Heterogeneous Catalysis

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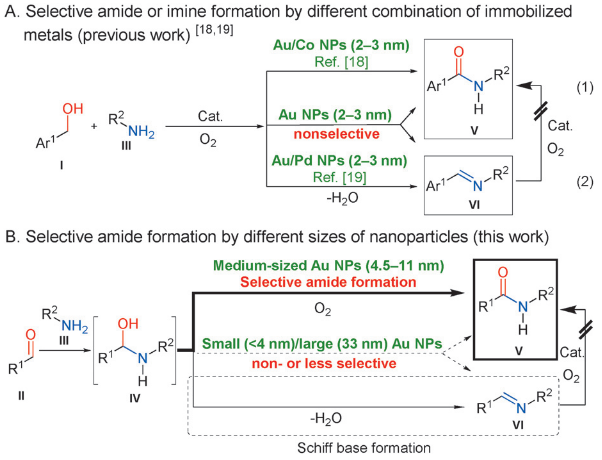
Size of Gold Nanoparticles Driving Selective Amide Synthesis through Aerobic Condensation of Aldehydes and Amines**

*Hiroyuki Miyamura, Hyemin Min, Jean-François Soulé, and Shū Kobayashi**

Abstract: *Metal nanoparticles (NPs) have attracted much attention in many fields due to their intrinsic characteristics. It is generally accepted that smaller NPs (1.5–3 nm) are more active than larger NPs, and reverse cases are very rare. We report here the direct aerobic oxidative amide synthesis from aldehydes and amines catalyzed by polymer-incarcerated gold (Au) NPs. A unique correlation between imine/amide selectivity and size of NPs was discovered; Au-NPs of medium size (4.5–11 nm) were found to be optimal. High yields were obtained with a broad range of substrates, including primary amines. Au-NPs of medium size could be recovered and reused several times without loss of activity, and they showed good activity and selectivity in amide formation from alcohols and amines.*

Metal nanoparticles (NPs) and nanoclusters (NCs) have received much attention as catalysts because of their distinct characteristics, which differ from those of both bulk metals and metal complexes.[1] Among various metal NP/NC catalysts, Au-NPs/Au-NCs have been investigated as efficient catalysts for aerobic oxidations.[2,3] One of the important factors that affect catalytic activity is the size of the Au-NPs/Au-NCs.[4] In the case of Au-NCs (<2 nm), each reaction has an optimal size or number of Au atoms that yields the best result.[5] On the other hand, intensive studies on the size effect of Au-NPs (>2 nm) have established that the catalytic activity generally increases with decreasing size, and that smaller NPs usually show better performance.[6] Examples of the reverse phenomenon, in which activity increases with increasing particle size, are very limited.[7] We previously observed such a reverse phenomenon in the aerobic oxidation of amines to imines;[8] however, the reasons for this tendency (i.e., particles with larger diameter being more efficient) remain unclear.

The abundance of amide bonds in organic compounds has led to intense efforts to develop new methods for their synthesis over the last few decades.[9] Amide bonds were traditionally generated by condensation of carboxylic acids with amines;[10] however, stoichiometric amounts of activators or condensation reagents are required, and a large amount of waste is formed.[11] Alternatively, oxidative or dehydrogenative approaches from aldehydes or alcohols and amines are desirable methods from the viewpoint of green sustainable chemistry.[12,13] Aerobic oxidative reactions, in which molecular oxygen is used as an oxidant, are particularly efficient because the use of stoichiometric amounts of explosive oxidants can be avoided and because water is the only by-product (Scheme 1).[14,15] Despite these advantages, direct oxidative amide synthesis from aldehydes and amines is still challenging due to various possible side products.[15] The use of a combination of primary amines and aldehydes is particularly difficult because these substrates undergo facile formation of Schiff bases (Scheme 1B, Eq. (2)). To our knowledge, only one example of the use of formaldehyde under aerobic oxidative conditions with a quasi-homogeneous catalyst has been reported and, in this case, substrate generality was limited.[15]



Scheme 1. Aerobic oxidative amide synthesis with Au NPs.

