

***AB INITIO* REACTION KINETICS SIMULATIONS OF CATALYTIC METHANOL SYNTHESIS THROUGH CO₂ HYDROGENATION**

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Abstract

An overview of *ab initio* and kinetic multi-scale modeling is given on the example of heterogeneous catalytic synthesis of methanol on various copper-based surfaces. Combining density functional theory (DFT) and kinetic Monte Carlo (kMC) simulations, we study Cu(111) and Cu/metal oxide surfaces (Cu/Zn₃O₃, Cu/Cr₃O₃, Cu/Fe₃O₃, Cu/Mg₃O₃), and propose to study Cu/perovskite substrate surfaces (Cu/CaTiO₃, Cu/SrTiO₃, Cu/BaTiO₃, Cu/PbTiO₃) and a stepped Cu surface. We simulate an extensive reaction scheme for methanol formation, including gas adsorption/desorption, the formate pathway, the RWGS pathway, and surface diffusion. The acquired selectivity, turn-over frequency (TOF), apparent activation energies, selectivities, and reaction rates at industrially-relevant operating conditions (varying the temperature, pressure, and reactant molar ratios) allow us to compare the studied catalyst surfaces in terms of catalytic performance and activity.

Keywords

carbon dioxide reduction, renewable methanol production, copper-based heterogeneous catalysis, kinetic Monte Carlo (KMC), density functional theory (DFT), multi-scale modeling.

Introduction

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Catalytic CO₂ hydrogenation to methanol represents an innovative way of carbon fixation and CO₂ emission decrease. Methanol synthesis at thermal power stations, which use fossil fuels, or from residual steel gases from blast furnace, using hydrogen from electrolysis running on renewable power sources (wind/solar power) or surplus electricity, represents a green fuel solution and a resource for the production of useful chemicals.

The catalysts of choice are Cu-based materials, where the activity and selectivity is improved with secondary metal oxide alloys, dopants, and supports. Here we present a theoretical study on various Cu motifs as catalyst models for methanol synthesis, with DFT and kMC simulations. We confirm that pure copper is not efficient catalyst, but when alloyed with other metals (either as oxides or perovskites), the selectivity and activity are greatly improved. Similarly, the catalytic performance increases when adding the defect (periodic step) to Cu(111) surface.

Methods

Using DFT, we simulate the methanol synthesis via CO₂ hydrogenation reaction scheme (see Figure 1 for the mechanism). The obtained results identify the stable catalyst structures, as well as the energetics for all elementary steps in the pathway, shown in a potential energy surface (PES) diagram (Figure 2). These energies are then used as an input for kMC simulations to study the dynamics of the process, and reveal the selectivity, turnover frequency (TOF), apparent activation barriers, *etc.* on the studied catalysts at industrially-relevant operating conditions (the temperature of 420-600 K, pressure 0.001-100 bar and different reactant ratios).

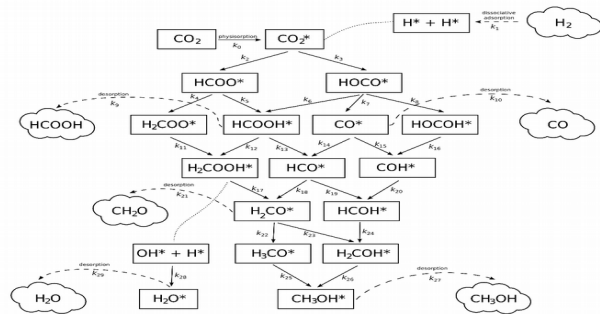


Figure 1: The proposed pathway for methanol synthesis via CO₂ hydrogenation.

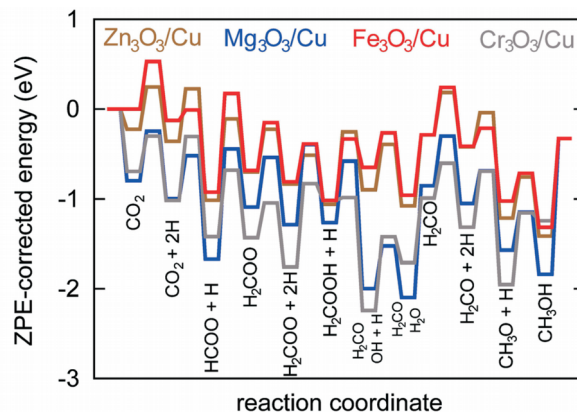


Figure 2: Calculated potential energy surface diagrams for the most probable reaction route on Cu/metal alloy catalysts (Huš et al. 2017).

DFT calculations were performed using Quantum Espresso software and Vienna Ab Initio Simulation package (VASP), while the kMC simulations were done using Zacros (a graph-theoretical kMC package). Details of the calculations are given in Huš et al. (2017), Kopač et al. (2017), Huš et al. (submit.), and Kopač et al. (in prep.).

