

(1) 履歷書 (Curriculum Vitae)

Dr. S. M. A. Hakim Siddiki

Personal Details:



Dr. S. M. A. Hakim Siddiki

Date and place of birth: 5th July 1977; Dhaka, Bangladesh

Nationality: Bangladeshi

Current address: Institute for Catalysis, Hokkaido University,
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Current position:

Nov. 2012-:

Postdoctoral Research Fellow

Graduate School of Engineering, Kyoto University, Japan

Working place: Institute for Catalysis, Hokkaido University, Japan

Education:

Oct. 2007-Mar. 2011:

Ph.D. in Organic Chemistry, University of Hyogo, Japan

Thesis title: *Study of chiral pentanediol induces asymmetric radical cyclization and metathesis reactions.*

Oct. 2005- Sept. 2007:

M. S. in Organic Chemistry, University of Hyogo, Japan

Thesis title: *Efficiency and stereoselectivity in 2,4-pentanediol tethered radical cyclization.*

Oct. 2000-Sept.2002:

M. S. in Organic Chemistry, University of Dhaka, Bangladesh

Thesis title: *Reactions of diarylideneacetone with acyclic active methylene compounds.*

Oct. 1995-Sept.1999:

B. S. in Chemistry, University of Dhaka, Bangladesh

Employment/Positions

2012-: Postdoctoral Research Fellow, Graduate School of Engineering Kyoto University, Japan.

2011-2012: Postdoctoral Research Fellow and Researcher, Graduate School of Science, Kyoto University, Japan.

2003-2005: Research and Development Officer, Beximco Pharmaceuticals Company Ltd., Dhaka, Bangladesh: *Conducted research on cost effective synthetic route for API (active pharmaceutical ingredients) and generic drugs.*

(2) 研究業績 (Research Achievements)

a. Publications in Refereed Journals:

1. Direct Olefination of Alcohols with Sulfones by Heterogeneous Platinum Catalysts; S. M. A. Hakim Siddiki, Abeda Sultana Touchy, Kenichi Kon, Ken-ichi Shimizu, *Chem. Eur. J.* **2016** (manuscript accepted).
2. Hydrogenation of sulfoxides to sulfides by Pt and MoO_x co-loaded TiO₂ catalyst; Abeda Sultana Touchy, S. M. A. Hakim Siddiki, Kenichi Kon, Wataru Onodera, Ken-ichi Shimizu, *Green Chem.* **2016** (manuscript accepted).
3. Amidation of carboxylic acids with amines by Nb₂O₅ as a reusable Lewis acid catalyst; Md. Ayub Ali, S. M. A. H. Siddiki, Wataru Onodera, Kenichi Kon, Ken-ichi Shimizu, *ChemCatChem.* **2015**, 7, 3555–3561.
4. A Heterogeneous niobium(V) oxide catalyst for the direct amidation of esters; Md. Ayub Ali, S. M. A. Hakim Siddiki, Kenichi Kon, Ken-ichi Shimizu, *ChemCatChem.* **2015**, 7, 2705–2710.
5. Acceptorless dehydrogenative synthesis of benzothiazoles and benzimidazoles from alcohols or aldehydes by heterogeneous Pt catalysts under neutral conditions; Chandan Chaudhari, S. M. A. Hakim Siddiki, Ken-ichi Shimizu, *Tetrahedron Lett.* **2015**, 56, 4885–4888. (*highlighted in Synfact*).
6. Synthesis of indoles *via* dehydrogenative *N*-heterocyclization by supported platinum catalysts; Sondomoyee Konika Moromi, Abeda Sultana Touchy, S. M. A. Hakim Siddiki, Md. Ayub Ali, Ken-ichi Shimizu, *RSC Adv.* **2015**, 5, 1059–1062.
7. Selective *N*-alkylation of indoles with primary alcohols by Pt/HBEA catalyst; S. M. A. Hakim Siddiki, Kenichi Kon, Ken-ichi Shimizu, *Green Chem.* **2015**, 17, 173–177.
8. Acceptorless dehydrogenative synthesis of 2-substituted quinazolines from 2-aminobenzylamine with primary alcohols or aldehydes by heterogeneous Pt catalysts; Chandan Chaudhari, S. M. A. Hakim Siddiki, Masazumi Tamura, Ken-ichi Shimizu, *RSC Adv.* **2014**, 4, 53374–53379.
9. Acceptorless Dehydrogenative Coupling of Primary Alcohols to Esters by Heterogeneous Pt Catalysts; Sondomoyee Konika Moromi, S. M. A. Hakim Siddiki, Md. Ayub Ali, Kenichi Kon, Ken-ichi Shimizu, *Catal. Sci. Technol.* **2014**, 4, 3631–3635.
10. Versatile and sustainable alcoholysis of amides by a reusable CeO₂ catalyst; S. M. A. Hakim Siddiki, Abeda Sultana Touchy, Masazumi Tamura, Ken-ichi Shimizu, *RSC Adv.* **2014**, 4, 35803–35807.
11. Heterogeneous Pt Catalysts for Reductive Amination of Levulinic Acid to Pyrrolidones; Abeda Sultana Touchy, S. M. A. Hakim Siddiki, Kenichi Kon, Ken-ichi Shimizu, *ACS Catal.* **2014**, 4, 3045–3050.
12. Versatile and Sustainable Synthesis of Cyclic Imides from Dicarboxylic Acids and Amines by Nb₂O₅ as a Base-Tolerant Heterogeneous Lewis Acid Catalyst; Md. Ayub Ali, S. M. A. Hakim Siddiki, Kenichi Kon, Junya Hasegawa, Ken-ichi Shimizu, *Chem. Eur. J.* **2014**, 20, 14256–14260.
13. Sustainable heterogeneous platinum catalyst for direct methylation of secondary amines by carbon dioxide and hydrogen; Kenichi Kon, S. M. A. Hakim Siddiki, Wataru Onodera, Ken-ichi Shimizu, *Chem. Eur. J.* **2014**, 20, 6264–6267. (*highlighted in Synfact*)
14. Self-Coupling of Secondary Alcohols and α -Alkylation of Methyl Ketones with Secondary Alcohols by Pt/CeO₂; Chandan Chaudhari, S. M. A. Hakim Siddiki, Ken-ichi Shimizu,

