

Atomistic understanding catalytic reactions from first principles calculations

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Advancing green transition and fighting climate change require new chemistry, the development of novel catalytic materials, and close interplay between experiments and calculations. Today various computational methods are extensively used to understand the properties of catalytic materials and the influence of a reaction environment on surface-catalyzed reactions. In this presentation, I will discuss a few examples, where we have employed density functional theory calculations alone or together with a microkinetic analysis to understand the atomistic details of catalytic reactions and potential impact on catalyst development.

Single atom catalysts form an interesting class of materials, which has shown that miniaturization may imply new phenomena like dynamic charge transfer between isolated metal atoms and a host oxide, difficult to verify experimentally. Employing the integrated DFT-microkinetic approach, we have explored CO oxidation on Pt₁/CeO₂ [1]. The left panel of Fig.1 shows turn-over frequency for CO oxidation at experimentally relevant reactions conditions. Our results agree with experimentally available kinetic data in the literature and demonstrate that turn-over frequency depends on the presence or absence of polarons. Computational findings highlight that CO oxidation activity on Pt₁/CeO₂ is tunable via the electronic properties of the oxide support and provides an alternative approach for modifying the performance of the low-temperature oxidations in single-atom catalysts.

Single metal atom-based acid modifiers can also be used to tune acid-base properties of metal catalysts. The competitive glycerol conversion to 1,2 propanediol and 1,3 propanediol was explored with the DFT calculations [2]. The thermodynamic and kinetic analysis of glycerol dehydration on the bare and ReOH-acid modified Rh surfaces show that C-H bond breaking is followed by the C-OH bond cleavage, and the experimentally observed preference towards 1,2 propanediol is related to highly favorable secondary C-H cleavage. DFT results demonstrate that while ReOH reduces the barrier for a C-OH bond breaking step, 1,2 propanediol production is still favored, see Fig.1 right panel. Stronger acid with lower H binding energy could reverse selectivity to desired 1,3 propanediol. Overall, we find that the atomic-level understanding of interplay between acid, metal, and studied reaction chemistry is needed to guide development efforts on acid catalysis.

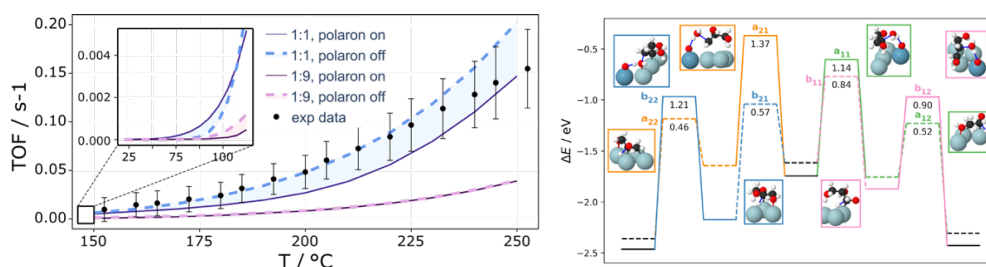


Fig. 1. Left: Steady state turn-over frequency as a function of temperature at 1 atm pressure and 1:1 CO:O₂ ratio. Right: Potential energy surface for glycerol dehydration on ReOH-Rh(111).

[1] M.M. Kauppinen, N. Daelman, N. Lopez, and K. Honkala Journal of Catalysis **423**, 26 (2023)

[2] V. Korpelin, G. Sahoo, R. Ikonen and K. Honkala Journal of Catalysis **422**, 12 (2023)