We have developed aerobic oxidations by using heterogeneous Au-NPs immobilized in a copolymer containing cross-linking moieties (copolymer **A** in Table S1) either with or without carbon black (CB) as a stabilizer; the resulting material was referred to as polymer-incarcerated Au-NPs (PI(CB)-Au).[6b,16] We have also demonstrated the viability of incorporating these PI(CB)-Au and related bimetallic NP catalysts into tandem oxidation processes (TOPs),[17] and found that the formation of amides and imines from alcohols **I** and primary amines **III** could be controlled by using different

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[*] Dr. H. Miyamura, H. Min, Dr. J.-F. Soulé, Prof. Dr. S. Kobayashi
Department of Chemistry, School of Science
The University of Tokyo
Hongo, Bunkyo-ku, Tokyo, 113-0033 (Japan)
E-mail: shu_kobayashi@chem.s.u-tokyo.ac.jp

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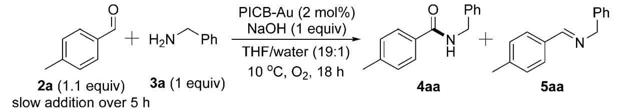
Table 1: Oxidative amidation—optimization and size effect.



Entry	Cat.	**4 aa**[a]	**4 aa/5 aa**[a]	Entry	Cat.	**4 aa**[a]	**4 aa/5 aa**[a]
1[b,d,e]	**1 a**[c]	36%	36:64	9	**1 e**	**96% (93%)**	**96**:4
2[b,d,e]	**1 a**	45%	45:55	10	**1 f**	64%	64:36
3[b,e,f]	**1 a**	65%	71:29	11	**1 g**	93%	93:7
4[b,f]	**1 a**	77%	89:11	12	**1 h**	92%	92:8
5	**1 a**	88%	88:12	13	**1 i**	92%	92:8
6	**1 b**	86%	86:14	14[g]	**1 e**	92%	93:7
7	**1 c**	89%	89:11	15[h]	**1 e**	91–96%	91:9
8	**1 d**	90%	90:10				96:4

[a] Determined by ^{1}H NMR analysis with respect to tetrachloroethane as internal standard; the isolated yield of **4 aa** is given in parentheses. [b] Reaction time, 12 h. [c] 1 mol%. [d] No slow addition. [e] Reaction was performed at room temperature. [f] Slow addition over 8 h. [g] Reaction was performed with 0.25 equiv NaOH. [h] Catalyst was recovered and reused three times after the experiment in entry 9.

combinations of immobilized metals: Au/Co for amide **V** synthesis[18] and Au/Pd for imine **VI** synthesis[19] (Scheme 1 A). In contrast to our previous observation, we report herein that the size of the Au-NPs controls the selectivity of the oxidative amide synthesis from aldehydes and alcohols (Scheme 1 B).

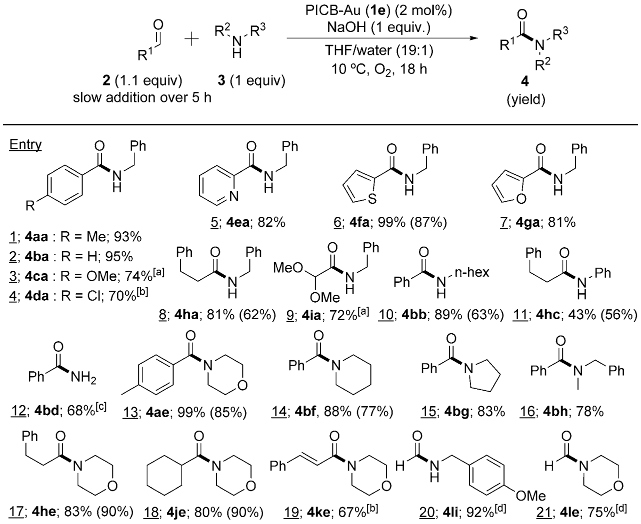
Firstly, we prepared different cluster sizes of PICB-Au catalysts: **1a:** 2.9 ± 1.0; **1b:** 3.4 ± 1.5; **1c:** 4.5 ± 1.4; **1d:** 6.0 ± 3.3; **1e:** 7.2 ± 2.5; **1f:** 33 ± 11; **1g:** 4.8 ± 1.9; **1h:** 5.2 ± 1.9; **1i:** 11 ± 4.9 nm (see the Supporting Information (SI), Table S1). Generally, small Au-NPs were formed at mild reduction temperature, whereas larger sizes of Au-NPs were obtained at increased temperature for addition and reduction of Au^I source (**1a**–**f**). Cross-linking conditions (existence of solvents) also affected the size of Au-NPs (**1g**–**i**).