- Catalyst, *Top Catal.* **2014**, *57*, 1042–1048.
15. Direct synthesis of quinazolinones by acceptorless dehydrogenative coupling of *o*-aminobenzamide and alcohols by heterogeneous Pt catalysts; S. M. A. Hakim Siddiki, Kenichi Kon, Abeda Sultana Touchy, Ken-ichi Shimizu, *Catal. Sci. Technol.* **2014**, *4*, 1716–1719.
 16. C-3 alkylation of oxindole with alcohols by Pt/CeO₂ catalyst in additive-free conditions; Chandan Chaudhari, S. M. A. Hakim Siddiki, Kenichi Kon, Atsuko Tomita, Yutaka Tai, Ken-ichi Shimizu, *Catal. Sci. Technol.* **2014**, *4*, 1064–1069.
 17. *N*-alkylation of ammonia and amines with alcohols catalyzed by Ni-loaded CaSiO₃; Ken-ichi Shimizu, Shota Kanno, Kenichi Kon, S. M. A. Hakim Siddiki, Hideyuki Tanaka, Yoshihisa Sakata, *Catalysis Today* **2014**, *232*, 134–138.
 18. Fe³⁺-exchanged clay catalyzed transamidation of amides with amines under solvent-free condition; Md. Ayub Ali, S. M. A. Hakim Siddiki, Kenichi Kon, Ken-ichi Shimizu, *Tetrahedron Lett.* **2014**, *55*, 1316–1319 (*highlighted in Synfact*)
 19. Heterogeneous Ni Catalysts for *N*-Alkylation of Amines with Alcohols; Ken-ichi Shimizu, Naomichi Imaiida, Kenichi Kon, S. M. A. Hakim Siddiki, Atsushi Satsuma, *ACS Catal.* **2013**, *3*, 998–1005.
 20. Alkylation of 2-methylquinoline with alcohols under additive-free conditions by Al₂O₃-supported Pt catalyst; Chandan Chaudhari, S. M. A. Hakim Siddiki, Ken-ichi Shimizu, *Tetrahedron Lett.* **2013**, *54*, 6490–6493. (*highlighted in Synfact*)
 21. CeO₂ as a versatile and reusable catalyst for transesterification of esters with alcohols under solvent-free conditions; Masazumi Tamura, S. M. A. Hakim Siddiki, Ken-ichi Shimizu, *Green Chem.* **2013**, *15*, 1641–1646.
 22. General and selective C-3 alkylation of indoles with primary alcohols by reusable Pt nanocluster catalyst; S. M. A. Hakim Siddiki, Kenichi Kon, Ken-ichi Shimizu, *Chem. Eur. J.* **2013**, *19*, 14416–14419.
 23. Size- and support-dependent Pt nanocluster catalysis for oxidant-free dehydrogenation of alcohols; Kenichi Kon, S. M. A. Hakim Siddiki, Ken-ichi Shimizu, *J. Catal.* **2013**, *304*, 63–71.
 24. Acceptor-free dehydrogenation of secondary alcohols by heterogeneous cooperative catalysis between Ni nanoparticles and acid–base sites of alumina supports; Ken-ichi Shimizu, Kenichi Kon, Katsuya Shimura, S. M. A. Hakim Siddiki, *J. Catal.* **2013**, *300*, 242–249.
 25. An Efficient Synthesis of Chromene derivatives through a tandem Michael addition-cyclization reaction; Zinia Jaman, Khorshada Jahan, Kawsari Akhter, U. K. R. Romman, S. Mosaddeq Ahmed, S. M. A. Hakim Siddiki, M. Giasuddin Ahmed, *J. Bang. Chem. Soc.* **2013**, *26*, 75–82.
 26. Stereocontrol in radical cyclization: change in rate-determining step; S. M. A. Hakim Siddiki, Takashi Sugimura, *Org. Lett.* **2010**, *12*, 3626–3629.
 27. Ring closing metathesis using chiral template consisting of hard and soft parts; S. M. A. Hakim Siddiki, Takashi Sugimura, *Macromol. Symp.* **2010**, *293*, 10–14. (*cover page article*)
 28. Carbanion vs. carbon radical in tandem 1,4-addition to two connected units of acrylate or methacrylate; Shinya Nagano, S. M. A. Hakim Siddiki, Takashi Sugimura, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2011–2013.

