ACS Catalysis
EDITORIAL
pubs.acs.org/acscatalysis

Highlights of Biocatalysis and Biomimetic Catalysis

Biocatalysis generally refers to the use of enzymes or whole cells as catalysts for synthetic chemistry. Because of its connection with reduced energy consumption, greenhouse gas emissions, and waste generation, biocatalysis is increasingly used in pharmaceutical, chemical, food, energy, and agricultural industries. Compared to chemical catalysis, one of the biggest advantages of biocatalysis is that biocatalysts are often highly selective (regio-, diastereo-, enantio-, or chemo-), which can circumvent the need for many blocking and deblocking steps that are required in asymmetrical synthesis. In addition, biocatalysts can operate at mild and environmental-friendly conditions, which may significantly reduce energy input and waste generation. This special issue of *ACS Catalysis* on biocatalysis and biomimetic catalysis contains 15 articles which can be broadly grouped into three categories, including developing new tools for biocatalysis, exploring biocatalysis for practical applications, and learning from biocatalysis—biomimetic catalysis.

■ DEVELOPING NEW TOOLS FOR BIOCATALYSIS

Thanks to recent advances in functional genomics and bioinformatics, numerous enzymes capable of catalyzing a wide variety of biological reactions have been identified. For example, Dadashipour and Asano contributed a comprehensive review focusing the enzymology, discovery, and engineering of hydroxynitrile lyases capable of producing cyanohydrins. Cyanohydrins are key intermediates in the synthesis of valuable pharmaceuticals and agrochemicals. Wackett and co-workers used bioinformatics to identify a novel enzyme that can hydrolyze biuret, an intermediate in the metabolism of the herbicide atrazine in environmental bacteria, and carried out detailed biochemical characterization. Stewart and co-workers reported the screening of alkene reductases for α/β-unsaturated carbonyl compounds toward new substrates, Baylis—Hillman adducts whose reduction products are useful chiral synthons. Berglund and co-workers were particularly interested in studying and engineering ω- transaminases, enzymes capable of interconverting ketones and amines, for the production of pharmaceutically important chiral amines. To this end, they reported an efficient method to quantify the active enzyme fraction in a given ω- transaminase preparation.

There is no doubt that more and more enzymes will continue to be discovered. However, naturally occurring biocatalysts are often not optimal for many specific industrial applications, because of low stability and activity. Moreover, naturally occurring biocatalysts may not catalyze the reaction with the desired non-natural substrates or produce the desired products. Therefore, protein engineering is often required to address these limitations. Quin and Schmidt-Dannert provided a comprehensive and systematic review on the various strategies used for engineering naturally occurring enzymes, while Zhang proposed the concept of cell-free synthetic pathway biotransformation (SyPaB) for biocatalysis by in vitro assembly of stable enzymes and (biomimetic) coenzymes. In parallel to naturally occurring enzymes, designing artificial enzymes also represents an attractive strategy for discovery and engineering of novel biocatalysts. Lu and co-workers reported systematic investigations of the effect of different covalent attachment or anchoring positions on reactivity and selectivity of the artificial cofactor MnSalen-containing myoglobin enzymes.

■ EXPLORING BIOCATALYSIS FOR PRACTICAL APPLICATIONS

As mentioned above, enzymes have been increasingly explored for practical applications in various industries. In his comprehensive review, Patel described many examples and case studies on the use of enzymes for the synthesis of single enantiomers of key intermediates used in the development of pharmaceuticals. In contrast, Kelly and co-workers outlined an interesting new strategy for engineering a CO_2 fixation pathway in a hyperthermophilic host with the goal of using hydrogen from a renewable resource to produce biofuels or value-added chemicals. Mukherjee and Martinez reported the screening and application of commercial lipases as biocatalysts for the efficient synthesis of a wide range of optically active precursors of β-substituted-γ-amino acids. In a related work, Turner and co-workers described the use of a hydantoinase to prepare enantiomerically pure β-amino acids from a range of racemic 6-substituted dihydrouracils, which provides a new and practical method for the preparation of enantiomerically pure β-amino acids.

In addition to synthesizing small molecules, enzymes can also be used to prepare polymers, as demonstrated by Gross and co-workers in their use of proteases to catalyze oligomerization of L-lysine ethyl ester in aqueous solution. Finally, as reported by Cooney and co-workers, enzymes have also been used in the design of a hybrid biofuel cell in which combination of enzymatic and microbial bioelectrocatalysis merges the advantages of the two fields in one device.

■ LEARNING FROM BIOCATALYSIS: BIOMIMETIC CATALYSIS

Biomimetic catalysis generally refers to chemical catalysis that mimics certain key features of enzymes. These features include high enzyme—substrate binding affinities, high catalytic turnovers of enzyme-catalyzed reactions, and substantial rate accelerations relative to uncatalyzed reactions. In their review, Levine and Marchetti focused primarily on catalysis using organic macrocycles and polymers, which like enzymes, create a supramolecular environment that differs from the environment of the bulk medium. The relationship of biomimetic catalysts to the newer research area of organocatalysis was also discussed. As an example of biomimetic catalysis, Que and co-workers described the synthesis and characterization of a new iron(II) complex containing a cyclam-type ligand and its application as a catalyst for the oxidation of alkenes with H_2O_2 as the oxidant. This work

Special Issue: Biocatalysis and Biomimetic Catalysis for Sustainability

Published: August 17, 2011

dx.doi.org/10.1021/cs200425r | *ACS Catal.* 2011, 1, 1119–1120

was inspired by the mechanisms of the Rieske dioxygenases that catalyze the *cis*-dihydroxylation of aromatic C═C bonds in the biodegradation of arenes.

Biocatalysis has emerged as a powerful tool for synthetic chemistry. As new tools for enzyme discovery, characterization, and engineering continue to advance, the applications of biocatalysis are likely to increase rapidly. In addition, biocatalysis will be increasingly combined with homogeneous catalysis, heterogeneous catalysis, and electrocatalysis to explore the potential synergy between different forms of catalysis. Fundamental understanding of enzyme catalysis will facilitate the design of more efficient and selective biomimetic catalysts, which in turn improves our understanding of enzyme catalysis. The breadth and depth of knowledge in biocatalysis is undoubtedly still limited when compared to traditional chemical catalysis. However, the expanding biocatalytic toolbox will make it easier for both specialists and nonspecialists to explore biocatalysts for practical applications.

Huimin Zhao*

Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana—Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801, United States

AUTHOR INFORMATION

Corresponding Author

*Phone: (217) 333-2631. Fax: (217) 333-5052. E-mail: zhao5@illinois.edu.

dx.doi.org/10.1021/cs200425r | *ACS Catal.* 2011, 1, 1119–1120