

論文の内容の要旨

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)

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Introduction

Immobilized catalysts have been of great interest due to several advantages, such as simplification of product work-up, separation, isolation, and reuse of catalysts. However, there are several disadvantages such as diminished catalytic activity when compared to the corresponding original catalysts and leaching of catalysts from supports. To solve these problems, we have been investigating new immobilization methods of metal catalysts: microencapsulated catalysts and polymer-incarcerated (PI) catalysts.

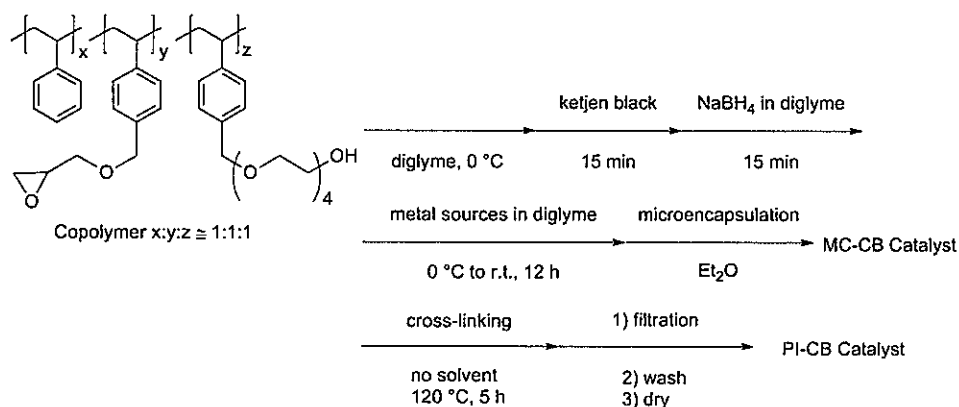
Selective oxidation of alcohols is one of the most important transformations in organic synthesis since the resulting carbonyl compounds possess higher energy and reactivity to allow many kinds of carbon-carbon bond-forming and other transforming reactions. While several metal-based oxidizing reagents have been developed, these protocols usually require stoichiometric amounts of the metal oxidants and thus a large amount of waste is formed in many cases. In this context, alcohol oxidation using molecular oxygen catalyzed by reusable heterogeneous catalysts under mild conditions is desired from the viewpoints of atom economy and energy efficiency. Recently, aerobic oxidation of alcohols catalyzed by gold nanoclusters has been widely investigated. We have also reported the aerobic oxidation of alcohols and the direct oxidative ester formation of primary benzyl alcohols catalyzed by PI Au and PI Au/Pt. During these investigations, bimetallic nanocluster catalysts showed distinctive activity compared with monometallic nanoclusters. However, to the best of our knowledge, there have been no reports that the reaction pathways in gold nanocluster catalysis can be changed dramatically by combining it with a second metal.

Flow systems are crucial for large-scale industrial synthesis, high-throughput organic synthesis related to combinatorial library generation, and automation of multistep transformations. Moreover, unique reactivity and selectivity are sometimes expected under short residence time in flow. In addition, a flow system is one of the methods for reaction integration (space integration) where, for example, unstable intermediates can be available for further reactions.

In this study, I have explored the preparation and characterization of novel carbon-stabilized polymer-incarcerated (PI-CB) bimetallic nanocluster catalysts and the aerobic oxidation of alcohols catalyzed by these bimetallic nanocluster catalysts in various reaction environments.

Catalyst Preparation

PI-CB/Au-Pt and PI-CB/Au-Pd were prepared by the formation of bimetallic nanoclusters from the corresponding metal salts under reductive conditions in the presence of a polystyrene-based polymer and carbon black (Scheme 1). The following features of the bimetallic catalysts have been discovered from scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) analyses: (1) the size of the clusters is almost the same in PI-CB/Au-Pt and PI-CB/Au-Pd (around 2-2.5 nm); (2) the size distribution is a bit narrower for PI-CB/Au-Pt when compared with PI-CB/Au-Pd; (3) the Au-Pt clusters contain an ~1:1 ratio of gold to platinum in alloy clusters and this ratio is consistent with the metal loading determined by inductively coupled plasma-atomic emission spectrometry (ICP); (4) although the metal loading determined by ICP is almost 1:1, the Au-Pd clusters contain an ~4:1-3:1 ratio of gold to palladium in alloyed clusters (Figure 1).



