

Spotlights on Recent JACS Publications

■ NOT A DROP IN THE BUCKET: WATER'S ROLE IN HETEROGENEOUS CATALYSIS

The presence of even a few layers of water on the surface of a heterogeneous catalyst can have a profound effect on its activity, boosting or slowing reaction rates sometimes by orders of magnitude. However, achieving atomic-level insight into chemical reactions in wet reaction conditions has been a long-standing challenge in heterogeneous catalysis and electrocatalysis due to the complexity of the system. Matteo Farnesi Camellone, Stefano Fabris, and co-workers gain insight on this phenomenon using computer simulations involving CeO₂-supported platinum nanoparticles, key heterogeneous catalysts in fuel production and purification, environmental chemistry, and the chemical industry (DOI: [10.1021/jacs.6b03446](https://doi.org/10.1021/jacs.6b03446)).

Their results suggest that when water contacts the catalytic surface, a fraction of it quickly dissociates into hydroxide ions and protons. While the protons diffuse across the surface, the hydroxide ions remain partially tethered to the surface through electrostatic interactions, clustering around the platinum nanoparticles. There, these anions drive a substantial charge transfer across the metal/oxide surface, and this movement of electrons significantly influences the platinum nanoparticles' interaction with the oxide support and the activity of the catalyst as a whole. The authors note that these findings highlight the complex dynamics of wet conditions in heterogeneous catalysis and their effects on reaction mechanisms and rates.

Christen Brownlee

■ WASTE-FREE SHORTCUTS TO ANILINE AND PHENOL

Aniline and phenol are two essential fine chemicals in the manufacture of agrochemicals, pharmaceuticals, dyes and pigments, and other industrial chemicals. Their production often requires multi-step energy-consuming procedures or severe reaction conditions, generating large amounts of toxic wastes. Searches for more efficient and environmentally benign production alternatives are extensive, but current processes remain far from ideal. Now, Li-Zhu Wu, Chen-Ho Tung, and colleagues report a new strategy that enables one-step amination of benzene to aniline with ammonia and one-step hydroxylation of benzene to phenol with water in excellent yields and high selectivity (DOI: [10.1021/jacs.6b05498](https://doi.org/10.1021/jacs.6b05498)).

The reaction consists of two redox cycles: photocatalytic electron-transfer oxidation of benzene and the hydrogen-evolving system using cobalt catalysis. The cross-coupling hydrogen-evolution transformation proceeds at ambient conditions without any additional reagent, and therefore it yields no byproduct except for hydrogen gas. This study presents a highly feasible and atom-efficient pathway for aromatic C–H functionalization. With potential to be adopted for industrial production, the method is not only green but also substantially value-adding with hydrogen collected as a clean fuel.

Xin Su, Ph.D.

■ THE LESS STUDIED SIDE OF NITROGENASE

Nitrogenase is the central enzyme that catalyzes nitrogen fixation, the reduction of nitrogen to ammonia. Humans mimic the reaction to make fertilizer, but the process is highly energy-intensive, and chemists aim to identify milder conditions under which nitrogenase produces ammonia. So far, nearly all nitrogenase research has focused on the FeMoco cluster where the nitrogen reduction takes place. Another cluster in the enzyme, the P-cluster, which is also critical in the reaction, has received little attention. F. Akif Tezcan and colleagues shed light on how the P-cluster mediates electron transfer to FeMoco in the nitrogenase catalytic pathway (DOI: [10.1021/jacs.6b06783](https://doi.org/10.1021/jacs.6b06783)).

The researchers find that the P-cluster has a set of O- and N-based ligands capable of controlling the oxidation state and the reduction potential of the cluster in a switchable fashion, allowing it to gate electron flow to the FeMoco cluster. This result answers vital questions about how electrons are directed to the FeMoco cluster within nitrogenase to support the challenging and energy-demanding nitrogen reduction reaction. It also highlights how enzymes can use clusters to introduce electron gating in multi-electron reactions.

■ SINGLE-MOLECULE OBSERVATION OF A MECHANICALLY ACTIVATED REACTION SEQUENCE

The field of mechanochemistry unites chemical and mechanical phenomena on the molecular scale. Researchers have looked to covalent polymer mechanochemistry for its potential to unlock otherwise inaccessible chemical reactivity, to trap transition states and intermediates for reaction dynamics studies, and to study the force required to perform chemical transformations, such as ring-opening reactions. Now, Stephen Craig and colleagues report the single-molecule observation of an unexpected solvent-dependent, two-stage reaction sequence that is triggered by mechanical force (DOI: [10.1021/jacs.6b06452](https://doi.org/10.1021/jacs.6b06452)).

In a previous study, the researchers used single-molecule force spectroscopy to quantify the force required to open *cis*-gem-difluorocyclopropane in methyl benzoate solvent (*Nature Chemistry*, DOI: [10.1038/nchem.2185](https://doi.org/10.1038/nchem.2185)). Here, the team performs the same study in a different solvent—toluene—and finds several surprising differences in the reaction path and outcomes. Most notably, they observe the rare, mechanically induced *cis*-to-*trans* isomerization. The work provides a glimpse at the relationship between the mechanochemical reaction outcomes and the underlying principles of physical organic reactivity. These results also spark the concept of multi-step, in situ formation and activation of a new mechanophore that may be useful for covalent polymer mechanochemistry applications, such as stress-sensing, catalysis, and small-molecule release.

Christine Herman, Ph.D.

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