b. **Status of securing competitive research funding:** not applicable

c. **Others:**

Awards/Fellowships/Scholarships:

- Since 2012: Postdoctoral Research Fellow under "ESICB (Elements Strategy Initiative for Catalysts and Batteries)" project of MEXT Japan.
- 2011-2012: Postdoctoral Fellow and Researcher under "High-Performance Organocatalyst" project by JSPS Japan.
- 2007-2011: Research Assistant, under GCOE program.
- 2005-2010: "Monbukagakusho"(MEXT) Scholarship, Japan.
- 2009: Awarded by travel allowance (International Symposium on Olefinic Metathesis, Leipzig, Germany, August 02-07, 2009)
- 2000-2002: Syed Saadat Ali Scholarship (For academic excellence in Graduate program, Dhaka University, Bangladesh)
- 1995-1999: Dhaka University Merit Scholarship (For academic excellence in Undergraduate program)
- 1992-1994: Education Board Scholarship (For academic excellence in Higher Secondary School program)
- 1987-1992: Education Board Scholarship, Junior Scholarship and Primary School Scholarship

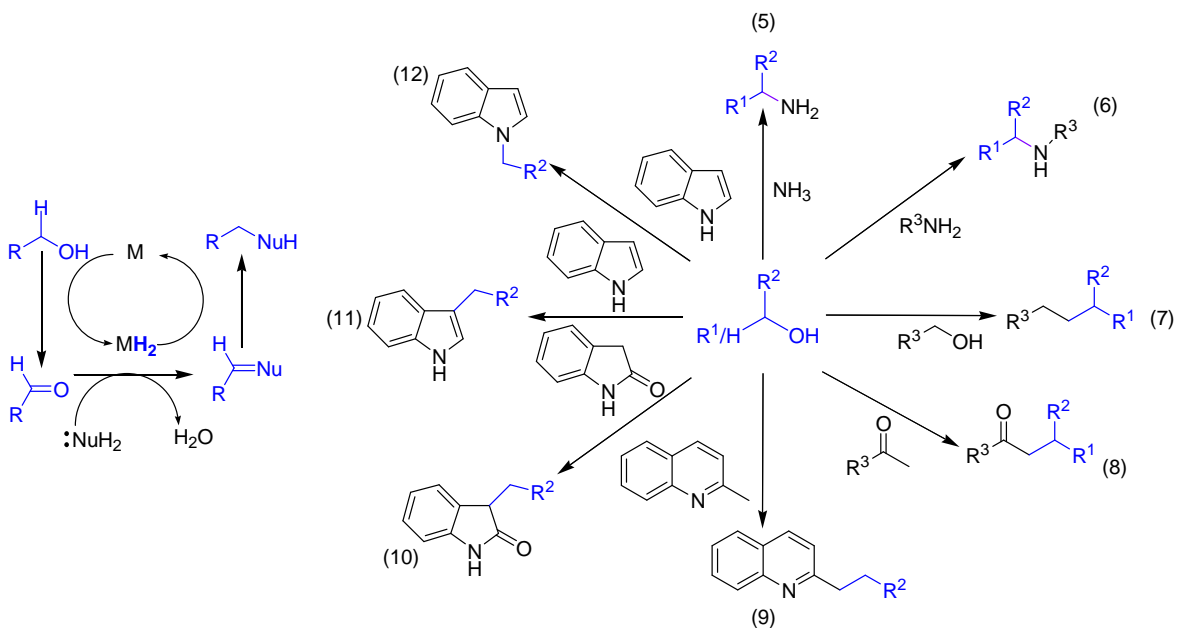
(3) 現在までの研究の概要 (Summary of Research Achievements)

Catalytic green synthesis of chemicals

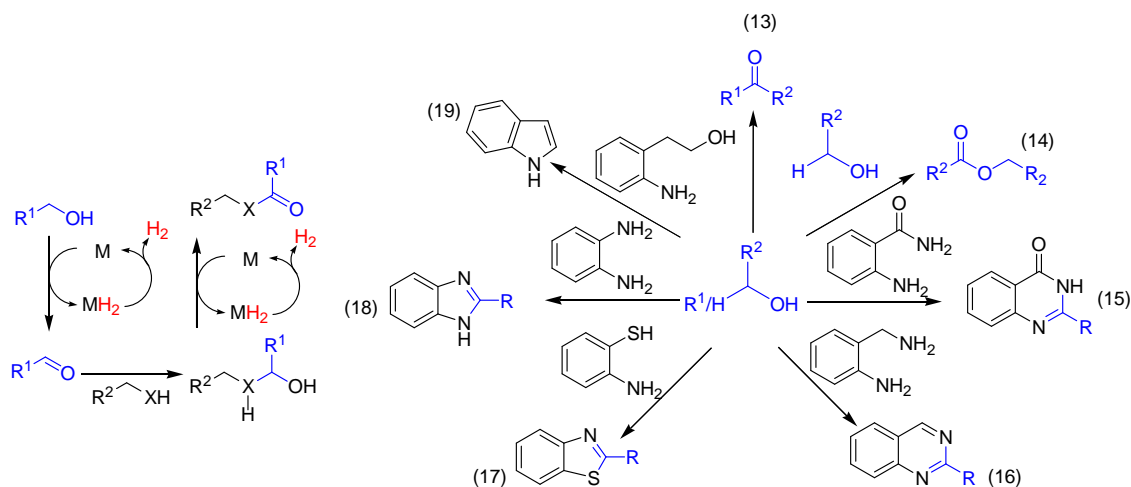
