



Digest paper

Recent developments on artificial switchable catalysis

Joyanta Choudhury



Organometallics & Smart Materials Laboratory, Department of Chemistry, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal 462 066, India

ARTICLE INFO

Article history:

Received 15 October 2017

Revised 21 December 2017

Accepted 23 December 2017

Available online 26 December 2017

Keywords:

Switchable catalysis

Light

Redox

pH

Coordination

ABSTRACT

This Digest letter aims to stimulate the readers with some recent developments in the field of artificial switchable catalysis achieved during the last couple of years. The significance of this young but burgeoning field was emphasized with the help of these latest examples.

© 2017 Elsevier Ltd. All rights reserved.

Contents

Introduction	487
Light-stimulated systems	488
Redox-stimulated systems	489
pH-stimulated systems	491
Metal-ion coordination-stimulated systems	492
Electrochemically-stimulated systems	493
Multi-stimuli systems	493
Conclusion	494
Acknowledgments	494
References	494

Introduction

Science is driven by imagination and knowledge. For any future scientific development, while knowledge provides the necessary input, an imagination reflects the potentiality of the output. The 2016 Nobel Prize in Chemistry truly portrays it. Artificial molecular machines, that garnered this recognition, are synthetic molecules which perform various stimuli-controlled ‘machine-like’ tasks.¹ Nature uses a bunch of smart biological machines for carrying out uncountable parallel processes with an unimaginable level of proficiency. This fascinating truth has inspired catalysis researchers also to explore their knowledge and imagination in designing and constructing artificial stimuli-controlled catalysts. Such inspi-

ration derived from Nature is, of course, inherently associated with an obvious demand in modern-day catalysis as it plays a pivotal role in the synthesis of valuable chemicals and materials. Eventually, the research field of ‘artificial switchable catalysis’ has emerged with a goal of offering advanced and controllable catalytic output in terms of reaction-rate, chemo-/regio-/stereo-selectivity, tandem and orthogonality, and even bi-/multi-functionality etc.²

Typically, the artificial switchable catalysts are equipped with smart structural features that respond reversibly to external stimuli such as light, pH, redox event, metal-ion coordination, or any other physicochemical trigger, to induce an on/off-type regulatory function related to one or more chemical events during catalysis. With the help of this sophisticated chemistry, therefore, one can achieve a good degree of control over the outcome of catalytic reactions. The most common type of ‘control’ achieved so far in majority of the reported switchable catalysis is that on the reaction

E-mail address: joyanta@iiserb.ac.in

rate, that is, switching the catalysis 'on' (upregulation) or 'off' (downregulation) in response to the applied stimulus. However, examples of more advanced control such as modulation of other stereochemical outcomes or orthogonal control of different catalysts/catalytic processes are slowly emerging.

Although the field of 'artificial switchable catalysis' is young but the advances in this budding research area have already started to emerge. Leigh et al. elucidated the state-of-the-art developments in this field and elegantly covered various types of stimuli-switchable catalysis in an overall comprehensive review in 2015.^{2a} A perspective on exclusively photoswitchable catalysis was also published in 2013 by Neilson and Bielawski.^{2b} Similarly, an extensive review by Bielawski et al. in 2016 focusing exclusively on switchable polymerization catalysis highlighted the significance of this rapidly-growing field.^{2c} Very recently, in 2017, Luisi et al. emphasized the important developments in switchable chiral catalysis along with the advantages of stimuli-driven dynamic control of enantioselectivity.^{2d} Therefore, this Digest focusses only on some of the latest and novel developments in this field to underscore the power of artificial switchable catalysts both on the conceptual as well as application facets. It is to be mentioned here that several important works have been reported in literature in which only enhancement of catalytic activity induced by stimuli (e.g., redox, light, cation, anion, or guest molecules) was shown without reversible switching of the activity between on and off or high and low. These examples have been excluded from the discussion here.

Light-stimulated systems

Light has been an attractive stimulus to switch the state of a catalyst by either incorporating a photoresponsive function within it via simple structural manipulation or using a separate photochemically active co-catalyst as an additive. The advantages of using light include its non-invasive nature, choice of desired wavelength depending on the chromophoric unit, excellent spatiotemporal control, and ease of operation. The primary concept of light-induced switching of activity/selectivity of a catalytic reaction is based on the controlled perturbation at the catalytic site (s) through some sorts of cooperative, steric (blocking/shielding) or electronic effect.^{2a} The commonly-applied catalyst-design principle to induce such effects relies on attaching a suitable functionality which shows an *E/Z*-photoisomerization (e.g., azobenzene unit) or photocontrolled ring-closing/ring-opening (e.g., diarylethene unit) process.^{2a,2b} Several systems have been reported using these simple concepts to achieve photoswitchable catalysis with excellent modulation of not only rate but also chemo- and/or regioselectivity of different organic reactions including Morita–Baylis–Hillman (MBH) reaction, Knoevenagel condensation, Michael addition, aza-Henry reaction, olefin cyclopropanation, transesterification, hydroboration etc. (Fig. 1).^{2a}

