Revisiting Grasselli's site-isolation principle – Distinguishing coupled and decoupled active sites in catalytic reactions

Christoph Sprung[1]*, Gregory S. Yablonsky[2]

1 Stirnerstr. 12, 12169 Berlin/Germany; 2 Department of Energy, Environmental & Chemical Engineering, McKelvey School of Engineering, Washington University, St. Louis, MO 63130, USA

**Corresponding author: kinetics@active-sites.de*

Highlights

- Testing Grasselli's site isolation principle for granularity to distinguish CO and CO_2 formation.
- Kinetic distinction between coupled and decoupled active sites.
- Combination of Rational Kinetic modeling, Monte-Carlo simulation, and Thermodynamic calculation.
- Normalized formation rates reveal high information density and kinetic sensitivity.

1. Introduction

In catalytic reactions, the active site is of central interest to facilitate chemical reactions between molecules with often complex reaction mechanisms and reactions, that are different in their chemical nature. The site isolation principle was observed to allow for selectivity, avoiding over-oxidation due to a limited availability of oxygen on one active site compared to another.[1,2] The structural concept for the proof of the requirement of site isolation was presented by Grasselli et al. [2]. CO and CO_2 have been grouped together into one category. The question arises, how many decoupled active sites do exist? And, how can they be distinguished kinetically? For the selective oxidation of propane, such kinetic distinction could be shown and the presence of active sites be linked to the kinetic fingerprints of products.[3] This concept shall here be applied to test the granularity of the site isolation principle.

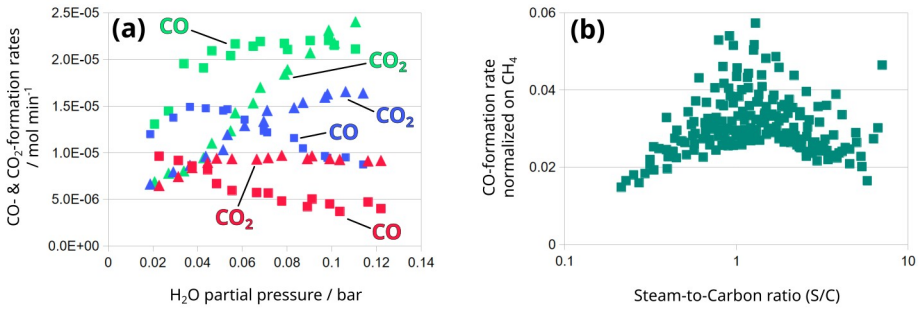

Figure 1. Experimental data: (a) CO- and CO_2-formation rates of three different CH_4 partial pressure levels. (b) CO-formation rate (all partial pressure levels) normalized with respect to CH_4 inlet flow.

In methane steam reforming the trends of CO- and CO_2-formation rates were observed to be significantly different as a function of H_2O partial pressure (see Fig. 1(a)). This leads to the question, whether both products form on the same active site or whether their formation is independent of each other.

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.[4] Normalized formation rates (shown for CO in Fig. 1(b)) were derived and taken as a benchmark due to their individual trend and high information content. Rational kinetic modeling [5], model-free simplified Monte-Carlo simulation, and thermodynamic calculation were performed independently of each other to assess whether the achieved data trends resemble the experimentally observed ones. This was taken as a measure to prove plausibility of CO and CO_2 formed on one (coupled) site or on two (decoupled) sites.

3. Results and discussion

Fig. 2 shows the most prominent trends of the simplified Monte-Carlo simulations and the thermodynamic calculations, which is the CO formation rate normalized with respect to the CH_4 partial pressure (in the feed).

The trends of the simplified Monte-Carlo simulations (Fig. 2(a)) appear with a clear distinction between a one- and two-site approach, with the former being observed with a maximum and the latter as continuous increase. The same observation can be seen in Fig. 2(b) for the thermodynamic calculations, where "one site" translates into the equilibrium composition of all (five) methane-steam-reforming components and "two sites" into considering either CO or CO_2 included as the carbon oxidation product (thus in total four components each).

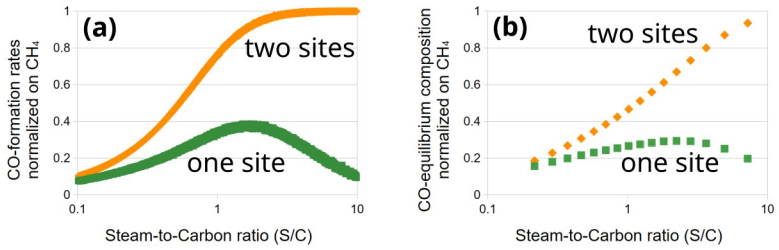

Figure 2. Collection of results and their data trends for (a) simplified Monte-Carlo simulations, and (b) thermodynamic calculations. The concave trend for one-site formation resembles the experimental observation (in Fig. 1(b)).

An asymptotic analysis was performed for the rate equations of the rational kinetic modeling approach at infinitely high $p(CH_4)$ and $p(H_2O)$ partial pressures, which translates to infinitely low and high steam-to-carbon ratios, respectively. For a one-site formation the analysis approached zero for either extreme end of the scale, thus there is/has to be a maximum in between. The two-site mechanism is observed with a continuous increase from zero to one.

All approaches are independent of each other and point into the same direction. The resulting trends of normalized CO formation rates for the one-site mechanisms (Fig. 2) resemble the experimentally observed trend shown in Fig. 1(b). Furthermore, it could be shown, that the CO_2 formation has to be significantly faster than the CO formation.

4. Conclusions

It could be proven through three independent approaches, namely rational kinetic modeling, model-free simplified Monte-Carlo simulations, and thermodynamic calculations, that CO and CO_2 are formed on the same active site during methane steam reforming. The data and mathematical trends of the three approaches prove the plausibility of the products formed through a coupled mechanism as plausible, and reject a two-site mechanism.

The application of normalized product formation rates are presented as information-rich and kinetically sensitive data trends, which proved their suitability to investigate the granularity of Grasselli's site-isolation principle even for the chemically very similar CO and CO_2 formation.

References

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Keywords
Rational kinetics ; Active-site coupling ; Model-free simulation ; Normalized formation rates