With different cluster sizes of PICB-Au catalysts in hand, we next conducted oxidative amide synthesis from 4-tolualdehyde (**2a**; 1.1 equiv) and benzylamine (**3a**; 1 equiv) as model substrates in the presence of NaOH under ambient conditions (10 °C to rt, atmospheric oxygen; Table 1). After optimization of the reaction conditions with **1a** (entries 1–5), *N*-benzyl-4-methylbenzamide (**4aa**) was obtained as a major product (**4aa**/**5aa** = 88/12) at 10 °C using slow addition of **2a** over 5 h (entry 5). We then tried different sizes of the catalysts and found a strong dependence of the selectivity on the NP size (the **4aa**/**5aa** ratio; entries 5–13). A moderate selectivity was observed with catalysts containing small NPs (**1a** or **1b**), whose diameters were between 2.9–3.6 nm (entries 5 and 6). The selectivity increased to 90/10 (the **4aa**/**5aa** ratio) using the catalyst with NPs of medium size (**1c** or **1d**; entries 7 and 8). The best result was obtained using catalyst **1e** with an average diameter of 7.2 nm, and the desired amide **4aa** was isolated in 93% yield with a selectivity of 96/4 (entry 9). With the catalyst containing larger NPs (**1f**), the amide selectivity dramatically dropped (entry 10). When catalysts were used that contain other NPs of medium size (4.5–5.5 nm; **1g** and **1h**), which were generated by different preparation methods, excellent selectivities were also observed. Accordingly, the size of the NPs is an important factor for the selectivity regardless of the preparation method (entries 11 and 12). With catalyst **1i**, which has Au-NPs with around 11 nm average diameters, a good selectivity was also obtained (entry 13).

The use of Au-NPs of medium size (4.5–11 nm) resulted in good selectivity for amide formation; contrary to the poor results obtained with both smaller (2–4 nm) and very large (> 30 nm) Au-NPs. Moreover, only a catalytic amount of base (0.25 equiv) was sufficient when **1e** was used (entry 14). To demonstrate the stability and reusability of **1e**, four cycles of recovery and reuse experiments were successfully performed with stable activity (entries 9 and 15).

We then examined the substrate scope (Table 2). By using slightly modified conditions depending on the aldehyde substitutions, we could employ various benzaldehyde analogues (entries 1–4). Electron-rich *p*-methoxybenzaldehyde (**2c**) reacted well to give amide **4ca** in good yield (entry 3), whereas electron-poor *p*-chlorobenzaldehyde (**2d**) gave the corresponding amide at 0 °C (entry 4). Heteroaromatic aldehydes also reacted well with **3a** (entries 5–7). Aliphatic aldehyde **2h** was oxidized smoothly (entry 8), and an aldehyde containing an acetal moiety was also a suitable substrate (entry 9). As for the scope of the amine partners, aliphatic primary amine **3b** reacted smoothly with benzaldehyde (**2b**; entry 10), but less basic amines such as aniline (**3c**) showed moderate reactivity (entry 11). A primary amide could be obtained by using aqueous ammonia solution (entry 12). Cyclic secondary amines, morpholine (**3e**), piperidine (**3f**), and pyrrolidine (**3g**), reacted well with **2b** (entries 13–15). The noncyclic secondary amine *N*-methyl-

Table 2: Scope of the reaction.

