

学位論文（要約）

**Preparation and Characterization of Polymer-immobilized
Bimetallic Nanoclusters and Their Application
to Organic Synthesis**

（高分子カルセランド型二元金属ナノクラスター触媒の
調製、物性評価および有機合成反応への応用に関する研究）

平成 23 年 12 月 博士（理学）申請

東京大学大学院理学系研究科

化学専攻

貝塚 互輔

Abstract

Preparation and Characterization of Polymer-immobilized Bimetallic Nanoclusters and Their Application to Organic Synthesis

Kosuke Kaizuka
Department of Chemistry
Graduate School of Science
The University of Tokyo

インターネット公表に関する共著者全員の同意が得られていないため、および一部について今後学術論文への投稿を予定しているため、全文公表を控えさせていただきます。

【Publications related to the thesis】

1. “Remarkable Effect of Bimetallic Nanocluster Catalysts for Aerobic Oxidation of Alcohols: Combining Metals Changes the Activities and the Reaction Pathways to Aldehydes/Carboxylic Acids or Esters”
Kaizuka, K.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2010**, *132*, 15096-15098.
2. “高分子カルセランド型二元金属ナノクラスター触媒を用いるアルコール類の高選択的酸素酸化反応”
貝塚互輔, 宮村浩之, 小林修, 高分子論文集, **2011**, *68*, 493-508.
3. “Multiphase Flow Systems for Selective Aerobic Oxidation of Alcohols Catalyzed by Bimetallic Nanoclusters”
Kaizuka, K.; Lee, K.-Y.; Miyamura, H.; Kobayashi, S. *J. Flow Chem.* **2012**, *2*, 1-4.

Introduction

Section 1: Introduction

Homogeneous catalysts and heterogeneous catalysts

In organic synthesis, catalysts are essential to obtain desired compound and chemists have been investigating more efficient catalysts for long time. Catalysts can be classified into two groups; homogeneous catalysts and heterogeneous catalysts. These two types of catalysts have characteristic properties. Homogeneous catalysts such as transition metal catalysts usually show high reactivity and selectivity, and design of catalysts is facile in homogeneous environment. In contrast, recovery and reuse of homogeneous catalysts are difficult or impossible in many cases. From the environmental view point, homogeneous catalysts are not suitable due to large amounts of undesired co-product, in other words, high E-factor. Heterogeneous catalysts such as zeolite and immobilized catalysts have been of great interest due to several advantages, such as simplification of product work-up, separation, isolation, and reuse of catalysts.¹ However, there are several disadvantages such as less diminished catalytic activity when compared to than the corresponding original catalysts and leaching of catalysts from supports. To solve these problems, development of new generation immobilized catalysts is strongly required.

In this aspect, our laboratory has recently been reinvestigating immobilized catalysts mainly from two aspects. First, chemical processes with little waste are expected using immobilized catalysts, because they can be recovered and reused. This leads to more environmentally benign chemical processes, and immobilized catalysts can play a central role in more sustainable chemistry. Second, the use of immobilized catalysts is expected to be a key to high throughput organic synthesis. Recent advances in combinatorial chemistry have required synthesis of large numbers of structurally distinct compounds (compound library) efficiently. For this purpose, new methodologies are needed. While solid-phase syntheses provide one of the efficient methods, a new method for the synthesis of compound library using immobilized catalysts is promising combined with automation/robotic synthesis.

Polymer-immobilized catalysts

Through those recent research works, our laboratory have recognized the importance of developing truly efficient polymer-supported catalysts, and reached an idea of microencapsulated (MC) catalysts.^{1c} Microcapsules have been used for coating and isolating substances until such time as their activity is needed, and their application to medicine and pharmacy has been extensively studied. Recently, much progress has been made in this field;

for example, the size of microcapsule achievable has been reduced from a few micrometers to nanometers. Our idea is to apply this microencapsulation technique to the immobilization of catalysts onto polymers. That is, the catalysts would be physically enveloped by polymer thin films, and at the same time, immobilized by the interaction between π -electrons of benzene rings of the polystyrene used as a polymer backbone and vacant orbitals of the catalysts.

