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学位論文題目 Size and Interfacial Effect on Gold Nanocluster Catalysts

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論文内容の要旨
Summary of thesis contents

Since the discovery of catalytic activity of nanogold catalyst for CO oxidation reaction by Prof. Haruta, nanogold catalyst becomes one of the novel catalysts for various types of oxidation reactions. In the field of catalysis, the nanogold have been developed to overcome the many difficulties by their excellent activity and selectivity against the reactions. In this current thesis, the size-controlled synthesis in both quasi-homogeneous and heterogeneous gold nanoclusters and understanding interfacial interaction between matrix and gold's surface have been described with the aim for further development of the gold nanocluster catalysts.

The novelty of nanoscale materials arises from the fact that with the decreasing size so-called "quantum size effect". It is well known that the catalytic activity of nanogold is highly dependent on its size and in general, smaller sized-nanogold shows superior activity. For example, previous reports from the author's laboratory demonstrated that the poly(*N*-vinyl pyrrolidone) (PVP)-stabilized colloidal gold nanoclusters (Au:PVP) (K-30)-catalyzed *p*-hydroxybenzyl alcohol oxidation using the clusters with 2 nm or less in mean size was extremely faster, and the catalytic activity increased rapidly with decreasing of core size. Moreover, matrices incorporation alters the nanomaterials' properties such as catalytic activity, reaction selectivity and electronic property. Typical system of homogeneous nanoclusters is constituted with the stabilizing polymers, which is important to inhibit agglomeration of the clusters through the steric bulk of the framework and bind weakly to the cluster surface via heteroatom as ligand in molecular complex. Previous experimental and theoretical studies have revealed that such kind of interaction between the stabilizing polymer and the nanogold induces the negative charge on the nanogold surface, which play an important role in the aerobic oxidation. Besides, the general perspective on gold nanoclusters based on the size and interfacial effects were described in chapter 1.

In chapter 2, the size-selective preparation of quasi-homogeneous gold nanoclusters is described. The author performed the preparation of gold nanoclusters stabilized by hydrophilic polymers with high viscosity; PVP (K-90) and star 2-methoxyethyl vinyl ether ((MOVE)₂₀₀) by utilizing micro-mixer. Since it has long been known that gold nanoclusters having smaller size exhibit better catalytic activity. However, in the synthesis of colloidal nanogold, there is a serious problem that the viscosity caused by the polymers impedes the kinetic control of agglomeration due to inefficient physical mixing. Therefore, the realization of small size of nanogold with highly viscose stabilizing polymer is quite difficult. To overcome this difficulty, the author successfully established the practical and reproducible method for the preparation of small-sized colloidal gold nanoclusters stabilized with highly viscose polymers by utilizing a micro-mixer. This method realized to produce smaller gold nanoclusters, which would have more catalytic superiority than those obtained by conventional batch methods. It should be noted that the mean size and size distribution were highly dependent on the type of micro-mixer employed, as well as the flow rate of the precursors' solutions. These results clearly indicate that the appropriate apparatus/reaction conditions should be considered carefully according to the application, for which the resulting gold nanoclusters are used.

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In order to carry out the polymer matrix effect, various and wide range of size of the clusters in the presence of the different types of polymers as well as the small size of them is necessary. Two important methods for the size-selective preparation of relatively large sized clusters have been reported, a seed-mediated growth method and a slow reduction method. By using seed-mediated growth method, the cluster size of different molecular weight of PVP; PVP (K-15), PVP (K-30), PVP (K-60) and PVP (K-90), have been prepared. By using 1.3-1.5 nm Au:PVP as seed, subsequent reduction of Au salt by Na_2SO_3 yielded a series of larger Au:PVP ranging from 5-9 nm. The larger particle size can also be obtained by the slow reduction method. The reduction by NaBH_4 in the presence of Na_2SO_3 , the 2.5 nm of Au:PVP could be obtained by the slow reduction method. This observation arose from the reduction of $\text{Na}_2\text{S}_2\text{O}_4$ which generated from the reaction between NaBH_4 under the presence of Na_2SO_3 caused slightly larger size.

Different from quasi-homogeneous gold nanoclusters, the size-controlled preparation is still not well developed in case of heterogeneous gold nanoclusters. The catalytic activity of heterogeneous gold nanoclusters is also markedly depending on the size and preparation method. However, most of the conventional preparation techniques yielded large gold nanoclusters with the diameter above 5 nm. In chapter 3, a new method for size-controlled synthesis of gold nanoclusters on metal oxide supports through trans-deposition process using various sized Au:PVP as gold precursors is discussed with focusing on the weak interaction of PVP with gold nanoclusters. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP) was used as the metal oxide support. The developed trans-deposition method realized the successful removal of PVP resulting in bare gold nanoclusters deposited on HAP. The size of gold nanoclusters from 1 to 8 nm scale was well preserved under the preparation conditions, which were confirmed by TEM measurement. The thus-obtained Au:HAP can be used for the oxidation of both primary and secondary alcohols toward corresponding oxidized product with excellent catalytic activity, selectivity and recyclability. The specific size around 5.2 nm exhibited highest catalytic activity.