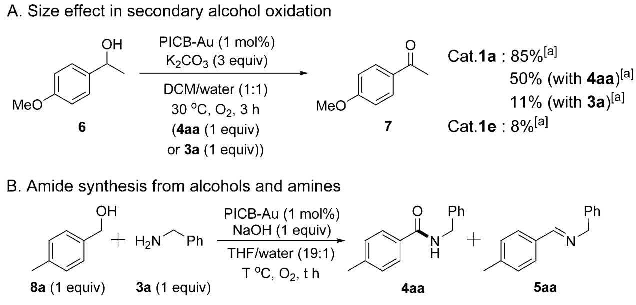


Yields are those of isolated products. [*] The number in parenthesis is the yield of the isolated product with 0.25 equiv of NaOH. [a] Reaction was performed at 25 °C. [b] Reaction was performed at 0 °C. [c] 6 equiv of aqueous ammonia was used. [d] 1.5 equiv of aqueous formaldehyde was used.

N-benzylamine (**3h**) also reacted well (entry 16). Aliphatic aldehydes **2h** and **2j** gave tertiary amides with **3e** in high yields (entries 17 and 18). High amide yields obtained with aliphatic aldehydes without undesired enamine formation and concomitant aldol products also highlight another useful feature of our catalytic systems (entries 8, 9, 17, and 18). Cinnamaldehyde (**2k**) gave amide **4ke** at 0 °C with complete integrity of the double bond (entry 19). Almost 1:1 mixtures of aldehydes and amines were sufficient to obtain amides effectively in most cases. In addition, a catalytic amount of base was enough to achieve satisfactory results (Table 2, entries 6, 8, 10, 11, 13, and 14). Moreover, in the cases of aliphatic aldehydes with a secondary amine or aniline, improved yields were obtained, probably because of suppressed side-reactions (Table 2, entries 11, 17, and 18). Finally, formylation reactions using formalin worked well (entries 20 and 21), hence the reaction proceeds through a hemiaminal intermediate. This mechanism is similar to that reported by Sakurai et al. using Au:PVP,[15c] but is at odds with mechanisms proceeding via methylformate as a major intermediate, as proposed by Ishida et al. and by Tanaka and Asao et al. using Au-NPs and Au nanopore.[14d,20]

Further investigations using Au-NPs of medium size were carried out as shown in Table 3 (also see SI, Schemes S1–S4). In the oxidation reaction of 4-methoxy-α-methylbenzylalcohol (**6**) to 4-methoxyacetophenone (**7**) (Table 3 A),[16d] very different oxidation rates were observed for Au-NPs with different sizes; the oxidation rate with **1e** was much slower than **1a** (8 vs. 85 % yield of **7**), indicating that Au-NPs of medium size have less activity than small Au-NPs in a simple alcohol oxidation. Different activity depending on the size of the NPs was also observed in amide synthesis from 4-methylbenzylalcohol (**8a**) and benzylamine (**3a**; Table 3 B). With **1a**, the starting materials were almost completely consumed after 12 h, but the major product was imine **5aa** (entry 1). On the other hand, **1e** gave a higher yield of **4aa** and better selectivity than **1a**, despite a lower conversion (entry 2), and good yield of **4aa** was obtained under slightly optimized reaction conditions (entry 3). In contrast, the use of **1f** resulted in a very slow reaction rate and poor selectivity (entry 4). The substrate scope of amide synthesis from alcohols and amines by using Au-NPs of medium size is shown in the SI (Table S2).

Table 3: Further investigations with catalyst **1e**.