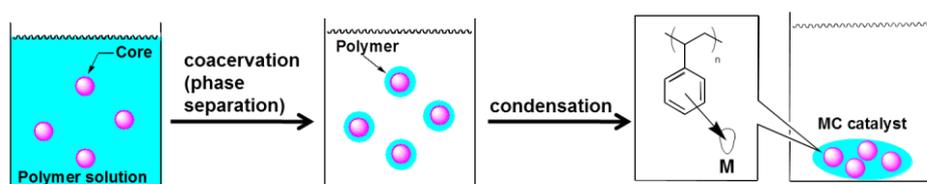


Figure 0-1. Microencapsulated (MC) catalysts

The polymer-incarceration method is based on two procedures; microencapsulation and cross-linking. Whilst the MC technique, as mentioned above, is efficient for keeping metal catalysts stable, interaction between metal catalysts and benzene rings in polymers is enough strong to prevent leaching of metal catalysts, but not too strong to deactivate the catalysts. On the other hand, microencapsulated catalysts dissolve in some solvents, and in those cases recovery and reuse are difficult. In order to address this issue, cross-linking was introduced in the polymer, and new “polymer incarcerated (PI) catalysts,” were developed.² The PI catalyst can be used in most of solvents without leaching of metal sources. In addition to the feature of solvent tolerance, metal catalysts are strongly trapped in the polymer network.

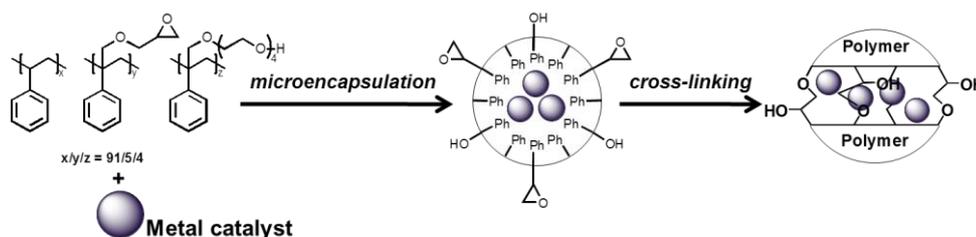


Figure 0-2. Polymer-incarcerated (PI) catalysts

Metal nanoclusters

Metal nanoclusters consist of several or more metal atoms and possess specific physical and chemical properties which are different from metal atoms or bulk metals. In general, the smaller the cluster size, the less metallic features they have because the energy gaps go into discrete. Because of such characteristic features, metal nanoclusters can show variable reactivity or selectivity in chemical reactions depending on their sizes or shapes. For examples, better reactivity of the smaller clusters is usually assumed to be attributed to their increasing

specific surface area. In addition, it can be mentioned as one of the reasons that, considering its small surface, there are relatively many metal atoms which are catalytically active, like edge atoms or corner atoms. On such atoms, there are less metal-metal bonds, and it is easy for substrates to approach catalysts because of the sterically larger space. As a result, the reactivity of the smaller clusters should be increased.

In general, metal nanoclusters have high surface energy, and they are thermodynamically unstable. Therefore, they tend to aggregate to form large clusters in order to minimize their surface energy. It is assumed that this thermodynamic stabilization would be attributed that the aggregation leads to degeneracy of orbitals and formation of band, then delocalization of electrons can occur and it will stabilize the clusters. However, such large clusters show low activity as stable catalysts.