After completion of my PhD work for synthetic and catalytic studies, I moved to Kyoto University and started new part of my research carrier. Considering the environmental issues to build a sustainable society, idea of green chemistry for chemical synthesis is a recent growing area and developments of catalytic process for green chemistry are essentials. In contrast to the conventional homogeneous catalysis, one-pot synthesis of chemicals with heterogeneous catalysis is prospective as it ensures the decrease in energy consumption and recycling of the catalysts. Ideal organic synthesis requires catalytic activity, selectivity, atom-economy and step-efficiency, which courage us to develop new heterogeneous catalytic methodologies for chemical synthesis.

1. Catalytic transformation of alcohols by metal nanoparticles (ref: 5-9, 14-17, 19, 20, 22, 23)

I have developed size-controlled supported Ni/Pt nanocluster catalysts highly effective for hydrogen-borrowing type reactions (Scheme 1) and acceptorless dehydrogenative coupling reactions (Scheme 2) of alcohols for construction of C-C, C-O, C-N and C-S bonds. Conventionally homogeneous Ru and Ir complexes are effective for this type of reactions. Heterogeneous catalysts design concept is based on the multifunctionality of metal loaded acidic and/ or basic supports, where the acid and/or base sites on the supports selectively catalyzes condensation steps and metal catalyzes transfer dehydrogenation of alcohols/amines and transfer hydrogenation of condensation products.



