1-2014

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Abstract
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Keywords
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Disciplines
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Room Temperature Hydroamination of Alkynes Catalyzed by Gold Clusters in Interfacially Cross-Linked Reverse Micelles

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Supporting Information

ABSTRACT: The microenvironment around a catalyst could have profound influence on catalysis. Gold clusters encapsulated within interfacially cross-linked reverse micelles catalyzed hydroamination of alkyne at room temperature instead of at 100 °C commonly required for gold nanoparticles. Different metal oxides introduced into the micelle core by sol−gel chemistry interacted with the gold clusters and modulated their catalysis, with silicon oxide being the most effective cocatalyst.

KEYWORDS: Au cluster, hydroamination, alkyne, sol−gel chemistry, catalysis, reverse micelle

Gold nanoparticles (AuNPs) can catalyze a wide range of reactions, including hydrogenation, oxidation, carbon−carbon bond formation, and C−N bond formation. In recent years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest. In comparison with years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest.

An important reaction catalyzed by gold catalysts is hydroamination of alkyne, an atom-economical reaction to a wide range of fine chemicals. Although the intramolecular reaction occurs rather readily, intermolecular hydroamination is quite challenging. The latter could be catalyzed by homogenous Au(I) or Au(III) complexes in the presence of acid promoters and special ligands. The acid promoters were reported to be replaced by acidic sites when Au(III) complexes were supported on Sn-containing MCM-41; the same report was supported on silica support, AuNPs could catalyze intermolecular hydroamination of alkynes, although rather harsh conditions (100 °C for 22 h) were required. Very recently, AuNPs supported on TiO2 were found to catalyze similar hydroamination at mild temperatures (40 °C) under visible light irradiation.

We recently reported a simple method to capture reverse micelles (RMs) by covalent fixation. Unlike dynamic RMs that constantly exchange surfactants and internal contents with one another, the interfacially cross-linked RMs (ICRMs) are stable core−shell organic nanoparticles with tunable properties. The size of their hydrophilic core, the alkyl density on the surface, and internal contents can be changed systematically either during the synthesis or through postmodification.

Herein, we report that gold clusters encapsulated within ICRMs are efficient catalysts for hydroamination of alkynes at room temperature. The benefit of Au,Ag,Ag@ICRMs (i.e., gold clusters encapsulated within ICRMs) is that the ICRM serves as both the template and the support for the catalysts, and the microenvironment around the catalyst could be tuned through introducing metal oxide into the ICRM core.

The synthesis and characterization of ICRMs from cross-linkable surfactants 1 and 2, as well as the template synthesis of Au@ICRMs, have been documented in detail previously. Briefly, the cross-linkable surfactant was dissolved in a heptane/chloroform mixture in the presence of a small amount of water (Scheme 1). The size of the water pool in the middle of the RM was determined by the water/surfactant ratio. UV irradiation in the presence of dithiothreitol (DTT, a hydrophilic cross-linker) and 2,2′-dimethoxy-2-phenylacetophenone (a photoinitiator) for 10−15 min was generally sufficient to cross-link the core of the RM to afford the ICRM. When a solution of the ICRM in chloroform was stirred with an aqueous solution of HAuCl4, the aurate ions exchanged with the bromide in the ICRM core and underwent a two-step elimination disproportionation reaction (eqs 1 and 2) to afford gold clusters, with the overall reaction shown in eq 3.

The size of the gold clusters (Au4 to Au23) was mainly controlled by W0 and the aurate loading (aurate/surfactant ratio) in the template synthesis. The gold clusters stayed inside the ICRM core probably because the overall Au−bromide complex was anionic and needed to stay inside the ICRM to help the ammonium-lined ICRM core to maintain charge neutrality. At high aurate loading (>50%), not all aurate was reduced to Au(0), according to our previous study.

\[
\text{AuX}_n^- + \text{AuX}_m^- + \text{X}_2 \rightarrow \text{AuX}_x^- + \text{X}_2
\]

Received: December 19, 2013
Revised: January 21, 2014
Published: January 22, 2014
Scheme 1. Preparation of Au\textsubscript{n}@ICRM

3AuX\textsubscript{2}\textsuperscript{−} ⇌ AuX\textsubscript{4}\textsuperscript{−} + 2Au(0) + 2X\textsuperscript{−}  \hbox{(2)}

2AuX\textsubscript{4}\textsuperscript{−} ⇌ 2Au(0) + 3X\textsubscript{2} + 2X\textsuperscript{−} \hbox{(3)}

Our model hydroamination was between 1-octyne and aniline. To our delight, the alkyl corona of the ICRMs made Au\textsubscript{n}@ICRMs freely soluble in the reactants and allowed us to carry out the reaction under solvent-free conditions. The reaction was performed at room temperature for 18 h with 1 mol % Au as the catalyst. Similar to what was reported in the literature,\textsuperscript{6} because some of the imine product hydrolyzed under typical reaction conditions, we added water at the end of the reaction to hydrolyze the product into ketone to facilitate determination of the yield by \textsuperscript{1}H NMR spectroscopy (Figure S1, Supporting Information). In the absence of aniline, 1-octyne was recovered under the same reaction conditions; thus, the 2-octanone obtained at the end of the reaction was NOT a result of simple hydration of alkyne catalyzed by gold.

