (simplified Monte Carlo) and statistic (thermodynamic calculation), the latter shown in Fig. 2(c). It appears, that methane steam reforming might proceed without a dedicated mechanism as a reaction pathway.

4. Conclusions

Utilizing most sensitive data trends and combining those to unique kinetic fingerprints allows for a rigorous plausibility test of kinetic models against the experimental data. Established mechanistic models, like graph theory, steady-state kinetic, and microkinetic approaches fail to resemble the experimental kinetic fingerprint data trend. Conversely, model-free stochastic and statistic approaches, however, do resemble the experimental kinetic fingerprints and, thus, appear plausible in describing the features of how the CO formation reaction from CH$_4$ and H$_2$O over nickel might proceed.

References

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Keywords
Rational kinetics ; Kinetic fingerprint ; Model-free simulation ; Normalized formation rates