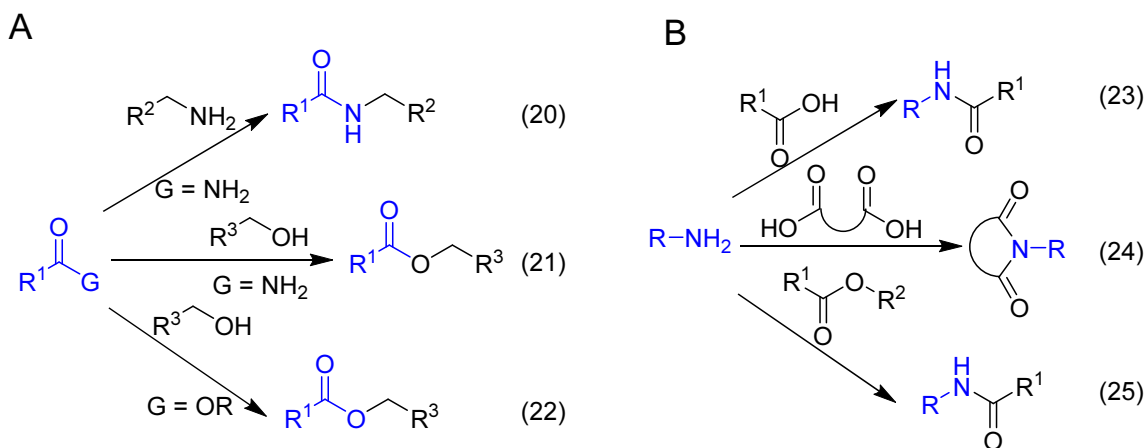
Scheme 1. Hydrogen-borrowing strategy with different successful reactions.



Scheme 2. Acceptorless dehydrogenative coupling reactions of alcohols.

2. Catalytic transformations of carboxylic acid derivatives by metal oxides (ref: 3, 4, 10, 12, 21)

I have jointly found that Lewis acid catalysts (CeO_2 , Nb_2O_5) activate carboxyl groups in the coexistence of a base. On this basis, CeO_2 -catalyzed transamidation, transesterification and alcoholysis of amides were developed [eq. (20), (21), (22)]. I also took part in the development of Nb_2O_5 catalysis [eq. (23), (24), (25)] for condensation of carboxylic acids and amines to imides, amides and amidation of esters to amides.



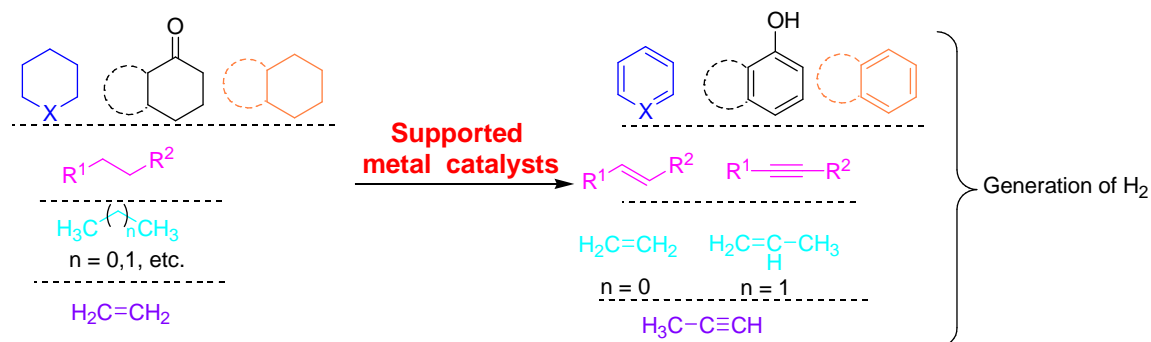
Scheme 3. (A) CeO_2 and (B) Nb_2O_5 -catalyzed reactions.