A high-utility process – ring-opening polymerization (ROP) has also been experimented with photoswitchable catalysts setting the target to achieve engineered microstructure and property of the resulting polymers.^{2c} However, only modulation of rate has been reported by utilizing the above-mentioned concepts. In one of the earlier designs, a cinnamoyl moiety was used as the tool to reversibly tune the steric hindrance around the catalytic center, thus either allowing or preventing a good polymerization rate of δ -valerolactone.^{2a} Electronic perturbation was also applied for *on/off* control of this type of polymerization catalysis along with other type of catalytic and non-catalytic processes with the help of dithienylethene-annulated photochromic N-heterocyclic carbene (NHC)-based catalysts.³ Considering the significance of

ROP catalysis, a recent development on switchable *rac*-lactide polymerization is worth to mention here. Wu et al. exploited the *E/Z* photo-isomerization capability of the azo-group within an azobenzene-based thiourea catalyst to discriminate the activity of the catalyst in two different states in terms of reaction rate. The UV light-generated *Z*-isomer was found to be inactive due to blocking of the thiourea catalytic site *via* intramolecular ($-\text{NO}_2$ $\text{HN}-$) hydrogen bonding caused in this configuration. A simple exposure of the system to ambient light generated the *E*-isomer which disrupted the hydrogen bonding and freed the catalytic site resulting in enhanced rate (Figure 2).⁴

The concept of switchable photoisomerization of azobenzene moiety was proved fascinating in many ways. The change of polarity of 4-(phenylazo)-benzoate group upon *trans-cis* isomerization was utilized elegantly by Prins and co-workers to control its affinity toward binding to Au nanoparticles (Au NPs) functionalized with a monolayer of 1,4,7-triazacyclononane (TACN): Zn^{2+} head-group-terminated C_9 -thiols. This chemistry led them to demonstrate an interesting photoswitchable 'nanozyme' catalyst for regulating the rate of transphosphorylation of 2-hydroxypropyl-4-nitrophenylphosphate (HPNPP) in aqueous buffer. The catalytic activity was found to be downregulated/inhibited with the *trans* isomer of the azobenzene compound which was ascribed to its higher binding affinity to the catalyst. On the other hand, the *cis* isomer, due to the increased polarity, disfavored its hydrophobic binding with the apolar part of the Au NP-attached monolayer, and thus increased the reaction rate. Although the authors found several operational limitations of this system, but the novelty of the work is promising to target biological systems (Fig. 3).⁵

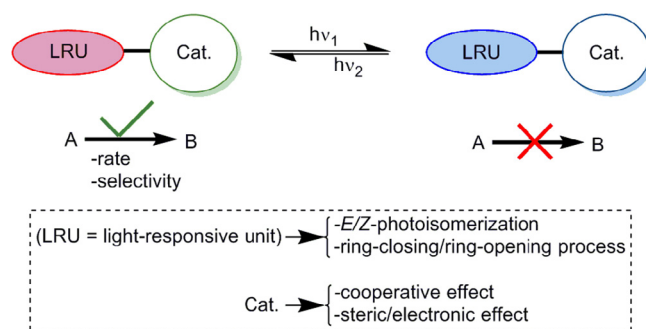


Fig. 1. Concept of photoswitchable catalysis.

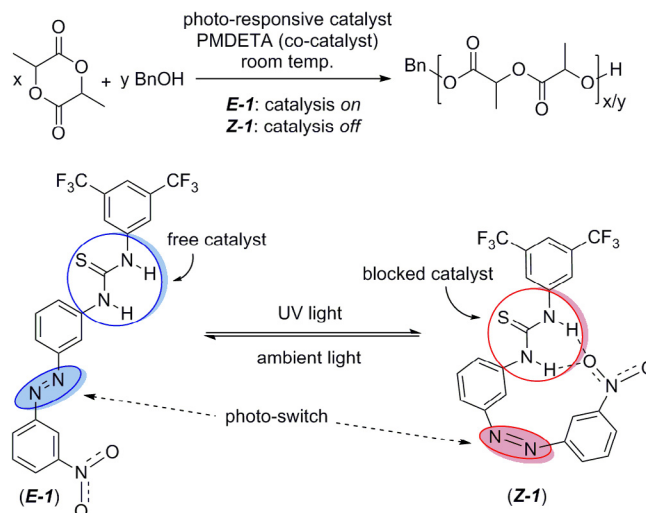


Fig. 2. Azobenzene-supported photoswitchable catalysis.⁴

Download English Version:

<https://daneshyari.com/en/article/7830656>

Download Persian Version:

<https://daneshyari.com/article/7830656>

[Daneshyari.com](https://daneshyari.com)