Simple Homopolymer-incarcerated Gold Nanoclusters Prepared by Self-assembled Encapsulation with Aluminum Reagents as Crosslinkers: Catalysts for Aerobic Oxidation Reactions

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Simple homopolymer-incarcerated gold nanocluster catalysts were developed using a self-assembled encapsulation strategy. In this method, Red-Al[®] acting as a reductant also played the role of an inter-crosslinker via the formation of tetraalkoxyaluminate with the hydroxy groups in a homopolymer. Gold nanoclusters could be immobilized at high loadings without aggregation, and high catalytic activities were observed in several aerobic oxidation reactions.

Heterogeneous metal nanoclusters as catalysts have attracted much attention because of their robustness and unique activity.¹ In particular, gold nanoclusters have been shown to possess remarkable catalytic activities for oxidation reactions and have been widely studied.² Our group has developed polystyrenebased copolymers with crosslinking moieties, which incarcerate gold nanocluster catalysts via microencapsulation and crosslinking.³ In this method, nanoclusters are formed by the reduction of gold salts with NaBH₄ in a solution of the polymer, and they can be stabilized by weak, but multiple, π interactions between the benzene rings of the polymer and the nanocluster surface. Addition of a poor solvent for the polymer to the mixture precipitates the microencapsulated catalyst. Precipitates containing gold nanoclusters prepared in this way are heated under neat conditions to afford a solid catalyst: polymerincarcerated Au (PI-Au). Using PI-Au, we have demonstrated various aerobic oxidation reactions.⁴ We then improved this technique by introducing spherical carbon black with high specific surface area as a second support to expand the surface area of the catalyst (PI/CB-M).5 Gold nanoclusters were highly dispersed over the polymer matrix that was stabilized on the surface of the carbon black and were immobilized at high loadings (ca. 0.28 mmol g^{-1}) without loss of catalytic activity. In contrast, PI-Au could not maintain high catalytic activity with such a high loading because of aggregation of the nanoclusters.^{3a} Using this method, we successfully demonstrated various interesting metal nanocluster-catalyzed reactions.⁶ None of the catalysts caused any significant metal leaching, and the catalysts were easily recovered and reused.

Although we have previously demonstrated a wide range of applications of our method, the preparation of copolymers from synthesized monomers is required. In our current strategy, both epoxy and hydroxy groups as internal crosslinkers were introduced into polymers to afford solid solvent-tolerant catalysts through an attack of hydroxy groups to open epoxy rings to form crosslinkages (Scheme 1a). Simplifying the structure of the polymer, an alternative approach to using an internal crosslinking strategy, such as an external addition of crosslinkers, may be beneficial. Recently, we achieved coimmobilization of a Au–Pd bimetallic catalyst and a boron catalyst using our PI method and performed sequential aerobic oxidation–Michael



Scheme 1. Polymers with crosslinkers.



Scheme 2. Preparation of PIAL-Au catalyst.

addition of 1,3-dicarbonyl compounds to allylic alcohols using this catalyst.^{6c} In this report, we found that tetraalkoxyborates, which are catalysts for Michael addition reactions, formed from the NaBH₄ and hydroxy groups in the polymer backbone. Although the borates could be flushed out by water, these results implied the possibility of crosslinking from the formation of metal alkoxides between reductants and polymers bearing hydroxy groups (Scheme 1b). For example, it is known that aluminum tetraalkoxide can be synthesized from alcoholysis of aluminum hydrides.⁷ Herein, we report a simple and readily prepared homopolymer-incarcerated gold nanocluster catalyst using self-assembled encapsulation and an aluminum reagent as a reductant and an inter-crosslinking agent.

We chose a (4-vinylphenyl)methanol-derived homopolymer as the support and sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al[®]) that has two roles: as a reductant to generate a metal nanocluster from a metal salt and as an inter-crosslinking reagent to form aluminates from the hydroxy groups in the polymer (Scheme 2). A reddish purple solid appeared immediately on addition of Red-Al[®] to a THF solution of the polymer and a gold salt. This indicated that reduction to form nanoclusters occurred immediately and that crosslinking occurred

OH PIAL-Au X (1 mol%) K₂CO₃ (3 equiv) rt. O₂. BTF/H₂O. 5 h Catalyst Target loading Au Actual loading Au/Al Yield Entry $/\text{mmol g}^{-1 a}$ /%^b X /mmol g⁻ 1 0.08 0.067/3.017 82 1 2 2 0.16 0.150/2.555 85 3 3 0.32 0.297/2.466 95 4 0.394/1.926 4 0.48 84

Table 1. Aerobic oxidation of an alcohol to a ketone with PIAL-Au

^aDetermined by ICP analysis. ^bDetermined by GC analysis. ^cThe catalyst was prepared from a 4-vinylphenol-derived polymer. ^dLiAlH₄ was used instead of Red-Al[®] during the preparation of the catalyst.

