学　位　論　文（要　約）

Well Designed, Heterogeneous Gold, Palladium, and Rhodium Nanoparticles as Catalysts for Organic Transformations

（精密に設計された不均一系金、パラジウム、
及びロジウムナノ粒子触媒の開発と
その有機合成への応用）

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I. Introduction

1. Green Chemistry

The industrial revolution changed our life significantly in many aspects, such as beginning of mass product, development of industrial technique and economy, but it also caused some serious problems including environmental pollution and insufficiency of energy resources. To solve these main problems with continuing advance in chemistry, the concept of 'green chemistry' have been paid much attention.

Green chemistry is a beneficial idea for environment and human being by encouraging the development of product or process, which minimized the use of energies and generation of harmful substances. This concept including eco-friendly precess to reduce waste and solvent, minimize energy consumption using mild conditions, design of environmetally benign catalysts or reactions which have high atom efficiency and so on. The details are shown well in the '12 principles of green chemistry' as shown in below.[1]

<u>12 principles of green chemistry</u>

- **Prevention**
  It is better to prevent waste than to treat or clean up waste after it has been created.
- **Atom Economy**
  Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- **Less Hazardous Chemical Syntheses**
  Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- **Designing Safer Chemicals**
  Chemical products should be designed to affect their desired function while minimizing their toxicity.
- **Safer Solvents and Auxiliaries**
  The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- **Design for Energy Efficiency**
  Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- **Use of Renewable Feedstocks**
  A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- **Reduce Derivatives**
  Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or

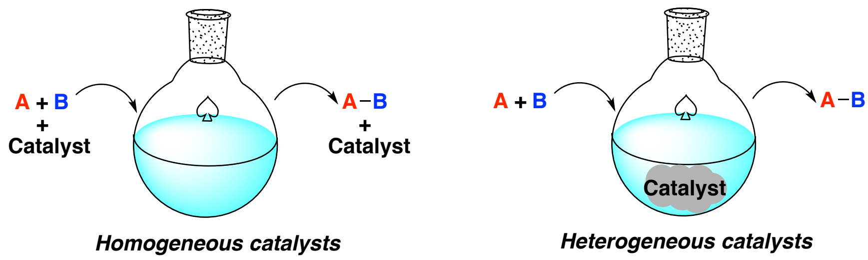
avoided if possible, because such steps require additional reagents and can generate waste.

- **Catalysis**
  Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- **Design for Degradation**
  Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- **Real-time analysis for Pollution Prevention**
  Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- **Inherently Safer Chemistry for Accident Prevention**
  Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires

2. Heterogeneous Catalysts

As shown in 12 principles of green chemistry, catalytic reaction is desirable way and superior compared with stoichiometric reactions due to use of less amount of substances and decreased consuming energies.

Figure 1-1. Homogeneous catalysts and heterogeneous catalysts



The catalyst is developed as ‘homogeneous catalyst’ firstly, which is dissolved in solvent, and existed as homogeneous form with the other substances. The most well know catalytic system is metal complex, sometimes with the presence of ligand, which showed excellent activities in various reactions including cross-coupling reactions. Even homogeneous catalysts have high activity and there are many examples and information about those catalytic systems, there are some drawbacks. The most significant disadvantage of homogenous catalyst is difficulty in recovery of catalysts; some metal catalysts (moreover, some reactions require ligands for better activity and selectivity) are expensive, therefore, the addition of precious catalyst in every run is cost-burden. Also, it causes serious toxic metal contamination of product; removing catalyst and no contamination of metal in product are very important point especially in medicines because remained metal catalyst can act as poison in human body.