Scheme 1. Preparation of PI-CB catalysts

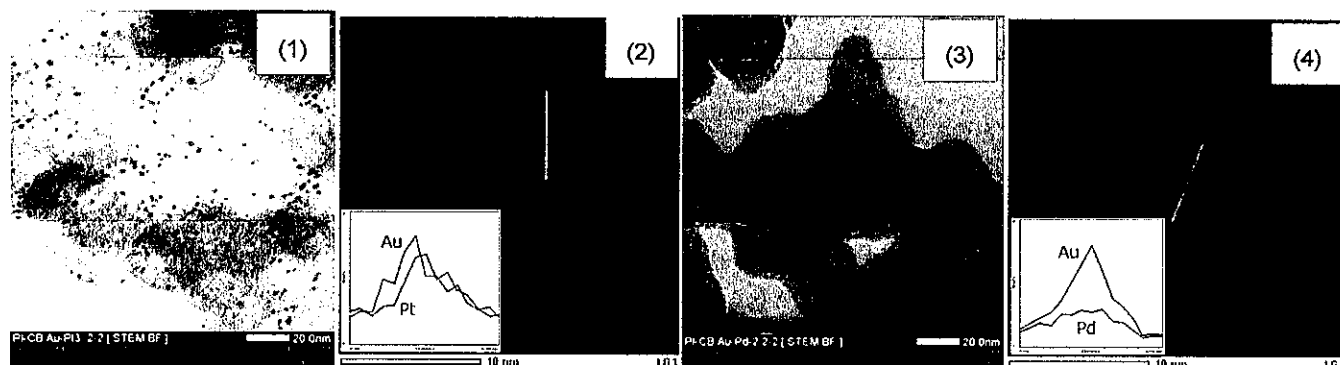
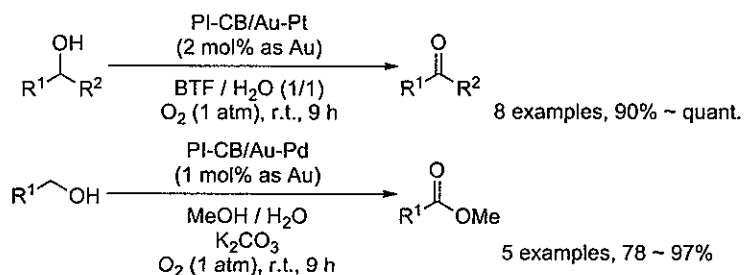


Figure 1. STEM and EDS analyses of PI-CB catalysts: (1) Typical STEM image of PI-CB/Au-Pt; (2) EDS analysis of a cluster of PI-CB/Au-Pt; (3) Typical STEM image of PI-CB/Au-Pd; (4) EDS analysis of a cluster of PI-CB/Au-Pd

Selective Aerobic Oxidation of Alcohols Catalyzed by PI-CB Catalysts in Batch Systems

The catalytic activities of the prepared catalysts in the aerobic oxidation of alcohols were assessed using 1-octanol as a model substrate. Under neutral conditions in a benzotrifluoride (BTF)/water solvent system, PI-CB/Au-Pt oxidized 1-octanol to octanal in excellent yield (92%) and 1-octanoic acid in low yield (6%). In the presence of K_2CO_3 , the major product was 1-octanoic acid (94%). It is noted that overoxidation of 1-octanol to 1-octanoic acid was suppressed under neutral conditions. In contrast, direct oxidative methyl ester formation catalyzed by PI-CB/Au-Pd proceeded smoothly in methanol/water under basic conditions in a methanol/water solvent system (78%). The difference in the activity and the selectivity between PI-CB/Au-Pt and PI-CB/Au-Pd catalysts could be explained by the difference in the structure of the clusters. Because of their electronegativities, palladium is more positive than gold in the bimetallic clusters. I assume that the oxidation reaction pathways to

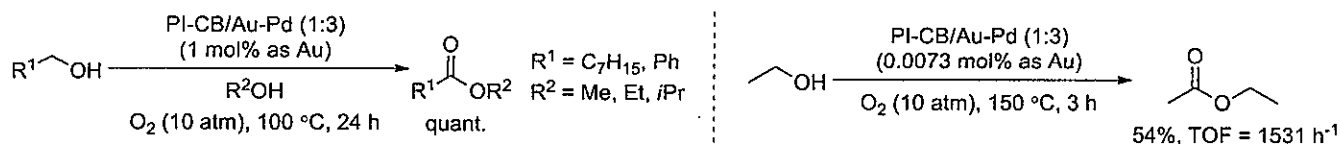
carboxylic acids or esters are dependent on hydration or hemiacetal formation from aldehydes. It is likely that in the presence of the Au-Pd clusters containing the acidic palladium, hemiacetal formation occurred preferentially. These reaction systems could be applied to various alcohols. Primary aliphatic alcohols and primary benzylic alcohols were smoothly converted to the corresponding aldehydes and esters in high yields. Secondary alcohols were also oxidized to the corresponding ketones in excellent yields.



