CaRMeN: Catalytic Reaction Mechanisms Network – A Novel Tool for the Evaluation of Kinetic Data and Mechanisms

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Highlights

- Novel software tool for digitalization and archiving of experimental and modeling data in reaction kinetics
- Compatible with various reactor configurations and simulation codes
- Automated and easy testing of kinetic models in a *plug-and-play* fashion
- Featured case-study: Conversion of methane over Rhodium catalysts

1. Introduction

Given a particular chemical reaction system of interest, the literature usually contains a very large number of experimental and modeling studies, which are difficult to assess as a whole. Kinetics of heterogeneously catalyzed reactions, such as the conversion of methane over rhodium catalysts can serve as a prime example: Over the years, this system has been studied in many reactor configurations including, but not limited to, fixed beds, monoliths, and stagnation-flow setups. These experiments were carried out at different conditions (total/partial oxidation, steam/dry reforming), and have been modeled using over a dozen different reaction mechanisms, each with their own set of rate expressions. The published mechanisms tend to have a special focus on the particular application for which they were developed, and the quality and potential of that mechanism under differing conditions is either not known or hard to judge.

CaRMeN is a software tool that addresses these problems by providing a platform to archive and evaluate structured experimental data and kinetic models. This platform can be a first step towards organizing the vast amounts of data available in the literature. Within this platform, these data can be conveniently compared with the results of any simulation code under the matching experimental conditions. Reaction mechanisms can then be developed faster and their quality and applicability increased.

In this contribution, the approach and capabilities of the software are illustrated using data for the conversion of methane over rhodium catalysts at very different conditions and reactor configurations.

2. Methods

CaRMeN provides a database that contains measured data from any experiments in tabulated form, e.g. CH_4 oxidation over Rh-based catalysts, including all conditions of the experiment. Any other files such as a human-readable description along with images or PDFs can also be attached to the experiment file to understand its background and the experimental setup. The measured data are for instance end-of-pipe compositions, light-off curves, spatial and temporal species and temperature profiles, or catalyst oxidation states as a function of operating conditions in different reactor types.

Metadata are associated with the experimental dataset, and provide the information required to run the numerical simulation under conditions matching those of the experiment. CaRMeN is not restricted to a particular simulation software, but can be used with any simulation code, provided a *simulation driver* for that code has been configured. While it is in general possible to run any simulation code, we currently provide drivers (and tools to easily create more drivers) for DETCHEM and CHEMKIN. This approach enables the use of a wide variety of computer codes that can numerically simulate the catalytic reactors

(batch, tubes, monoliths, fixed beds, stagnation flow, etc.) using varying levels of complexity. Furthermore, a comparison between different implementations of the same reactor model is easily carried out.

Figure 1 shows two screenshots of the graphical user interface. An arbitrary number of different experiments can be chosen to be simulated using a user-specified surface reaction mechanism or other physical model (e.g. plug flow versus parabolic flow in a channel). As results, comparisons of experimental and numerically predicted conversion, selectivities, species profiles, or any other relevant measurable variables are presented as shown in the figure on the left. Parity plots provide a clear and concise comparison of multiple experiments and their corresponding simulations in a single graph (Fig. 1, right).

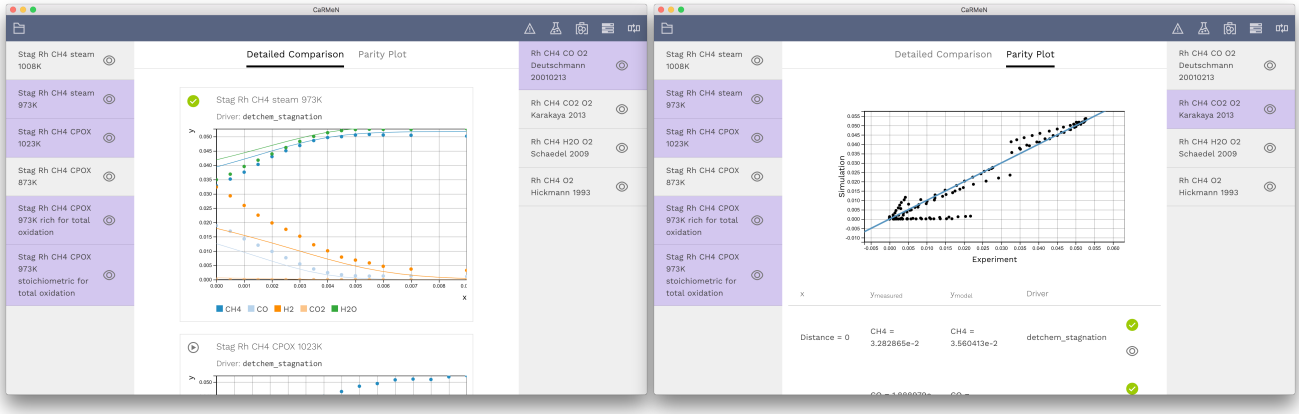

Figure 1. Screenshots showing detailed comparison between measured data obtained from a stagnation point flow reactor and simulated data using DETCHEM^{STAGNATION} (left). The right image shows a parity plot of the same experiments as on the left simulated with a different mechanism [5].

3. Results and discussion

Several mechanisms for the conversion of methane over rhodium catalysts have been proposed in the literature, e.g. [1-4]. This contribution presents comparisons between the different mechanisms applied in simulations of a wide variety of experimental setups and conditions. On one side, the applicability of the mechanisms is evaluated, their potentials and limitations are visualized. On the other side, different reactor models are tested showing the level of detail needed to adequately simulate mass and heat transport in the reactor setup. Furthermore, comparing a vast number of experiments studying methane conversion over rhodium elucidates experiments that are likely to bare high experimental uncertainties.

References

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Keywords
Digitalization; Reaction mechanism; Rhodium; Methane