One of the most common methods to prevent metal nanoclusters from aggregation is the immobilization on supports. There are mainly two types of methods to create metal nanoclusters; physical and chemical methods. In the former case, broken-apart pieces of bulk metals are immobilized on supports. This is based on the formation of the layer of adsorbed molecules near the surface by van der Waals' force between such molecules and supports. Usually, it is easy to prepare catalysts in these methods. However, there are some problems; for example, leaching of metals caused by effect of ligands or decrease of activity because of difficulty to approach substrates and catalysts each other. On the other hand, in the latter case, metal nanoclusters which are prepared by reduction of metal salts are stabilized by coordination of ligands. The disadvantages of chemical methods are decrease of freedom of metal catalysts in case of stronger coordination with ligands and degradation of reactivity or selectivity caused by steric hindrance of supports themselves. In addition, the oxygen and moisture in the air can deteriorate the ligands, then the degradation could be accelerated.

In order to keep the metal nanocluster immobilized catalysts highly active, it would be necessary to make weak interactions between supports and metal nanoclusters, however, also enough strong to prevent the metals from leaching out. Then, aforementioned problems will be solved by utilizing the weak bonds between each metal nanoclusters and support, at the same time, strong as a whole because of multiple interactions. To address these issues, we have applied PI methods for immobilization of metal nanoclusters. Metal nanoclusters are stabilized by the interaction between metal catalysts and benzene rings in polymers, and strongly "locked up" in the polymer network and do not aggregate any more to keep high reactivity.

In my Ph.D study, I have explored the preparation and characterization of novel carbon-stabilized polymer-incarcerated (PI-CB) bimetallic nanocluster catalysts (PI-CB

catalysts), and the aerobic oxidation of alcohols catalyzed by these bimetallic nanocluster catalysts in various reaction environments.

Section 2: References

1. a) Gladysz, J. A. *Chem. Rev.* **2002**, *102*, 3215. b) McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275. c) Kobayashi, S.; Akiyama, R. *Chem. Commun.* **2003**, 449. d) Ertl, G.; Kno"tzinger, H.; Weitkamp, J. Eds. *Handbook of Heterogeneous Catalysis*; Verlag Chemie: Weinheim, Germany, 1991, Vol. 5. e) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557. f) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans.* **2000**, *1*, 3815. g) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109. h) Frechet, J. M. J. *Tetrahedron* **1981**, *37*, 663. i) Anastas, P. T.; Warner, J. C. in *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998. j) Anastas, P. T.; Kirchoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686. k) Lee, A.; Ley, S. V. *Org. Biomol. Chem.* **2003**, *1*, 3263. l) Dolle, R. E. *J. Comb. Chem.* **2004**, *6*, 623. m) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815. o) Trindade, A. F. P.; Gois, M. P.; Afonso, C. A. M. *Chem. Rev.* **2009**, *109*, 418. p) Climent, M. J.; Corma, A.; Iborra, S. *Chem. Rev.* **2011**, *111*, 1072. q) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. *Chem. Rev.* ASAP. r) Heitbaum, M.; Glorius, F.; Escher, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4732. s) Shylesh, S.; Sch"unemann, V.; Thiel, W. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 3428. t) Benaglia, M. Ed.; *Recoverable and Recyclable Catalysts*; Wiley-VCH: Weinheim, Germany, 2009.
2. Akiyama, R.; Kobayashi, S. *J. Am. Chem. Soc.* **2003**, *125*, 3412.

Chapter 1: Development of Carbon-stabilized Polymer-incarcerated Bimetallic Nanocluster Catalysts and Selective Oxidation of Alcohols

Selective oxidation of alcohols catalyzed by novel carbon-stabilized polymer-incarcerated bimetallic nanocluster catalysts using molecular oxygen has been developed. Aldehydes and ketones were obtained by the gold/platinum catalyst in benzotrifluoride.

インターネット公表に関する共著者全員の同意が得られていないため、および一部について今後学術論文への投稿を予定しているため、全文公表を控えさせていただきます。

Chapter 2: Direct Oxidative Ester Formation Reactions

Selective oxidation of alcohols catalyzed by novel carbon-stabilized polymer-incarcerated bimetallic nanocluster catalysts using molecular oxygen has been developed. Esters were formed by the gold/palladium catalyst in methanol. To the best of our knowledge, this is the first example that the reaction pathway has been changed dramatically in gold catalysis by combining with a second metal. The differences in the activity and the selectivity are considered to be derived from the difference in the structure of the bimetallic clusters.