HAP is known to have good profile as metal oxide support for various types of metals. HAP-supported gold nanoclusters prepared in chapter 3 were used as catalyst for aerobic homocoupling reaction of trifluorophenylboronate (PhBF_3K), which can suppress the generation of phenol byproduct as observed in case of using phenylboronic acid ($\text{PhB}(\text{OH})_2$). In chapter 4, the unusual yield profile of aerobic homocoupling of PhBF_3K observed in the course of study on the reactivity and the reusability of Au:HAP catalysts is described. After intensive characterization by XRD, TEM and EDX analysis, the transformation of metal oxide support's structure from HAP to fluorapatite (FAP) partially, then finally to calcium fluoride (CaF_2) was found. This structure transformation also affected to the catalytic activity of gold nanoclusters, which afforded the unusual yield profile in the reuse studies. Direct comparison of catalytic activity of gold nanoclusters deposited on HAP and F-contained supports (F-HAP) clearly showed the better catalytic activity of F-HAP than parent HAP with excellent reaction selectivity and stability. The partially fluoride-substituted HAP (F-HAP) is the best support for the above purpose. The F-HAP support satisfies both properties: the effective stabilization of AuNCs by phosphate moiety and the activation of C-B bond transmetallation through B-F interaction. In addition, the results suggested that the Au:F-HAP is superior catalyst to Au:HAP while Au: CaF_2 was found to be the one with the lowest

activity, reusability and stability.

As shown in chapter 1, nanogold with smaller size exhibits higher in catalytic activity due to quantum size effect because the electronic effect is preferred in smaller core size of nanoclusters due to more electronic charge distribute in orbitals of nanogold. Besides, the electronic properties of nanogold are also affected by polymer matrix. The experimental and calculation studies revealed that the interaction between C=O group of PVP monomer unit and gold surface plays an important role to lead negative charge on the gold surface, which promoted the catalytic activity of nanogold. In addition, it is long known that the molecular weight of stabilizing polymer can control the stability of nanoclusters. However, only a few reports are available about nanogold stabilized by different molecular weight as well as morphology or rheology of the same polymer. In chapter 5, the catalytic activity of various sized nanogold on aerobic oxidation based on the different molecular weight of PVP (K-30, K-60, K-90) is discussed to investigate the intrinsic ability of stabilizing polymers depending on their molecular weight. The size-controlled preparation of gold nanoclusters was performed by our original method discussed in chapter 2. The results obtained from the electronic and colloid structure studies clearly showed the generation of the anionic character on gold surface is highly dependent on molecular weight of PVP. Morphology effect overtook the size effect to control the catalytic activity. It is promising that not only the cluster size but polymer matrix also plays an important role on the catalytic activity of nanogold in terms of the broadening the variety of highly active gold nanoclusters catalysts. The experimental result revealed the 7 nm Au:PVP (K-90) exhibited up to 5 times larger than that of 1.3 nm Au:PVP (K-30). The extremely high negativity of the 7 nm Au:PVP(K-90) was caused by high surface coverage of PVP (K-90) on the gold surface. With this study, the new tactic can be established by correct matching of nanogold and PVP interaction which extremely enhance the catalytic activity of gold nanocluster catalysts.

The author could obtain the results that strong interface interaction can be induced if the chain length of the stabilizing polymers and the core size of the metal clusters are matched accordingly. It highly motivated the author to investigate that reaction control/selectivity on the surface reaction of the clusters by the influence from the structure and morphology of the stabilizing polymers only through the weak non-bonding interaction. Chirality induction should be a good research topic to elucidate this hypothesis because the chiral ligands such as phosphines, commonly used for the asymmetric metal complex catalyst, cannot be used for the cluster surface reaction due to the inhibition of the catalytic activity by their strong coordination. In chapter 6, preliminary study of a new insight into the chirality induction of gold nanoclusters by chiral polymer is described. Various types of copolymers between chiral-vinylpyrrolidone (chiral-VP) and vinylpyrrolidone (VP) were prepared in different molecular weight. A new chiral PVP has been developed by the co-polymerization of the *N*-vinylpyrrolidone (NVP) with the chiral substituted NVP at 4 position, which is prepared from the amino acid. The resulting chiral polymers (chiral-PVP) were used as stabilizing polymer on different size of nanogold clusters. Although the optical activity in metal-based electronic transition (MBET) was significantly weak compared with those observed in case of capping agent, the chiral-PVP-protected gold nanoclusters can act as the catalyst and give high enantio-selectivity toward hydroamination reaction only in case of particular metal core

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size and the polymer chain length. The fact possibly indicates as expectedly, that the strong interface interaction induces the chirality on the surface of AuNCs, inducing the chirality in the hydroamination reaction. However, it is also true that there are several contradictions. Therefore, further studies should be requested to prove the possibility of the chiral induction only through the non-bonding interaction from the polymer matrix.