Scheme 2. Selective aerobic oxidation of alcohols catalyzed by PI-CB catalysts

Direct Oxidative Ester Formation Reactions Catalyzed by PI-CB/Au-Pd under Neutral Conditions

In batch systems, methyl ester formation from primary alcohols catalyzed by PI-CB/Au-Pd proceeded smoothly. However, ethyl and isopropyl ester formation reactions afforded poor reactivity because of their steric hindrance. Even increasing the amount of K_2CO_3 , the selectivity of ester did not improve and the yield of the undesired carboxylic acid increased. Bases seemed to accelerate the formation of acetal, not hemiacetal. To prevent the use of bases and to improve the reactivity, reactions under high pressure and temperature in autoclave were examined. As I expected, the reactions proceeded well and the desired esters were obtained quantitatively under neutral conditions under 10 atm oxygen atmosphere, at 100 °C (Scheme 3, left part). I also examined the ethyl acetate formation from ethanol in autoclave, and it was found that PI-CB/Au-Pd afforded ethyl acetate effectively under 10 atm oxygen atmosphere, at 150 °C (Scheme 3, right part).



Scheme 3. Aerobic Oxidation of 1-Octanol Catalyzed by PI-CB Catalysts

Aerobic Oxidation of Alcohols Catalyzed by PI-CB Catalysts in Flow Systems

Application to flow system is one of advantages of immobilized catalysts. As for flow systems for aerobic oxidation of alcohols using heterogeneous catalysts, there are only a few reports of multiphase reactions in microreactor systems, capillary systems, multichannel reactor systems, and only one report of a conventional packed flow system. In addition, while gas–solid, liquid–liquid or liquid–solid biphasic conditions are common in flow systems, examples of gas–liquid–solid multiphase

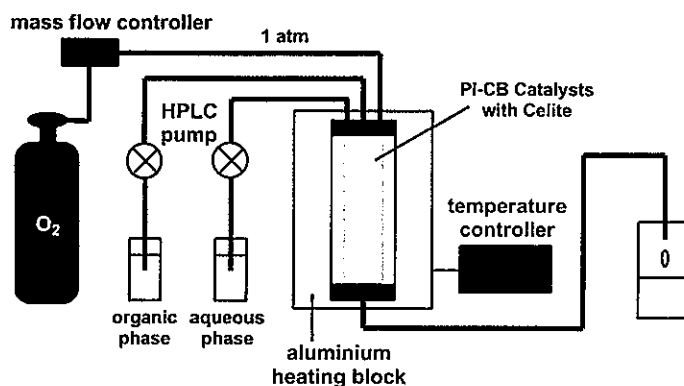


Figure 2. The gas–liquid–liquid–solid multiphase flow system

conditions are very rare. I examined the aerobic oxidation of alcohols catalyzed by PI-CB catalysts in gas-liquid-solid multiphase flow systems (Figure 2). As a result, flow systems were found to show higher conversion and selectivity than batch systems. In the case of selective oxidation to an aldehyde, the batch system gave a higher yield (92%) than the flow system (81%); however, the selectivity of the flow system (98%) was higher than that of the batch system (92%). On the other hand, in the case of direct oxidative ester formation, the flow system showed much higher yield and selectivity (87% yield, 95% selectivity) than the batch system (78% yield, 90% selectivity). These results showed the advantages of flow systems because overoxidation could be prevented by controlling the residence time in the column. In addition, space-time-yield of flow systems was about 5 to 10 times higher than that of batch systems, which shows higher productivity in flow systems. It is also noted that the activity of the catalyst inside the column could be maintained and the yield and the selectivity were constant for several days.

Conclusion

Novel carbon-stabilized polymer-incarcerated (PI-CB) bimetallic nanocluster catalysts, PI-CB/Au-Pt and PI-CB/Au-Pd, were prepared and their properties were characterized. These catalysts were then applied for the selective aerobic oxidation of alcohols. While PI-CB/Au-Pt catalysts provided aldehydes/carboxylic acids, PI-CB/Au-Pd catalysts gave esters. Differences between Au-Pt and Au-Pd clusters were considered to be key for selective formation of aldehydes/carboxylic acids and esters. These catalysts could be applied to reactions in flow systems and those in autoclave, and these reaction environments showed characteristic reactivity and selectivity compared to those in batch systems.

【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.