I have also jointly found Pt and MoO_x co-loaded TiO_2 ($Pt-MoO_x/TiO_2$) catalyst highly active for methylation of secondary amines by CO_2 and H_2 eq. (26), reductive amination of levulinic acid by H_2 and hydrodeoxygenation of sulfoxides to sulfides (ref. 11, 13). High catalytic activity can be attributed to Lewis acid–base interactions between the surface Mo cation and oxygen of $C=O$ and $S=O$, while the Pt is proposed to act as a H_2 dissociation site (ref. 2).

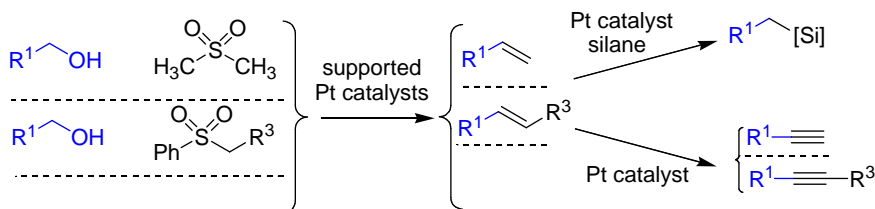
(4) 機構における研究計画 (Research proposal)

The prime concern of the modern civilization is the limited natural resources, energy and environmental issues. To solve these global problems I would like to play an active role through my future research. Considering the environmental issues to build a sustainable society, idea of green chemistry for chemical synthesis is a recent growing area and developments of catalytic process for green chemistry are essentials. As an academic point of view, I want to design and conduct research for the contribution to the global environmental issues.

I have successfully carried out conversion of alcohols to chemicals by heterogeneous Pt, Ni catalysts. As a specific research project, the development of unprecedented high performance heterogeneous catalysts based on specific cooperative action of solid surface could be demonstrate for chemical synthesis under sustainable green chemistry concept. Ideal synthesis requires catalytic activity, selectivity, atom-economy, step-efficiency, reusability and easy catalyst product separation options which encourage me to develop new heterogeneous catalytic methodologies for chemical synthesis. Recently studies on C-H bonds activation, aromatization (Scheme 1), olefination of alcohols followed by alkylation and silylation and alkenylation (Scheme 2), chemical production based on the carbon source of biomass, functional group conversion of natural carbon resources such as carboxylic acids and CO₂, are actively carried out by homogeneous catalysts and examples of heterogeneous catalysts are very small.



Scheme 1. Proposed supported metal catalyzed C-H activation reactions for chemical synthesis.

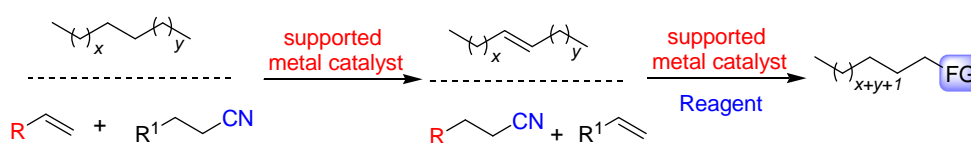


Scheme 2. Direct olefination, alkenylation, silylation of alcohols using supported Pt catalysts.

For economic efficiency, environmental compatibility challenges to one-pot synthesis of above chemicals with heterogeneous catalysts are prospective as it ensures the decrease in energy consumption and recycling of the catalysts. The mentioned reactions for organic synthesis can be

proceed using a facile heterogeneous catalysts if reuse and separation of catalyst and product allowed. Academic as well as industrial applications of this can be expected to have a significant impact.

Catalyst design can be done by taking the mechanistic consideration of existing homogeneous catalysts. It is aimed to build a mechanistic and structural research, where theory and surface chemistry should provide guidance of the solid catalyst design, through a interdisciplinary collaboration. Based on this feedback results, I want to developed catalysts by building a metallic nanoparticles. By utilizing a concerted action of the catalytically active species and the catalyst carrier or ligand, it is aimed to develop heterogeneous catalyst having activity and selectivity comparable to the homogeneous catalysts.



Scheme 3. Activation of neutral hydrocarbons and remote functionalization, catalytic transfer hydrocyanation using supported metal catalysts.

The above reactions are of interest as primary goal. In the future, based on acquired knowledge through these studies, it is also proposed to apply for neutral hydrocarbon activation as well as multifunctional reactions (Scheme 3) derived from the non-uniformity of the solid surface as a key to the new catalyst design that surpasses the enzyme, the challenge to the arbitrary control in a new idea to combine the surface science and organic synthesis.