

Eco-Catalysis Leads the Way to Green Synthetic Chemistry

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Editorial

Environmental problems caused by chemical industries, especially in the synthetic chemical processes, have aroused particular concern worldwide. However, our modern life is unimaginable without the myriad products of industrial organic synthesis, for examples, pharmaceuticals, cosmetics, synthetic plastics and fibers. Therefore, the concept of “Environmentally Benign Manufacturing” was appeared to address the dilemma of man-made pollution [1]. In the area of organic chemistry, the movement of developing green chemistry has also challenged chemists to consider the environmental impact of a chemistry process as an integral part of their program. Among them, catalysis is identified the most valuable contributor to improve the efficiency and minimize the use and generation of hazardous substances, which is the vital part of green chemistry.

Considering the environmental advantages of catalyzed processes, the decades have witnessed an explosive and impressive growth in this field with new catalysts and novel methodologies. In general, three concepts of catalysis: 1) bio-catalysis, 2) metal-catalysis, and 3) organocatalysis, were put forward. With respect to biocatalysis just by using natural enzyme and antibody, the advantages are obvious, such as very high chemoselectivity, regioselectivity and enantioselectivity; transformation under mild conditions and working in water as solvent. However, many limitations of biocatalysis have also been voiced: 1) enzymes often feature low reactivity, limited substrate specificity and instability at extreme temperatures and pH conditions. 2) The types of enzymes are limited and the time for developing new enzymes is long. For this reason, “metal catalysis” has been investigated in order to overcome weak points of the enzymes. Organometallics with transition metal-to-carbon bonds play the key role in the catalytic cycles; moreover, the metal center by means of oxidative/reductive cycles, metalcycles and metal-carbenes had showed excellent activity in organic reactions. In combination with well-defined ligands, the transition metal catalysts also achieved very high levels of selectivity. However, transition metal catalysts, especially precise metals possess other drawbacks such as the low moisture tolerance, air-sensitivity, the toxicity and difficulty of the waste disposal. Since the year of 2000, organocatalysis, defined as the catalysis by small organic metal-free compounds, was recognized and the field of organocatalysis experienced explosive progress. To date, thousands of catalysts and a large number of organocatalyzed reactions were reported in the literature [2]. After more than one decade of development, organocatalysis also showed some shortcomings: catalysts have low catalytic activity such as high catalyst loading and long reaction time. The substrates are generally limited to active substrates, such as aldehydes, imines and so on. As can be seen, until now, very rare organocatalytic cases of large-scale production are applied in the industry.

With the “eco-friendly” and “to be as efficient as possible” in mind, the chemistry by using the combination of both metal and organic catalysts are currently explored [3]. In this manner, the synthetically useful level of green process as a priority (eco-catalysis) should be emphasized. As the Nobel laureate Professor Ei-ichi Negishi pointed

out, “organic synthesis must be performed (i) in high yields (Y), (ii) efficiently (E), (iii) selectively (S), (iv) economically (E), and (v) safely (S), namely in Y(ES)² manner” [4]. In fact, Nature also employed some metals but not toxic ones, such as iron-based hemes, chlorophyll and so on, in their biosynthetic pathways. Inspired by Nature, “good and usable” metal elements are incorporated into organocatalysis and biocatalysis to design eco-friendly efficient catalysis, would have the great potential in the future. By studying the interactions between enzymes and/or proteins with substrate molecules, the elegant catalysis by enzymes can be well understood. The great challenge is to figure out these interactions and to engineer these specific interactions. So far, these interactions including ionic interactions, hydrogen bonding, hydrophobic interactions, π -stacking, covalent interactions, and even the metal-generated oxidative/reductive cycles were generally accepted. It can be certain that the existence of unknown interactions need to be discovered, which maybe critically important to design high efficient eco-catalysis (Figure 1).

Rational design and development of high efficient catalysts with an excellent selectivity (chem-, regional- and enantio-selectivity) have

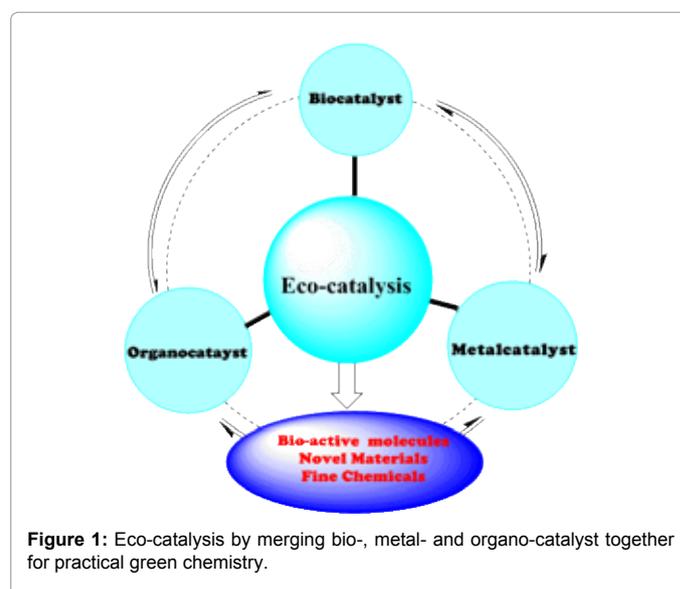


Figure 1: Eco-catalysis by merging bio-, metal- and organo-catalyst together for practical green chemistry.

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always received considerable attention, the ideal catalysts composed of green molecules including or combining with green metal element, which can be recycled, is highly desirable. Today, catalysis in the synthetic chemistry has already been a vital part of our core industrial infrastructure. Being able to create a practical level of eco-catalysis still remained a great challenge for us. Ecologically friendly procedures by high efficient catalysis (named eco-catalysis) are expected to be created to benefit the mankind. To this end, "Environmentally Benign Production" could be realized for chemical manufacturing; in doing so, we can achieve economic growth while protecting the environment.

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