הטכניון - מכון טכנולוגי לישראל

TECHNION - ISRAEL INSTITUTE OF TECHNOLOGY

הפקולטה להנדסה כימית
ע״ש וולפסון
The Wolfson Department of Chemical Engineering

Wolfson Department of Chemical Engineering Seminar

Monday, June 20th, 2022 at 13:30

Room #6

Molecular design of solid catalysts

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This colloquium will be divided into two applications parts, dealing with synthesis of supported molecular catalysts and solid catalysts for photoprotection. In the first of these areas, the relevant background is 3-D confinement of active sites, which has historically been used to achieve large rate accelerations in reactions via preferential solvation of transition states. However, while powerful, 3-D confinement is limited to sufficiently small reactants/products that can penetrate the microporous confines of zeolites. This is useful for molecules that are typically the size of a benzene ring (e.g., for a medium-pore zeolite). We highlight recent results from our research group, which quantify the effect of partial confinement on the external surface of a solid catalyst, in pockets there. Using epoxidation of olefins with organic hydroperoxide oxidants as a relevant probe reaction, we demonstrate the synthesis of catalysts that are up to 6-fold more active (on an active-site basis) compared with similar but unconfined active sites in industrial catalysts. [1,2,3] This demonstration provides a blueprint for enhancing reactivity on surfaces by synthetically controlling mechanical features of catalyst active-site environments.

In the second of these areas, reactive oxygen species (ROS) are associated with several human health pathologies and are invoked in the degradation of natural ecosystems as well as building materials that are used in modern infrastructure (e.g., paints and coatings, polymers, etc). Natural antioxidants such as vitamin E function as stoichiometric reductants (i.e. reaction with ROS synthesizes rancid oils). While enzymes such as superoxide dismutase working in tandem with catalase decompose decompose ROS to H_2O and O_2 through H_2O_2 as an intermediate, these enzymes are fragile and costly. Other non-stoichiometric commercial antioxidants that degrade ROS include hindered amine light stabilizers (HALS). Here, we demonstrate that cerium carbonate acts as a degradation catalyst for photogenerated ROS, and describe the performance and characterization of this new catalyst using X-ray photoelectron spectroscopy, and in comparison with HALS and stoichiometric reductants. Our results demonstrate catalytic antioxidant activity of cerium carbonate when dispersed in polymethylmethacrylate polymer. FTIR data demonstrate that a dispersion of 2 wt. % cerium carbonate within the polymer essentially stops degradation by photogenerated ROS, which otherwise cause oxidation of the polymer backbone, in the control polymer lacking cerium carbonate. Experiments with methylene blue dye in aqueous solution demonstrate that cerium carbonate decreases the rate of ROS degradation of dye, in the presence of UV irradiation and air by 16 fold. These effects become even more pronounced (over 600

fold decrease in rate of ROS dye degradation) when cerium carbonate is paired with a photoactive metal oxide. The mechanism involved in this latter case crudely mimics the enzyme tandem sequence referred to above.

[1] C. Schöttle, E. Guan, A. Okrut, N. A. Grosso-Giordano, A. Palermo, A. Solovyov, B. C. Gates, A. Katz*, Journal of the American Chemical Society, J. Am. Chem. Soc. **2019**, 141, 4010-4015.

[2] N. A. Grosso-Giordano, C. Schroeder, A. Okrut, A. Solovyov, C. Schottle, W. Chasse, N. Marinkoyic, H. Koller, S. I. Zones, A. Katz, Journal of the American Chemical Society **2018**, 140, 4956-4960.

[3] N. A. Grosso-Giordano, A. S. Hoffman, A. Boubnov, D. W. Small, S. R. Bare, S. I. Zones, A. Katz, Journal of the American Chemical Society **2019**, 141, 7090-7106.

[4] M. K. Mishra, J. Callejas, M. Pacholski, J. Ciston, A. Okrut, A. Van Dyk, D. Barton, J. C. Bohling, A. Katz, ACS Applied Nano Materials **2021**, 4, 11, 11590-11600.