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論文内容の要旨

Two decades have passed since the pioneering work by Prof. Haruta presented nanogold as a novel catalyst for CO oxidation reaction. Such groundbreaking, together with the subsequent employment of gold catalysis in the oxidation reactions opens a new exciting scenario in organic transformations. The novelty of nanoscale materials arises from their size effect so called “quantum size effect”. Gold is one of the very useful alloying metal elements due to its relatively low reactivity so that it has been used in bi-metallization with many metals. They are particularly important in the field of catalysis since they often exhibit excellent catalytic activities, which are superior to those of corresponding monometallic counterparts. In this thesis, a new method for the formation of carbon-carbon bond under ambient conditions by using gold or gold/palladium alloy bimetallic catalysts have been described.

In Chapter 2, the dual functions of matrices (chitosan and starch) such as stabilization of the metal nanoclusters as well as activation of the substrate in aerobic oxidative homocoupling of phenylboronic acids are described. To explore the dual function of “protective agents”, gold nanoclusters stabilized by polyhydroxy matrices including biopolymer (chitosan and starch) (Au:chit, 2.3 ± 0.2 nm, Au:starch 2.1 ± 0.6 nm) were prepared. Thus, prepared Au nanoclusters catalyzed oxidative homocoupling of arylboronic acids under acidic conditions of pH 4.57 (acetate buffer). As a result, up to 96% selectivity of biphenyl was achieved with trace oxidation products including phenol. The most remarkable finding regarding this reaction is that the homocoupling product was formed even in the absence of base, which is commonly required to activate the substrate before transmetalation. On the basis of the overall reaction trends, kinetics, and spectroscopic analysis, it was concluded that the hydroxyl groups of polymer interacts with phenylboronic acid and activated it before transmetalation on Au.

The hydroxyl groups of polymer which are located at the interface between the hydrophobic part of the matrix and the water solvent play an important role in dragging the boronic acid into the interior part of the catalyst near the gold surface by means of reversible binding. The competitive oxidation reaction is suppressed because the acidic reaction conditions favor the formation of the biphenyl. Catalyst Au:chit can easily be separated and can be reused up to three cycles.

In Chapter 3, anomalous effect of bimetallic Au/Pd nanoclusters in the activation of C-Cl bond toward Suzuki-Miyaura coupling reaction is described. The author describes a new mechanistic concept of bimetallic catalyst, which can easily activate the strong C-Cl bond in Suzuki-Miyaura coupling reaction under ambient conditions (room temperature, aqueous conditions). It is important to point out that this reaction does not proceed in the presence of monometallic clusters, indicating that synergetic effect of bimetallic system is crucial for coupling reaction to occur. For an example, equimolar amounts of chlorobenzoic acid and $\text{PhB}(\text{OH})_2$ were used as reactants for the reactions

catalyzed by Au_{0.5}Pd_{0.5}:PVP (1:1 ratio of Au and Pd) in the presence of 300 mol% K₂CO₃ at room temperature under degassed conditions. The Suzuki-Miyaura-type cross-coupling product was obtained along with homocoupling product of PhB(OH)₂ in 1:2 molar ratios. The homocoupling of PhB(OH)₂ should only be formed in the presence of oxidant. However, biphenyl was observed even in the absence of oxidant in fair competition with cross-coupling product. The constant ratios of cross-coupling and homocoupling products formed in each time interval suggested that both of products should be formed through single cycle. By careful monitoring of side product from boronic acid during the reaction, diboron was detected by ¹¹B-NMR, which confirmed that the homocoupling product was formed through formal metathesis-type reaction not by oxidative coupling mechanism.

Hence, the major finding of this research is Au/Pd alloy nanoclusters stabilized by poly (*N*-vinylpyrrolidone) catalyze two different reactions of phenylboronic acid with 4-chlorobenzoic acid at room temperature in a single reaction cycle.

In Chapter 4, a new method for activation of C-Cl bond at low temperature as a result of bimetallic Au/Pd synergy is described. The first example of Ullmann coupling of chloroarenes at room temperature was achieved. The Ullmann coupling of 4-chlorotoluene (0.1 mmol) in *N,N*-dimethylformamide (DMF)/ H₂O (1:2, 1 mL DMF, 2 mL H₂O) in the presence of 150 mol% KOH at 27 °C under argon atmosphere using nanoclusters of bimetallic Au/Pd alloy gave the 98% yield of coupling product. The kinetic isotope effect on the pseudo-first-order kinetics of decay of 4-chlorotoluene ($k_H/k_D = 7.0$) using DMF and DMF-d₇ showed that DMF participates in the rate-limiting step, which probably involve a hydrogen-transfer process.

Hence, no external reductant such as Zn or formic acid was necessary under the reaction conditions. However, the reaction of 4-bromotoluene was much slower than that of 4-chlorotoluene and reaction was incomplete even after 24 hours, and gave coupling product in only 65%. A comparison of the observed reaction rate for the decay of 4-chlorotoluene was nearly 3 times higher than that of 4-bromotoluene. The significant difference in the rates of decay of C-Cl and C-Br showed the opposite trend in the catalytic activity of bimetallic Au/Pd catalyst to that of usual transition-metal catalyst for transformation of haloarenes.