0.049/3.952

0.034/4.213

16

3

0.08

0.08

5°

6^d

5

6

between the alcohol moieties in the polymer and the tetravalent aluminum species. Addition of ether as a poor solvent to the polymer completed the precipitation, but the generated solid was partially soluble in THF. This is probably because of incomplete crosslinking. The precipitate was heated at 150 °C under neat conditions to accomplish crosslinking, washed with several solvents, and then reheated to afford the polymer-incarcerated aluminum and gold nanocluster catalysts (PIAL-Au 1-4). The solid catalysts obtained were completely insoluble in solvents such as THF, DCM, and water. Inductively coupled plasma (ICP) analysis revealed that most of the gold used during the preparation was immobilized on the catalyst. The alkoxide groups on the tetravalent aluminate may not have been fully exchanged with the alcohol moieties in the homopolymer before heating, and complete exchange of the alkoxides could be facilitated by heating to afford an insoluble solid catalyst. As a result, a high concentration of aluminum was also detected by ICP analysis, even after the catalyst had been washed with water. The borates could be easily washed out with water.^{6c} This indicates that the aluminate produced in the polymer matrix was much more stable than the borate in the presence of water, probably because of the higher coordination number of aluminum, which would facilitate the formation of multiple bonds between aluminum and the hydroxy groups in the polymer and/or prevent dissociation of the aluminum-alkoxide bonds by water.

The catalytic activity was evaluated using the aerobic oxidation of an alcohol to a ketone (Table 1),^{3a} and the desired ketone was obtained in high yield (Entry 1). We increased the metal loading to evaluate how much of the gold could be immobilized using this method (Entries 2–4). It was confirmed using scanning transmission electron microscopy (STEM) analysis that no aggregation of nanoclusters occurred and that the size of the nanoclusters was restricted to ca. 2 nm in PIAL-Au **3** (Figure 1). Surprisingly, very high loadings (around 0.3–0.4 mmol g⁻¹) could be achieved while maintaining a small size of nanoclusters (2–3 nm) and a high catalytic activity. This is in contrast to previous studies, which have indicated that increased loadings of gold caused aggregation and loss of catalytic activity.^{3a} In the current system, the nanoclusters were efficiently stabilized even at high loadings, probably because the formation



Figure 1. STEM image of PIAL-Au 3.



Scheme 3. Aerobic oxidation of a primary alcohol to an aldehyde.



Scheme 4. Aerobic oxidation of a hydroquinone to a quinone.

of aluminates occurred simultaneously during the reduction of gold salts, and thus, the gold nanoclusters would be encapsulated immediately and strongly stabilized after the formation of the gold nanoclusters. A 4-vinylphenol-derived polymer was examined as a control, but reduced metal loading was observed, probably because of the poor flexibility of the polymer, and the reduced nucleophilic nature of the hydroxy group made it difficult to form stable tetraalkoxyaluminate species (Entry 5). When lithium aluminum hydride was used instead of Red-Al[®], a low metal loading and poor catalytic activity were observed (Entry 6). STEM analysis confirmed the aggregation of the gold nanoclusters (see Supporting Information for more details). If a stronger reductant is used, then the rate of the reduction may be too fast and aggregation would occur before the formation of the tetraalkoxyaluminate species and subsequent stabilization of the nanoclusters.

We also tested PIAL-Au **3** for aerobic oxidation of a primary alcohol to an aldehyde^{3a} (Scheme 3), a hydroquinone to a quinone^{4b} (Scheme 4), an amine to an imine⁴ⁱ (Scheme 5), and aerobic oxidative methyl esterification from an alcohol in methanol^{4g} (Scheme 6). In all reactions, PIAL-Au **3** showed a high activity and the desired products were obtained in high yields.



Scheme 5. Aerobic oxidation of an amine to an imine.



Scheme 6. Aerobic oxidative methyl esterification from an alcohol.

In conclusion, we have developed PIAL-Au through the self-assembly of a simple homopolymer, a gold salt, and Red-Al[®]. In this simple preparation method to form polymerimmobilized gold nanoclusters, Red-Al® played two important roles: it reduced the gold salt to generate small gold nanoclusters, and it subsequently made it possible to form intercrosslinks of the side chains of the homopolymer by the formation of tetraalkoxyaluminate to afford microencapsulated gold nanoclusters while maintaining their small size. High loadings of gold could be achieved without aggregation of the gold nanoclusters and a high catalytic activity was confirmed in several aerobic oxidation reactions. This new class of immobilization method may make it easier to prepare various metal nanocluster catalysts. Detailed structural analysis and further application of this methodology to other catalytic reactions is ongoing in our laboratory.

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Supporting Information is available electronically on J-STAGE.

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