Performance of Cu and Cu/perovskite catalysts

Bi-functional catalysts improve the selectivity and activity compared to pure Cu catalysts. By comparing four copper-perovskite interfaces, Cu/(Sr/Ba/Ca/Pb)TiO₃, we show that upon a prudent choice of the secondary metal, they can outperform Cu(111) in terms of selectivity, TOF, and apparent activation energy. Figure 3 shows the CH₃OH TOF vs 1/T (Arrhenius plot) with the apparent activation energies provided in the plot legend. Cu/PbTiO₃ shows the best activity among all studied catalysts, while it also shows the best selectivity (similarly as Cu/SrTiO₃).

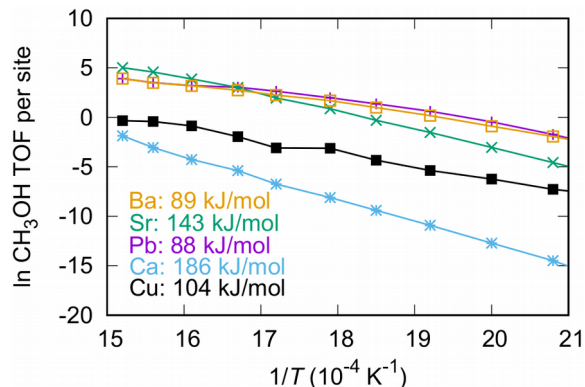


Figure 3: TOF vs 1/T for CH₃OH production, with the fitted apparent activation barrier.

Cu/metal alloy catalysts

Inverse catalyst models with strong metal support interaction are also studied for methanol synthesis. Figure 4 shows the selectivity towards methanol at various temperatures for each Cu/metal alloy catalyst. The selectivity peaks at 97% at low temperatures and drops with increasing temperature. The best catalysts in terms of selectivity are Cu/Cr₃O₃ and Cu/Zn₃O₃, which show the most stable behaviour across the whole temperature and pressure range. Trends in selectivity are in good agreement with experimental data (Huš et al. 2017). Performance of such catalysts is again better than of pure copper-type.

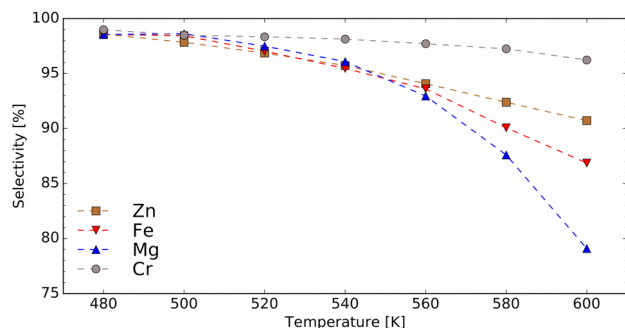


Figure 4: Selectivity vs T for four investigated Cu/(Zn,Fe,Mg,Cr)₃O₃ catalysts (Huš et al. 2017).

Sensitivity analysis

The effect of parameter sensitivity, in particular the elementary reaction step activation energy, is also studied. Results of kMC simulations are altered when perturbing the DFT-obtained Gibbs energies on the Cu(111) surface (Kopač et al. 2017). Even slight perturbation of the activation energies ($\pm 1\%$ of their values, normally distributed) can lead to 12% standard deviation in selectivity, and 40% standard deviation in TOF. The results are shown in Figure 5. This study serves as a proof of strong dependence of results on small differences in *ab initio* data and underscores the need for well converged and consistent results.

Conclusions

By studying various copper interfaces for catalytic methanol synthesis via CO₂ hydrogenation, we demonstrate that theoretical examination can often be paralleled with experimental results. We confirm that the pure Cu(111) surface exhibits low selectivity (especially at low pressures) and poor activity (low TOF) for methanol synthesis. However, on more complex Cu-based interfaces,

such as Cu/metal oxide or Cu/perovskite, which are often used in industry, the catalytic performance is strongly improved.

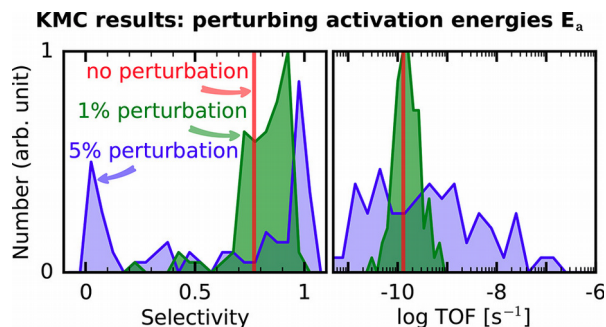


Figure 5: Distributions of selectivity and TOF when perturbing the activation energy by $\pm 1\%$ (green) and $\pm 5\%$ (blue) (Kopač et al. 2017).

The next step is to shift from electronic effects study to geometrical effect study, focusing on Cu defects (steps), Cu adatom, and Cu nanoparticles structures. We will concentrate on details, particularly on the surface geometry effects and the effects of finite surfaces.

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