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Electrochemical reduction of NO on Pt(100): a combined DFT and KMC study

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Electrocatalytic denitrification is a promising technology for the removal of NO_x species in groundwater. However, a lack of understanding of molecular reaction pathways that control the overpotential and product distribution have limited the advancement of NO chemistry to the same level of well-understood electrocatalytic processes like oxygen reduction reaction. Nitrate and nitrite electroreduction can produce a variety of different products but adsorbed NO has been considered a selectivity-determining species in the process. Experimentally, NO electroreduction has been studied under a variety of reaction conditions and the reaction demonstrates a rich chemistry with several possible reaction steps and intermediates. Thermodynamically, N₂ is the most favorable product but other products such as NH₄⁺ and N₂O are usually observed. Cyclic voltammetry experiments on Pt(100) demonstrate that NH₄⁺ is the only product in acid electrolyte and the onset potential of the reaction is 0.25 VSHE. Furthermore, NO reduction was proposed to proceed via the HNO intermediate together with the facile formation of ammonia after chemical N-O dissociation.

The DFT calculations were performed with the VASP code to address the thermodynamic and kinetic aspects for various possible elementary steps of NO electrochemical conversion to ammonia, nitrogen gas, and nitrous oxide both at low and saturated NO coverage on Pt(100). DFT results suggest that at low coverage a HNO intermediate dominates, while at experimentally observed NO coverages there is a significant thermodynamic and kinetic competition between two pathways proceeding either via NOH or HNO intermediates. Our kMC program employs the first reaction algorithm together with periodic boundary conditions, and takes the needed input parameters, which are reaction barriers and equilibrium constants for included elementary steps, directly from DFT calculations. Furthermore, we permit the formation of other products than NH₄⁺ in kMC but they were not observed during simulations. The potential-dependent kinetic Monte Carlo calculations were performed to simulate NO stripping experiments. We demonstrate how these profiles change as a function of the initial NO coverage dosed on Pt(100) and the calculated electrochemical NO stripping curve agrees well the measured one. Furthermore, simulations provide a mechanistic interpretation for observed peaks: high voltage results from NOH formation and conversion in simulations and the second peak originates from the coverage-dependent activation energy for NOH formation. Based on the large number of analyzed reaction pathways from kMC simulations and the calculated Tafel slope, we are able to identify a reaction mechanism, which consists of two consecutive proton electron steps which takes place after the initial

NO adsorption. Along the most probable reaction pathway, NOH protonates to HNOH, which undergoes a combined dissociation and protonation step forming NH and water. Finally, NH transfers to NH₃, which spontaneously forms NH₄⁺.

To conclude, the synergic DFT+kMC strategy provides detailed microscopic information to future development of denitrification technologies and it also offers a template to investigate and analyze other electrochemical transformations.

The reduction of NO has been identified as a key step in the electrochemical denitrification of nitrites and nitrates. We combine density functional theory calculations and kinetic Monte Carlo simulations to study the reduction reaction on Pt(100). This approach describes the effects of coverage-dependent adsorbate-adsorbate interaction, reaction thermodynamics, water-mediated protonation kinetics, and transient potential sweeps on product rates and selectivities. We are able to predict electrochemical NO stripping curves in nice agreement with experiments and provide an elementary mechanistic interpretation of observed current peaks. The combined methodology provides a full reaction profile and reveals the sensitive balance between thermodynamics and kinetics in NO reduction. However, the computational approach is sufficiently general to be applicable to other electrocatalytic processes on metal catalysts that are technologically and environmentally important.

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