Table 1 summarizes the reaction yields under different reaction conditions. We compared Au\textsubscript{n}@ICRMs prepared with the single-tailed surfactant 1 and the double-tailed 2. We also varied the amount of aurate loading in the template synthesis and W\textsubscript{0} for the ICRMs.

The most surprising result was the drastically different performance of Au\textsubscript{n}@ICRM(1) and Au\textsubscript{n}@ICRM(2). Regardless of the gold loading in template synthesis, Au\textsubscript{n}@ICRM(1) was completely inactive (Table 1, entries 1–2). In contrast, Au\textsubscript{n}@ICRM(2) displayed progressively higher activity with increasing gold loading in the core (entries 3–5). In addition to the alkyl density of the ICRM, the water/surfactant ratio was also critical to the catalysis. The reaction yield decreased at either W\textsubscript{0} = 2 or 20 for Au\textsubscript{n}@ICRM(2) while the gold loading in the ICRM core and the overall amount of gold were kept the same (entries 6–7). Without gold in the core, the ICRM was completely inactive, as expected (entry 8). Au(III) in the form of AuCl\textsubscript{4}\textsuperscript{−} was not a good catalyst itself, affording only 20% yield under the same reaction conditions, and formed gold black during the reaction (entry 9).

The main difference between ICRM(1) and ICRM(2) was the alkyl density on the shell. According to our previous study,\textsuperscript{8} ICRM(1), having a low density of alkyl groups, aggregates easily in many solvents (chloroform, THF, acetone) through alkyl interdigitation. ICRM(2), on the other hand, tends to exist as single nanoparticles. The same study also demonstrated that the template synthesis of gold clusters afforded similar results for the two ICRMs.

The enormously different reaction yields in Table 1 indicate that the catalytic hydroamination was sensitive to ICRM aggregation or some other differences between the two Au\textsubscript{n}@ICRMs. We noticed that gold black was formed in the case of Au\textsubscript{n}@ICRM(1) at the end of the reaction. Thus, the gold clusters encapsulated in the single-tailed ICRMs were not only inactive but also unstable under the reaction conditions. The formation of bulk gold suggests that the gold in ICRM(1) migrated out of the hydrophilic core in the presence of the reactants. Since both Au\textsubscript{n}@ICRMs are stable indefinitely in the absence of the reactants,\textsuperscript{8,10a} the gold migration/agglomeration might have been facilitated by the reactants (alkyne and amine) that could complex with gold and was understandably easier when the ICRMs aggregate.

The size of the gold clusters formed in the template synthesis with ICRMs depends on both the amount of aurate loading and W\textsubscript{0}.\textsuperscript{8,10a,11} Generally, the size of the gold clusters formed could be determined by the emission wavelengths of the particles.\textsuperscript{8,12} Our previous work indicates that, for ICRM(1) at W\textsubscript{0} = 5, 10% aurate loading in the template synthesis yielded mostly Au\textsubscript{9–10} clusters in the ICRM core, with an emission wavelength of 487 nm.\textsuperscript{10b} For Au\textsubscript{n}@ICRM(2) with W\textsubscript{0} = 5, the aurate/surfactant ratios (10, 30, and 50%) all afforded a main emission peak at 481 nm, indicative of similar gold clusters (Figures S2, Supporting Information). (As a reference, Au\textsubscript{8} clusters emit at ∼450 nm.)\textsuperscript{13} Meanwhile, a minor emission peak at 640 nm gradually increased with the increase in the gold loading, corresponding to the formation of Au\textsubscript{18} clusters.\textsuperscript{13} However, because the increase of W\textsubscript{0} from 2 to 5 to 20 progressively enhanced the 640 nm peak (Figure S3) but Au\textsubscript{n}@ICRM(2) with W\textsubscript{0} = 5 afforded the highest yield among the three, the catalytic activity of the gold clusters in the ICRMs was not simply a function of the cluster size. Other important parameters must also exist in the system.

In addition to cluster size, we examined the effects of different reduction methods in the template synthesis on the gold-catalyzed hydroamination. Our previous work already established that Au(III) could undergo the reaction shown in