インターネット公表に関する共著者全員の同意が得られていないため、および一部について今後学術論文への投稿を予定しているため、全文公表を控えさせていただきます。

Chapter 3: Application to Flow System Reactions

Au–Pt and Au–Pd bimetallic nanoclusters that catalyzed the aerobic oxidation of alcohols during a once-through pass through gas–liquid–liquid–solid flow systems were developed. Alcohols were converted to aldehydes and ketones in benzotrifluoride (BTF)/water media by Au–Pt catalyst or to the corresponding methyl esters in methanol/water media by Au–Pd catalyst. The flow systems were superior to the batch systems in terms of both yield and selectivity.

インターネット公表に関する共著者全員の同意が得られていないため、および一部について今後学術論文への投稿を予定しているため、全文公表を控えさせていただきます。

Overview

インターネット公表に関する共著者全員の同意が得られていないため、および一部について今後学術論文への投稿を予定しているため、全文公表を控えさせていただきます。

Experimental

インターネット公表に関する共著者全員の同意が得られていないため、および一部について今後学術論文への投稿を予定しているため、全文公表を控えさせていただきます。

References

1. Brown, H. C.; Mead, E. J.; Rao, B. C. S. *J. Am. Chem. Soc.* **1955**, *77*, 6209.
2. Lucchesi, C.; Inasaki, T.; Miyamura, H.; Matsubara, R.; Kobayashi, S. *Adv. Synth. Catal.* **2008**, *350*, 1996.

Publications

【Publications related to the thesis】

1. “Remarkable Effect of Bimetallic Nanocluster Catalysts for Aerobic Oxidation of Alcohols: Combining Metals Changes the Activities and the Reaction Pathways to Aldehydes/Carboxylic Acids or Esters”
Kaizuka, K.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2010**, *132*, 15096-15098.
2. “高分子カルセランド型二元金属ナノクラスター触媒を用いるアルコール類の高選択的酸素酸化反応”
貝塚互輔, 宮村浩之, 小林修, 高分子論文集, **2011**, *68*, 493-508.
3. “Multiphase Flow Systems for Selective Aerobic Oxidation of Alcohols Catalyzed by Bimetallic Nanoclusters”
Kaizuka, K.; Lee, K.-Y.; Miyamura, H.; Kobayashi, S. *J. Flow Chem.* **2012**, *2*, 1-4.

Acknowledgement

The author expresses his sincere thanks to Prof. Shu Kobayashi, The University of Tokyo, for his valuable suggestions, helpful discussions and support ranging over many subjects throughout the course of this work.

He also gratefully thanks Dr. Hiroyuki Miyamura and Dr. Ryosuke Matsubara for fruitful discussions, hands-on instructions and continuous encouragement throughout the course of this work.

He also thanks Dr. Yasuhiro Yamashita, Dr. Yuichiro Mori, Dr. Masaharu Ueno, Dr. Woo-Jing Yoo, Dr. Tetsu Tsubogo, Dr. Uwe Schneider, Dr. Miyuki Yamaguchi, Dr. Ryo Akiyama and Dr. Takashi Nagano for beneficial advice and discussions.

He is also grateful to Mr. Noriaki Kuramitsu for his excellent STEM and EDS analyses, to his co-workers, Dr. Ka-Young Lee and Mr. Yu Fukusato, and to all the members of the synthetic organic laboratory for various help, cooperation and motivation.

He also thanks the Fellowship of the Japan Society for Promoting Science, G-COE, NEDO and ERATO for their financial support.

At last, he also expresses his hearty thanks to his family and friends who have always warmly supported her.

March 2014

Kosuke Kaizuka

The University of Tokyo