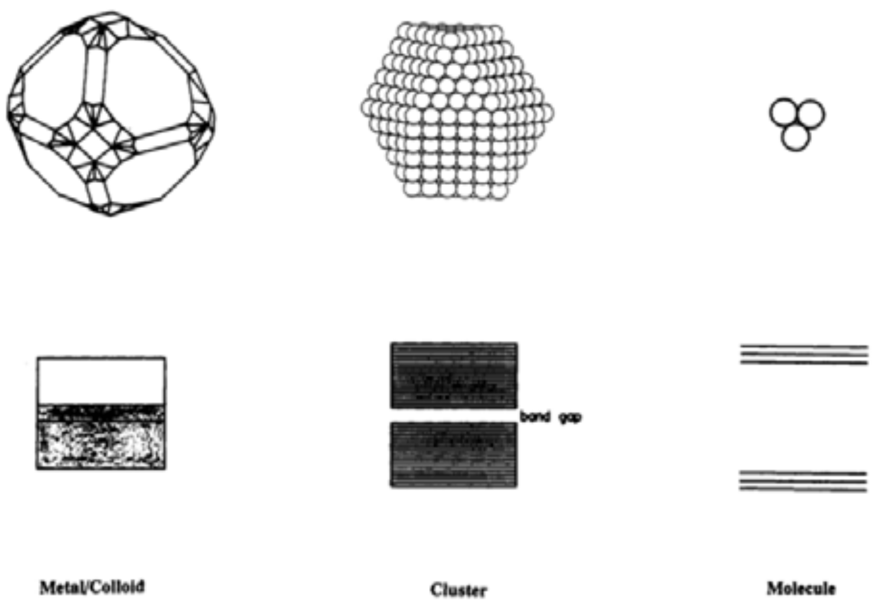
Heterogeneous catalysts have some advantages compared with homogeneous catalysts, especially in terms of recovery of catalyst as mentioned above. They can be easily separated from reaction systems by simple methods, such as filtration or use of magnetics, therefore, recovery and reuse of catalyst is possible. Also, heterogeneous catalyst can be applied in many fields of chemistry; the application in combinatorial chemistry leads the construction of useful tools for compound library,[2] and use of heterogeneous catalyst in flow reaction, which reactions are conducted in the stream of flow, makes flexible design of multistep reaction, application of biphasic systems, and large scale production.[3]

In spite of those advantages of heterogeneous catalysts, still there is hurdles to be jumped over; generally they are thought as less active than homogeneous catalysts probably because reaction would be proceeded only on the surface of catalysts and there is too strong interaction between their support for stabilization in the case of supported catalyst. Also, in the case of metal catalysts, sometimes metal leaching could occur and it would serious metal contamination of product. Though there are some problems that should be improved more, it is sure that heterogeneous catalysts are very attractive and efficient way.

3. Metal Nanoparticles/Nanoclusters

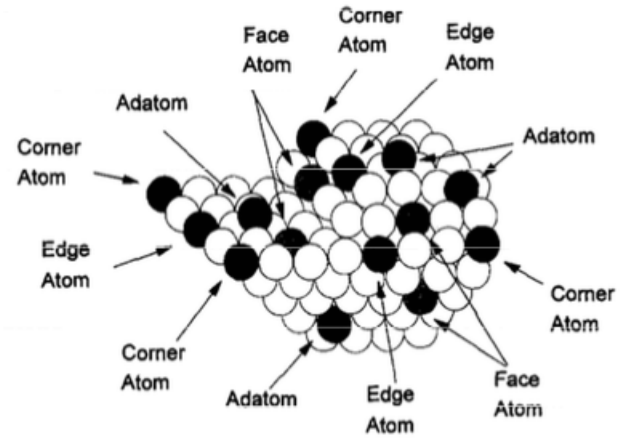
Metal nanoparticles/nanoclusters have been attracted as catalysts because of their unique characteristics different from metal complexes or bulk metals. This instinct features are derived from quantum size effect, which caused by decreased band gaps following the discrete energy level gap (Figure 1-2).[4]

Figure 1-2. Electronic state of bulk metal, clusters and molecules (adapted from *Chem. Rev.* **1992**, *92*, 1709)