Up to the present, there some difficulties with the development of the new type of organic polymer-stabilized metal nanocatalyst, because the simple coordination model of the monomer unit has been used for the explanation of the polymer effect. Although the principle concept could be established, this explanation cannot reflex to the total system. In addition, the polymer matrix effect must be compared by using the clusters having the same core size in order to exclude the size effect. However, it should be noted that in previous reports the comparison was not able to compare the reactivity between the different chain length of polymers by using the same size for the suppression of the size effect. In this current thesis, the practical size-controlled preparation on both quasi-homogeneous and heterogeneous gold nanoclusters. The various sizes of AuNCs ranging from 1-9 nm stabilized by different molecular weight of PVP have been prepared. The new concept based on interaction between matrix and nanogold's surface were also established. The detail studies that addressed the influence of the clusters size and interfacial effects are helpful to understand phenomena on the surface which enable to design a new type of gold catalyst with high activity and selectivity, and stable catalyst by matching between stabilizing polymer and gold nanoclusters.

Summary of the results of the doctoral thesis screening

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、クラスターサイズおよび保護マトリクスとの界面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、本研究の実施に不可欠な技術である、様々な保護マトリクスに対して一般に適応可能なクラスターのサイズ選択的調製法の開発について述べている。特に、これまで高粘度高分子マトリクスにおいて困難であった1 nm程度の微小クラスターの調製を、特定の形状を有するマイクロミキサーを用いることで可能にした。

第3章では、第2章でサイズ選択的に調製したポリ(ビニルピロリドン)(PVP)保護金クラスター(Au:PVP)を出発として、サイズを保持したままヒドロキシアパタイト(HAP)上に担持する技術の開発について述べている。従来の調製法では実現できなかった幅広いサイズのHAP担持金クラスター(Au:HAP)を同一の手法で作分けすることに成功した。また、これらの触媒を用いて、金触媒の典型的な反応であるアルコールの空気酸化反応についてサイズ依存性を調べ、5 nm程度のクラスターの活性が高いことも明らかにした。

第4章では、固体担持金クラスター触媒における界面効果について述べている。金クラスター触媒の典型的反応の一つである有機ホウ素化合物の酸化的ホモカップリング反応において、第3章で調製したAu:HAP触媒を用いた検討の最中に発見した構造変化を詳細に追跡した結果、最終的にHAPの一部をフッ素イオンに変換したF-HAP担持体が本反応に最も適しており、高い反応性と安定性を獲得することを明らかにした。この担持体はアパタイト骨格による金クラスターへの高い安定化効果とフッ素による炭素-ホウ素結合への高い活性化の両方の機能を併せ持っているためと考えられる。このように担持体の構造を精緻にデザインすることにより、高活性な触媒が開発できることを示した。

第5章では、高分子マトリクスのモルフォロジー効果について述べている。高分子を保護マトリクスとした場合の化学組成の影響についての研究例はあるが、鎖長の影響についてはほとんど研究されてこなかった。今回、第2章で開発した手法により様々な鎖長のPVPを用いた金触媒を用いて空気酸化反応の触媒活性に対する鎖長依存性を調べたところ、すべての反応において高分子量(平均分子量360,000)のPVPで保護した7 nm程度のサイズの触媒が他を圧倒して高活性であることを見出した。これは従来の「クラスター触媒はサイズが小さいほど活性である」という常識を大きく覆すものである。この触媒においては、特異的に金属表面が電子豊富な状態になっていることがX線光電子スペクトルにより確認されている。コロイドサイズ測定の結果と合わせ、高分子の鎖の長さでクラスターサイズがマッチすると顕著なモルフォロジー効果が発現し、マトリクスからの強い相互作用により活性が大きく向上する、という従来にはない触媒設計に対する提案を行っている。

第6章では、第5章までの知見に基づき、キラル高分子の合成及びそれを用いた金クラスター表面での不斉誘起の可能性について述べている。

以上の結果は、従来の金クラスター触媒の常識を覆す内容を含んでおり、新たな触媒デザインの可能性を切り拓くものとして、当該分野の研究の発展に大きく貢献する内容であ

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