In Chapter 5, the strong inhibitory influence of organic iodide (C-I) in colloidal gold and gold-based bimetallic catalyst was described. Since the discovery of the Ullmann coupling in 1901, and the following development of transition-metal catalyzed reactions, it was believed that the reactivity of the aromatic halides involving their oxidative addition process is in order C-I>C-Br>C-Cl. However, the finding of current result demonstrated that the Ullmann coupling of 4-chlorotoluene was relatively 3 times faster than 4-bromotoluene and no reaction was observed with 4-iodotoluene. So the reactivity of the Ullmann coupling of Ar-X catalyzed by Au_{0.5}Pd_{0.5}:PVP is C-Cl>C-Br>>C-I, completely opposite from the conventional catalysis. Further effort to find out the reason of no activity towards the 4-iodotoluene for Ullmann coupling reaction, it was found that the organic

iodides are selectively adsorbed on the surface of colloidal nanogold and completely inhibit the reaction rather than oxidative addition. UV-vis, Fluorescence spectra, XRD and SEM/EDS results showed that aryl iodides bind to the exposed surfaces of gold nanoclusters, thereby masking active sites for catalysis and acting as strong inhibitors.

In Chapter 6, some of the ongoing work of activation of C-Br bond by bimetallic Au/Pd alloy nanoclusters was described. Suzuki-Miyaura coupling reaction of 4-bromobenzoic acid with phenylboronic acid by using Au-rich bimetallic Au/Pd nanoclusters occurred on the surface of nanoparticles while leaching of Pd occurred by using Pd-rich bimetallic Au/Pd nanoclusters. The homocoupling product of phenylboronic acid was observed for Au-rich bimetallic catalyst even in the absence of oxidant and it was expected to occur by surface reaction. When the ratio of Pd was increased in bimetallic catalyst, the homocoupling product was decreased and cross-coupling product was increased which is probably due to leaching of Pd species in solution.

バルクの金が化学的に極めて安定で不活性であるのに対し、ナノメートルサイズのクラスター状態においては、酸素酸化などに対する極めて高い触媒活性が発現することが見出されて以来、金ナノクラスターの触媒機能ならびにその発現機構について精力的な研究が行われている。本学位論文は金ナノクラスター触媒活性を制御する手法として、保護マトリクスのデザインと異種金属の添加効果について記述され、序論（第1章）と結論（第7章）を含めて全7章で構成されている。

第2章では、キトサンやデンプンなどのヒドロキシ基を多く含む高分子で保護した金触媒の合成とその触媒活性について述べている。アリールボロン酸の酸化的ホモカップリング反応において、従来の触媒系より高活性かつ高選択的な反応が実現しており、その要因として、これらの高分子が金クラスターの保護だけでなく、ボロン酸の活性化に関与していることをNMR測定などから明らかにしている。この結果は、保護高分子を適切にデザインすることにより、触媒反応の精密制御が可能であることを意味しており、今後のクラスター触媒設計に対する新たな指針となりえる内容となっている。

第3章では、ポリ（ビニルピロリドン）で保護された金とパラジウムの合金クラスターの合成と、その鈴木-宮浦カップリング反応活性について述べている。芳香族塩素化物を反応基質としたカップリング反応は、通常過酷な条件が必要であり、実際に室温条件下フェニルボロン酸との反応では、金、パラジウムそれぞれ単独のクラスターでは全く反応が進行しない。一方、金/パラジウム合金クラスターを用いると室温でも反応が進行し、しかもその反応機構は従来知られている鈴木-宮浦カップリングとは全く異なることを見出している。本触媒反応は、金とパラジウムが協奏的に反応に関与することで初めて進行することを明らかにした。

第4章では、前章で見出した、金/パラジウム合金クラスター触媒が効率的に芳香族塩素化物を活性化する現象をUllmann反応へと応用した例について述べている。犠牲還元剤としてDMFを用いることで、これまで不可能だった芳香族塩素化物の室温でのUllmann反応を実現している。

第5章では、芳香族ヨウ素化物が金触媒あるいは金/パラジウム合金触媒に対する触媒毒になる現象について述べている。パラジウム触媒を用いた通常のカロスカップリング反応においては、一般には芳香族ヨウ素化物が最も反応活性であり芳香族塩素化物が最も不活性であるが、先のUllmann反応において、芳香族ヨウ素化物が触媒毒になること、さらにこの現象は金クラスター触媒一般に観測されることを見出した。紫外可視吸収スペクトル測定などにより、芳香族ヨウ素化物が金表面に安定に吸着することで、触媒を失活させていることを明らかにした。

第6章では、ヨウ素化物と塩素化物の中間の反応性を持つ、芳香族臭素化物の反応挙動について述べている。臭素化物を用いた場合、金とパラジウムの混合比によって臭素化物によるパラジウムのリーチングとの競争となり、クラスター表面での触媒反応と、原子状のパラジウムによる触媒反応が共に観測されることを見出している。この結果は、現在、パラジウムクラスターの真の触媒活性サイトに関して、金属表面か遊離原子状種かという議論があるが、それに対するひとつの回答を与えている。

以上の結果は、金触媒の科学に新たな展開をもたらしただけでなく、従来の触媒化学の概念を大きく変える内容も含まれており、当該分野の研究の発展に大きく貢献する内容である。これらの成果の一部は既に査読付きの国際学術雑誌に2報公表され、さらに2報が現在投稿中であり、語学力に関しても学位授与に十分なレベルに達していると判断された。よって、本論文は博士（理学）の学位論文に値するものと認められる。