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Models and Opportunities in Plasma-Catalytic Transformations

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Heterogeneous catalysis is essential to industrial chemical processes, from those that transform petroleum into fuels and chemicals to those, like the Haber Bosch process, that create fertilizers to feed the planet. The first heterogeneous catalysts were discovered empirically and improved through Edisonian experimentation. Within the last twenty years or so, however, the field has been transformed through the advent of catalysis science, which, using high fidelity synthesis and characterization coupled with molecular-level models, is able to understand and predict catalytic function.

Catalysis science has revealed that the most common heterogeneous catalysts, which include the later members of the d block transition metals, present a tableau of reactivity limited by intrinsic correlations between the various reaction steps that make up a surface catalytic reaction. These correlations rationalize the often observed Sabatier, or volcano, behavior in intrinsic catalytic function vs a single descriptor of a catalytic material. These correlations, coupled with the limitations imposed by thermodynamics, significantly limit the ability to optimize catalytic transforms. As an example, the synthesis of NH_3 from N_2 and H_2 must be carried out extreme conditions to achieve reasonable yields at reasonable rates.

Coupling of heterogeneous catalysts with non-thermal plasmas offers the potential to break these constraints.[1] While empirical evidence suggests that such combinations can enhance apparent catalytic function relative to plasmas or catalysts alone, the absence of basic models to rationalize this behavior and guide material and plasma selection has limited progress. In this talk I will describe our recent work to bridge this gap. As an example, Fig. 1 compares modeled thermal NH_3 synthesis turnover rates against rates under plasma-induced N_2 vibrationally

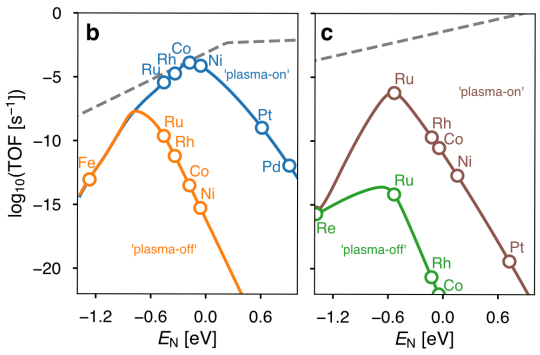

Fig. 1. Microkinetic model results for NH_3 synthesis from N_2 and H_2 over metal facets (left) and steps (right) at ambient conditions ("plasma off") and with N2 vibrationally excited ("plasma on").

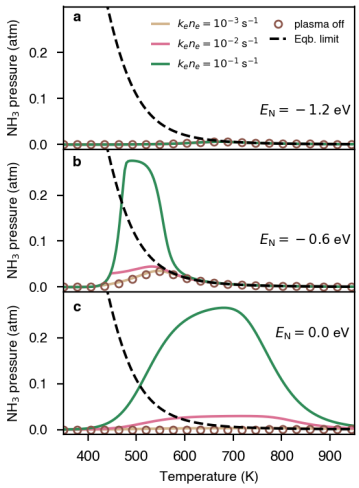

Fig. 2. Predicted NH_3 yields from N_2 and H_2 vs bulk temperature on three different materials and at three rates of plasma excitation of N_2 vibrations.

heating.[2] Evident is both the prominent enhancement in rates and the shift in optimal material. Predictions are in quality correspondence with observation.

A corollary to the non-equilibrium energy distribution in plasmas is the potential to realize product yields beyond those possible within a thermal regime. Fig. 2 presents predicted NH_3 yields under the same assumptions as Fig. 1 in a well-mixed reactor. With appropriate combination of catalytic material with a plasma energy deposition rate matched to the reactor, conversions are predicted to exceed those of the thermal reaction.

These model results illustrate potential opportunities to be realized through appropriate coupling of excited molecules with catalytic surfaces. Realizing these opportunities demands models and experiments coupled at a higher level of fidelity, incorporating both plasma-phase and surface chemistry at realistic conditions. We have recently extended this microkinetic modeling approach to N_2 oxidation to NO, incorporating both the plasma-phase Zeldovich chemistry with surface chemistry through series-coupled reactors. Results the interplay between both phases that limits regimes in which plasma and catalyst couple productively.

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References

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