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First-principles-based kinetic Monte Carlo simulations in heterogeneous catalysis: Application to water-gas shift reaction with several catalysts

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Heterogeneous catalysis employing solid catalysts for gas reactions has a huge impact in several applications in metallurgical and chemical industries. More than 90% of the chemical and energy industries utilize this type of catalysts. A better understanding of its kinetics aspects can help to improve the reactor working conditions and the type of catalysts. Heterogeneous catalytic reactions are complex reactions, which involve frequently a large list of several elementary surface processes, where one or several mechanisms can be competing in both main and side reactions. Mean-field microkinetic modelling and kinetic Monte Carlo (kMC) simulations [1,2] based on first-principles electronic structure calculations (i.e., Density Functional Theory) are two powerful and popular tools used currently in this area. We will present the assumptions, advantages and drawbacks of kMC method along with some practical guidelines to be applied for computational heterogeneous catalysis studies.

We will provide worked out examples mainly based on water-gas shift reaction (WGSR: $CO + H_2O \rightarrow CO_2 + H_2$) over Cu(111) [3], Cu(321) [4] and Au/MoC [5] catalyst. For WGSR on Cu(111) we observe that the COOH-mediated associative mechanism with assisted dehydrogenation through OH plays the main role for this reaction, being the water dissociation the main rate-limiting step. For WGSR on Cu(321) some interesting differences were revealed. First, two competitive mechanisms (redox and associative) were observed with different extension, being the CO_2 formation the main rate-limiting step. Second, the catalytic activity of Cu(321) was lower than Cu(111) surface (Fig. 1), which shows that stepped surfaces stepped surfaces do not necessarily have an overall larger catalytic activity. For the WGSR with bifunctional Au/MoC catalyst we studied different regions of the model catalyst (i.e., the bare MoC region, the Au region, and the Au-MoC interface). Hereby, we unravel the origin of the experimentally observed increased activity at low Au coverage, where a cooperative work between the different regions of the catalyst emerges as the clue for the experimentally observed increase in TOF.

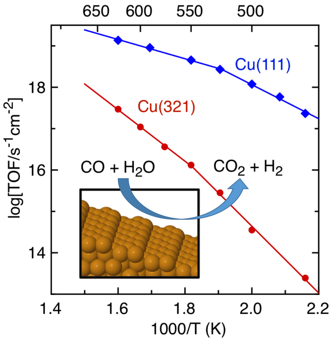

Figure1. Arrhenius plot of the WGSR on Cu(321) and on Cu(111) within the temperature range 463 – 625 K. Partial pressures of 26 and 10 Torr were used for CO and H_2O, respectively.

References
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