A. Size effect in secondary alcohol oxidation

B. Amide synthesis from alcohols and amines

Entry	Cat.	*T* [°C], *t* [h]	Conv.[b]	**4aa**[b]	**4aa/5aa**[b]
1	**1a**	25, 12	95%	45%	45:55
2	**1e**	25, 12	73%	66%	90:10
3[c]	**1e**	30, 24	**> 95%**	**94%**	**95:5**
4	**1f**	25, 12	63%	24%	50:50

[a] Determined by GC analysis with respect to anisole as internal standard. [b] Determined by ^{1}H NMR analysis with respect to tetrachloroethane as internal standard. [c] 2 mol% of **1e**.

We assume that there are two important factors that need to be considered to achieve excellent selectivity: efficiency in reaction integration and oxidation ability. First, oxidative amide formation from an aldehyde and an amine integrates two reaction steps: hemiaminal formation and oxidation. Friend et al. proposed a continuous reaction of hemiaminal formation and subsequent oxidation on an oxygen-covered metallic Au surface.[21] A similar cascade process without dissociation of a hemiaminal in the presence of molecular oxygen and an externally added base could proceed on Au-NPs of medium size (see SI, Figures S11 A and B). On the other hand, such efficient reaction integration may be difficult on the surface of small Au-NPs. It is well accepted that Au-NPs strongly interact with amide/amine,[22] and Tsukuda et al. reported that such interaction is larger with small NPs compared with large ones.[6c,23] We also confirmed that simple secondary alcohol oxidations using small Au-NPs were significantly suppressed by amide/amine (Table 3 A). Deprotonation of an amine adsorbed on NPs by a base, which is essential to the following hemiaminal formation,[24] is facilitated by electronic influence of molecular oxygen on the same surface, because various studies suggested partial electron transfer from ligated Au-NPs to adsorbed oxygen.[25] Available sites for oxygen adsorption are, however, decreased by strong interaction of amines with the surface, hence the hemiaminal formation becomes slower.[26] Large excess amines that have stronger interaction with the surface facilitate the hemiaminal desorption, thus the dissociated hemiaminal decomposes or is dehydrated to afford undesired imine. Generated amide also shows strong interaction with the surface of small NPs as Tsukuda et al. and Okumura et al. reported,[6c,22a] hence the slow dissociation of the amide decreases the available sites for catalysis and limits the turnover of the catalytic cycle.

Second, based on our previous studies[6b] and on the control experiments involving simple alcohol oxidation smaller/medium-sized Au-NPs possess higher oxidation ability than larger Au-NPs (Table 3 A).

It is assumed that these two factors are well balanced in Au-NPs of medium size, resulting in the smooth catalytic turnover and observed excellent amide selectivity (see SI, Figure S11 C).

On the other hands, in the case of amide formation from an alcohol, a lower oxidation ability to transform an alcohol to an aldehyde is preferred to avoid undesired background Schiff base formation, because slow but continuous supply of an aldehyde can be realized by the reduced oxidation rate of Au-NPs of medium size. This is similar to the effect of slow addition of an aldehyde.

In summary, we found a clear influence of Au-NPs size on amide formation from aldehydes and amines by using polymer-incarcerated Au-NPs and molecular oxygen. Au-NPs of medium size (4.5–11 nm diameter) were found to be optimal for the selective oxidative amidation from aldehydes and amines. A wide range of substrate combinations was applicable. In particular, the availability of formaldehyde, aliphatic aldehydes, and primary amines highlights the effectiveness of our catalytic system. To our knowledge, this is the first report of a highly selective amide synthesis from aldehydes and primary amines under aerobic oxidative conditions. We believe that our findings, especially the relationship between NP size and the reactivity and selectivity of catalysts, provide valuable information that can be used for the design of novel metal NP catalysts. Further mechanistic studies and applications of the size effect to other reactions are ongoing.

Keywords: aerobic oxidation · amide synthesis · gold nanoparticles · heterogeneous catalysis

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