Unifying electric field-mediated heterogeneous catalysis

by
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Electric fields in the catalytic active sites of enzymes, originating from charged amino acid residues in the protein scaffold, have been invoked as a key factor governing the extraordinary activities and selectivities of enzymes for catalyzing chemical transformations. Models and experimental measurements of these electric fields have been utilized to quantitatively rationalize reaction kinetics, understand active-site solvent structures, and design better enzymatic catalysts. Despite the success of using electric fields to study enzymatic systems, this electric field approach has not yet been widely used in studying liquid-phase heterogeneous catalysis, largely due to the difficulty in quantifying electric fields at active sites as well as challenges in designing heterogeneous catalysts with precise control of electric fields. In this thesis, we extend this electric field methodology into the realm of liquid-phase heterogeneous catalysis, both to accelerate heterogeneously catalyzed reactions and to understand solvent structures in catalyst pores.

First, we design an electrochemical basket reactor system to apply an electric field to the surface of Brønsted-acidic carbon nanotube catalysts via an applied potential, and we examine the effect of electric field on acid-catalyzed alcohol dehydration rates of 1-methylcyclopentanol to 1-methylcyclopentene in an electrolyte-containing acetonitrile solution. We observe that the reaction rate is remarkably sensitive to electric field, with reaction rates increasing ~100,000-fold over 0.5 V of applied potential, and we propose a model that explains the rate-potential scaling and dependence on ionic strength. In further support of our model, we experimentally observe a theorized “isokinetic potential” where the reaction rate is independent of ionic strength. Through reactive base titrations, we quantify the density of active sites and demonstrate that the rate promotion is due to increasing the site activity, rather than increasing the number of active sites.

Next, we demonstrate that this electric field effect does not require a special electrochemistry setup to manifest and can also be observed when a catalyst particle is simply touching another electrically conductive material. Through a carefully designed suite of experimental controls, we show that the intrinsic activity of acidic carbon nanotubes changes by an order of magnitude when they are in electrical contact with inert, thermally reduced carbon nanotubes, via the same mechanism that we previously observed when rates changed with an applied potential.

We then shift gears to examine solvent structures in confined zeolite pores using vibrational Stark spectroscopy, an infrared spectroscopic technique developed for measuring electric fields at enzyme active sites. Using Ti-Beta zeolite as a test case, we develop a method that quantifies the electric field experienced by a probe molecule at the Ti active sites in solvent-filled pores. We find that the electric field varies with solvent identity and also with zeolite hydrophobicity, indicating that the secondary sphere interactions of the solvent with the zeolite framework result in distinct solvent structures in the hydrophobic and hydrophilic zeolites. Furthermore, we observe that this method identifies distinct electric fields between hydrophobic and hydrophilic zeolites even in the absence of solvent, offering this technique as a method for distinguishing types of active site environments.

Finaly, we apply this approach to examine hydrogen-bonding interactions inside Ti-Beta zeolite pores when filled with secondary alcohol solvents, motivated by previous work which observed that intraporous solvent structures varied significantly with changes in zeolite hydrophobicity. Using an infrared liquid flow cell that we designed to achieve record signal-to-noise and in-pore selectivity, we find that hydrogen-bonding interactions between a probe molecule and solvent are different between the ensemble-average in-pore environment and at the zeolite active site, revealing that there may be a discrepancy between typically observed intraporous bulk solvent structures invoked to explain kinetic phenomena and the kinetically relevant active-site solvent structures.

Collectively, this thesis demonstrates that techniques and models of electric field-induced catalysis previously applied to understand biological systems can also be utilized to improve catalyst activity and understand the structure of solvent under confinement in liquid-phase heterogeneous catalysis. We hope that future work will expand on our methods, applying them to further investigate the effects of applied electric field on reactivity and utilizing vibrational probes to aid in understanding local structure at catalyst active sites.

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