One more important feature of metal nanoparticles/nanoclusters is their increased surface area to volumn ratio. Moreover, there are different types of surface atoms based on their positions and effects from near atoms, and actual active sites of catalysts is depending on kind of active surface atoms and reactions (Figure 1-3).[5]

Figure 1-3. Representation of some different types of surface atoms metal nanoparticle catalyst (adapted from *J. Mol. Catal. A. Chem.* **1995**, *95*, 277)



The combinations between different metals also can be considered; when two different metal nanoparticles were combined, sometimes very different features can be obtained because of various morphologies of them (Figure 1-4).[6] This manifestation of new feature could be explained by two different effects, ligand effect and ensemble effect. In the case of ligand effect, one metal changes the property of the other metal, by transferring electrons, and this effect is well seen in the case of core-shell structure. On the other hand, in ensemble effect, two different metals adsorb and activate different materials independently, and synergistic effect can be observed. Because of two different metals should adsorb different materials respectively, ensemble effect is normally shown in alloyed metal nanoparticles that both metal species can exist on the surface (Figure 1-5).

Figure 1-4. Various morphologies of bimetallic metal nanoparticles (adapted from *J. Am. Chem. Soc.* **2003**, *125*, 11034)

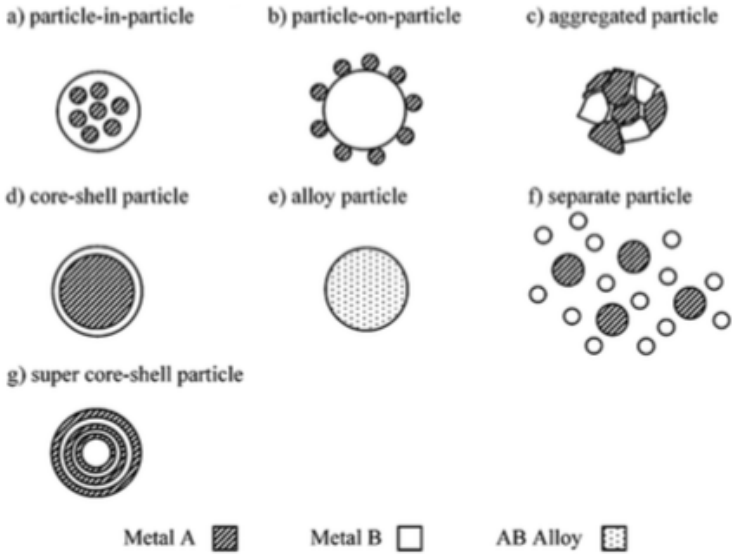
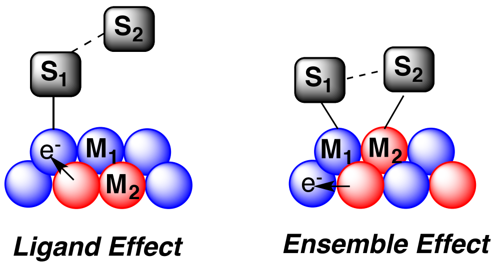


Figure 1-5. Ligand effect and ensemble effect



Due to the unique features as mentioned in above, various metal nanoparticles/nanoclusters have been used as efficient catalysts in many reactions. The activity of them is affected by various factors, such as size, composition, geometry, oxidation state, shape, morphology, and so on. To stabilize and prevent aggregation of metal nanoparticles/nanoclusters, supports are used in many cases, and the kind and property of supports are also one of the important factors to determine the activity of metal nanoparticle/nanocluster catalysts. Even they have been used as catalysts for many years, the effects of many factors mentioned above are unclear yet, therefore, there are still many rooms to research and develop the field of metal nanoparticle/nanocluster catalysts.

4. Polymer Incarcerated Metal Nanoparticle Catalysts (PI Catalyst)

Until now, various kinds of supports have been developed for metal nanoparticle catalysts due to thier lack of chemical stabilities. However, in some case, supported catalysts have lower activity compared with that of metal nanoparticle itself, because of interaction between metal nanoparticles and support, and decreased

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