Table 1. Hydroamination of 1-Octyne with Aniline Catalyzed by Au\textsubscript{n}@ICRMs\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>ICRM</th>
<th>Au loading, %</th>
<th>W\textsubscript{0}</th>
<th>yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ICRM(1)</td>
<td>30</td>
<td>5</td>
<td>0\textsuperscript{c}</td>
</tr>
<tr>
<td>2</td>
<td>ICRM(1)</td>
<td>50</td>
<td>5</td>
<td>0\textsuperscript{c}</td>
</tr>
<tr>
<td>3</td>
<td>ICRM(2)</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
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<td>30</td>
<td>5</td>
<td>49</td>
</tr>
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<td>ICRM(2)</td>
<td>50</td>
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<td>60</td>
</tr>
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<td>7</td>
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<td>50</td>
<td>20</td>
<td>42</td>
</tr>
<tr>
<td>8</td>
<td>ICRM(2)</td>
<td>0</td>
<td>5</td>
<td>0\textsuperscript{d}</td>
</tr>
<tr>
<td>9</td>
<td>HAuCl\textsubscript{4}</td>
<td>20</td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 0.25 mmol of 1-octyne, 0.25 mmol of aniline, and 1 mol % of catalyst at room temperature for 18 h. \textsuperscript{b}The reaction yield was determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{c}Metal black precipitates formed during the reaction. \textsuperscript{d}The reaction was carried out with the ICRMs only, without gold in the core.
eq 3 when bromide was the counterion in the ICRM core.\textsuperscript{10a} It is known that Au(III) undergoes reduction readily under UV irradiation.\textsuperscript{14} In our hands, because Au\textsubscript{n}@ICRM(2) with and without UV treatment gave identical yields in the hydroamination (Table 2, entries 1–2), the gold catalysts should be soluble in chloroform. In contrast, the same sol–gel synthesis in the absence of Au\textsubscript{n}@ICRM(2) yielded precipitate in the chloroform solution.

Table 3 shows that hydroamination was strongly influenced by the metal oxide around Au\textsubscript{n}@ICRM(2). In the absence of metal oxide, the hydroamination catalyzed by Au\textsubscript{n}@ICRM(2) gave 83% yield (with 2 mol % gold to substrate). SiO\textsubscript{2} was clearly the best cocatalyst, affording quantitative yield under the same conditions, possibly as a result of the acidity of the silica surface. A control experiment, with a physical mixture of Au\textsubscript{n}@ICRM(2) and SiO\textsubscript{2}@ICRM(2), showed no improvement in the reaction yield (data not shown). SiO\textsubscript{2}@ICRM(2) itself showed no activity (entry 6). Our study also showed that SnO\textsubscript{2} had little impact, and Al\textsubscript{2}O\textsubscript{3} lowered the yield slightly. The most unusual result was TiO\textsubscript{2}. In heterogeneous catalysis, TiO\textsubscript{2} is known to interact with AuNPs strongly to help the latter’s deposition and stability.\textsuperscript{25} In our hands, the small amount of TiO\textsubscript{2} completely shut down the catalysis. In addition, gold black was observed to form under the reaction conditions, indicating the instability of the gold clusters in the presence of TiO\textsubscript{2}.\textsuperscript{26} Our Au\textsubscript{n}–SiO\textsubscript{2}@ICRM(2) generally worked well for terminal alkynes and different substituted anilines (Table 4), all at room temperature and without any special ligands. Aliphatic amines did not show any reactivity (data not shown), possibly because of their stronger basicity and complexation with gold.\textsuperscript{5}

In summary, gold clusters encapsulated within ICRMs were found to be efficient catalyst systems for intermolecular hydroamination of alkynes. A unique feature of Au\textsubscript{n}@ICRM is the location of the gold clusters in the hydrophilic core of the cross-linked reverse micelles. Because reverse micelles are frequently used as templates to prepare inorganic nanoparticles,\textsuperscript{23} we could easily incorporate metal oxides in the ICRM core to fine-tune the catalysis.

To introduce metal oxide into the ICRM core, we first added 5 equiv of water\textsuperscript{24} relative to the surfactant to a chloroform solution of Au\textsubscript{n}@ICRM(2). A chloroform-soluble, hydrolyzable metal oxide precursor—e.g., Si(OMe)\textsubscript{4} for SiO\textsubscript{2}, SnCl\textsubscript{4} for SnO\textsubscript{2}, (s-BuO)\textsubscript{3}Al for Al\textsubscript{2}O\textsubscript{3} and Ti(OiPr)\textsubscript{4} for TiO\textsubscript{2}—was then added. Because the sol–gel reaction required water that was located in the ICRM core, hydrolysis was expected to occur near/inside the hydrophilic core. In general, hydrolysis was allowed to proceed for 24 h (48 h for SiO\textsubscript{2}) at room temperature and shown to be complete by the released alcohol side product monitored by \textsuperscript{1}H NMR spectroscopy. The metal oxide-modified Au\textsubscript{n}@ICRM(2) in all cases was completely soluble in chloroform.
hydroamination of alkenes at room temperature. The catalysts displayed a number of unusual features/trends from conventional AuNP catalysts, such as high activity, strong reliance on the bromide surface ligands, and unconventional interactions with locally introduced metal oxides (or their hydrates). Given the large tunability of metal-encapsulated ICRRMs, these metal cluster–ICRM composites may open new possibilities in catalyst design and applications.

**ASSOCIATED CONTENT**

Supporting Information
Experimential procedures, UV and fluorescence spectra for Au8@ICRRMs, and additional characterization data for the materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank the U.S. Department of Energy, Office of Basic Energy Sciences (Grant DE-SC0002142) for supporting the research. We thank Dr. Takeshi Kobayashi and Dr. Marek Pruski at the Ames Laboratory for acquiring the solid-state 29Si NMR spectra of Au8-SiO2@ICRM(2).

**REFERENCES**