JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Spotlights on Recent *JACS* Publications

HYDROGENATION PREFERENCE DOMINATED BY CATALYST INTERFACE

Competitive hydrogenation of benzene over heterogeneous catalysts usually favors hydrogenation of the more electron rich aromatic. By studying the arene hydrogenation activity of a series of organozirconium complexes chemisorbed on acidic oxides, Massimiliano Delferro, Tobin J. Marks, and their colleagues reveal the key factors accounting for the selective hydrogenation of benzene by these catalysts (DOI: 10.1021/jacs.5b03254). Often, heterogeneous catalyst performance significantly depends on its textural structure and surface morphology, among other factors. This principle is especially true for the single-site supported catalysts in this study, where the catalytic activity is enhanced by an electrostatic interaction between the Brønsted acidic oxide surface and the metal center.

In combination with catalytic data, several advanced spectroscopic techniques show that increased metal−surface distance generally leads to more active catalysts with higher selectivity toward benzene hydrogenation, an observation further supported by density functional theory predictions. These results help guide the development of highly selective benzene hydrogenation catalysts, providing efficient methods to remove carcinogenic benzene from gasoline. Meanwhile, these findings contribute useful insights for understanding the mechanisms of single-site supported catalysts, and they may also be extended to an even broader range of catalytic systems.

Xin Su, Ph.D.

UNRAVELING THE NEFARIOUS PROTEIN CLUMPS OF ALZHEIMER'S DISEASE

The fibrils of amyloid beta (Aβ) protein in the brains of people with Alzheimer's disease are signatures of the disease, but evidence suggests that the true toxic agents may be intermediate aggregates that form before the fibrils. To develop Alzheimer's disease medications, researchers must identify and characterize these toxic agents. However, structural details are scarce, due to the intermediates' notorious instability and heterogeneity. A team of researchers led by Yoshitaka Ishii use solid-state NMR spectroscopy to analyze one suspicious Aβ intermediate, amylospheroid (ASPD) (DOI: 10.1021/jacs.5b03373).

Previous research has found that the concentration of ASPD, a spherical cluster of misfolded Aβ protein, in the brains of people with Alzheimer's disease correlates with severity of disease. Using antibodies and transmission electron microscopy, Ishii's team establishes that a lab-derived version of ASPD matches ASPD from the brains of people with Alzheimer's disease. They then ^{13}C-label specific amino acids within the Aβ protein and perform a series of solid-state NMR experiments to evaluate the structure of synthetic ASPD. The Aβ protein in synthetic ASPD appears to exist as a single conformation formed of parallel beta sheets. Such site-specific structural characterizations are a first for amyloid intermediates directly associated with Alzheimer's, and may accelerate the development of treatments for this disease.

Erika Gebel Berg, Ph.D.

RESEARCHERS BUILD FUNCTIONAL APTAMERS USING SIX-BASE ALPHABET

The genetic alphabet comprises just four letters. This alphabet is enough to encode life but represents a limitation for the development of aptamers, oligonucleotide sequences that can bind to specific target molecules, often with associated biological activity. An expanded alphabet should allow a greater range of aptamer designs, and now Weihong Tan, Steven Benner, Zhen Huang, and their colleagues demonstrate the validity of that prediction (DOI: 10.1021/jacs.5b02251).

The team builds a randomized aptamer library from the four standard DNA nucleotides plus Z and P, additional nucleotides that the authors have recently shown can adopt a traditional Watson−Crick pairing geometry (10.1021/jacs.5b03482). The team subjects their library to multiple rounds of laboratory *in vitro* evolution (LIVE) to identify molecules capable of specifically binding HepG2 cancer cells. After 13 cycles of selection, mutagenesis, and PCR amplification (indicating the non-natural bases can be copied by a DNA polymerase), the team isolates several Z:P-containing aptamers with nanomolar affinity, stronger than aptamers lacking Z:P pairs.

The Z:P bases are critical to these aptamers' functionality, as replacing them with traditional nucleotides sharply reduces their affinity. "These data provide direct evidence, the first for any artificially expanded genetic information system, that a LIVE experiment can explore substantial fractions of sequence space in a six letter genetic system," the authors write.

Jeffrey M. Perkel

FOR CLEAN COLLOIDAL NANOCRYSTALS, THINK SAUNA

To build nanocrystals of precise size, shape, and composition, researchers often use organic ligands, which attach to and stabilize the nanocrystals as they grow. The downside of such colloidal synthesis is that the stabilizing molecules often remain bound to the crystal long after their work is done. For many nanoparticle applications, and catalysis in particular, exposed, clean nanoparticle surfaces are essential.

Christopher Murray and his team present a simple method to remove organic ligands from nanocrystal surfaces, without compromising the nanocrystals themselves (DOI: 10.1021/jacs.5b03333). The researchers show that a quick pop into a furnace at high temperature removes the ligands in air. The treatment activates the nanocrystals for catalytic reactions but does not provide enough time for large-scale atomic movements to change the nanocrystals' shape or size.

Highly uniform catalysts are important for investigating fundamental structure−behavior relationships. Even small amounts of ligands left on the nanomaterials can be very detrimental for catalysis. Previously, researchers had to choose between high uniformity and high activity in colloidal nanoparticles. This work provides a means to achieve both.

Jenny Morber, Ph.D.

Published: June 3, 2015

DOI: 10.1021/jacs.5b05438
J. Am. Chem. Soc. 2015, 137, 6725−6725