

Microkinetic Modeling of CO₂ Hydrogenation to Methanol on Perovskite Catalyst Materials

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Highlights

- Catalytic screening and characterization of the copper based perovskite catalyst.
- Selection of the reaction active sites for different reaction routes.
- Development of the multisite microkinetic model based on the DFT calculations

1. Introduction

The process of methanol production from carbon dioxide and hydrogen is industrially very important reaction. Excessive energy can be used to form hydrogen and later convert CO₂ emissions into methanol [1]. For efficient handling of these kinds of processes we need to have accurate model of reaction kinetics. This can be obtained from deeper knowledge about reaction mechanism on the surface of the catalyst. There are large number of empirical models which describes reaction rate of methanol formation for the copper catalyst [2], however models based on the first principles calculations are rare. The quantum chemical calculations, such as DFT, can provide the information about individual reaction steps with reasonable accuracy. However, catalytic structure used in the calculations may not comprehensively describe complex composition of the catalyst. For this reason, we use different experimental and theoretical techniques to create microkinetic model, which closely relates to the studied catalyst.

2. Methods

The perovskite catalyst was tested by different characterization techniques. Catalytic activity was measured at different temperatures, pressures, gas feed compositions and flow rates. All measurements were performed in the parallel reactor system (**Error! Reference source not found.**). The main crystal phases were determined by the Rietveld refinement of XRD patterns. The temperature programmed desorption was used to obtain types and amount of the active sites. Each type of active site was connected to the active site found in the DFT simulations.

Before we used data from different DFT microkinetic studies from the literature, we checked if those studies correlate to empirical findings about the reaction mechanism. Most empirical models are generally based on the rate determining step assumption of the main path of methanol production [2]. It was found, that the formation of methanol is generally limited by the hydrogenation of the adsorbed formate (HCOO*). Reaction rate constants from each DFT study was used to find the slowest reaction which determines the rate of methanol formation.

Microkinetic model with the reaction constants from DFT calculations was used to calculate molar fractions, which were compared with the molar fractions from the catalytic tests. Reaction rate constants from DFT simulations generally contain some error in the range of 0.05 eV for the activation energies in the range of 1eV. For this reason, we used those constants as the initial guesses for the fitting of microkinetic model to experimental data.

3. Results and discussion

Comparison of models shows that DFT microkinetic studies by Huš et al[3], Tang et al[4] and Studt et al[5] successfully predicts rate determining step. Formation of formate, which is the first reaction intermediate after CO₂ adsorption and reaction with adsorbed hydrogen, can be described by different mechanisms– H* reaction with adsorbed CO₂ or with gaseous CO₂. Appropriate reactions rate constant was used for the assembly of the microkinetic model. The model was later used in the simulation of the plug flow reactor (Figure 2). After variation of constants in bounds of predicted error we obtained constants which are ready for the fitting of the microkinetic model with experimental results.

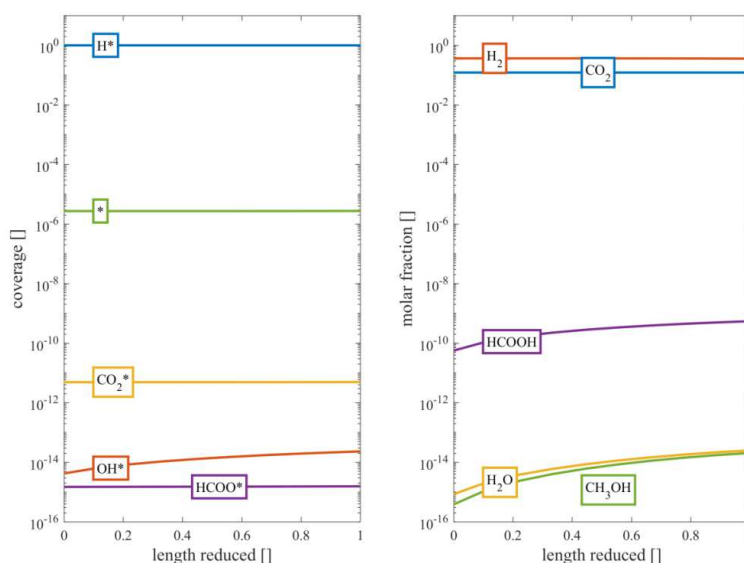


Figure 1: Example of the results from the microkinetic model with the original DFT reaction constants. The catalyst structure and reaction conditions prefer production of formic acid.

4. Conclusions

For an efficient synthesis of methanol we should use the kinetic model which accurately predicts reaction rates on the surface of the catalyst. With the combined use of experimental and theoretical methods, we obtained refined reaction rate constants, which can explain reaction mechanism.

References

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Keywords

Methanol production from CO₂; Mechanistic pathway analysis; Reaction microkinetics modelling; Perovskite catalyst materials