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

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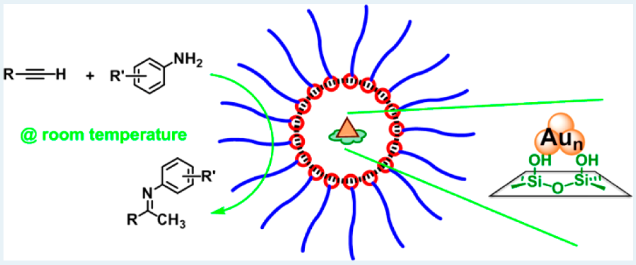
Supporting Information

ABSTRACT: The microenvironment around a catalyst could have profound influence on catalysis. Gold clusters encapsulated within interfacially cross-linked reverse micelles catalyzed hydroamination of alkynes 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.[1] In recent years, gold clusters, consisting of a few to tens of metal atoms, have attracted much research interest.[1,2] In comparison with their larger AuNP counterparts, metal clusters are characterized by an even higher surface-to-volume ratio. The abundance of low-coordinated gold atoms on the surface potentially could afford exceptional catalytic activity.[3]

An important reaction catalyzed by gold catalysts is hydroamination of alkyne, an atom-economical reaction to a wide range of fine chemicals.[4] Although the intramolecular reaction occurs rather readily, intermolecular hydroamination is quite challenging. The latter could be catalyzed by homogeneous Au(I) or Au(III) complexes in the presence of acid promoters and special ligands.[5] 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 indicated that colloidal gold displayed no catalytic activity under similar conditions.[5e] When deposited on a chitosan−silica support, AuNPs could catalyze intermolecular hydroamination of alkynes, although rather harsh conditions (100 °C for 22 h) were required.[6] Very recently, AuNPs supported on TiO_2 were found to catalyze similar hydroamination at mild temperatures (40 °C) under visible light irradiation.[7]

We recently reported a simple method to capture reverse micelles (RMs) by covalent fixation.[8] 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,[8] the alkyl density on the surface,[8,9] and internal contents[8,10] 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_n@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_n@ICRMs, have been documented in detail previously.[8,10a] 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 (i.e., W_0).

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 $HAuCl_4$, 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.[10a] The size of the gold clusters (Au_4 to Au_{23}) was mainly controlled by W_0 and the aurate loading (aurate/surfactant ratio) in the template synthesis. The gold clusters stayed inside the ICRM core probably because the overall Au_n−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.[10a]

$$AuX_4^- \leftrightharpoons AuX_2^- + X_2 \qquad (1)$$

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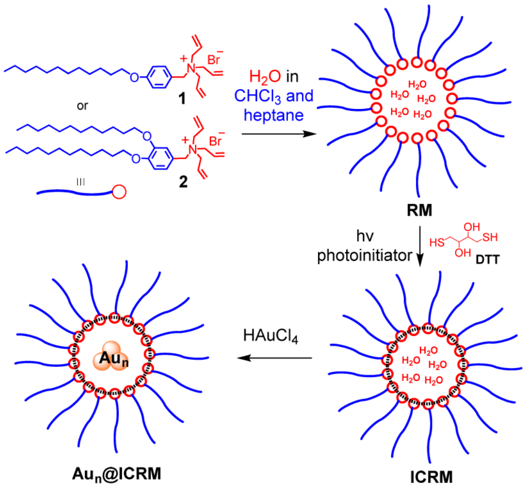
Scheme 1. Preparation of Au$_n$@ICRM



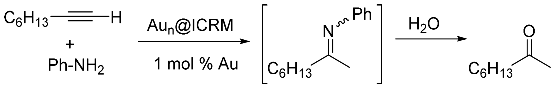
$$3AuX_2^- \leftrightarrows AuX_4^- + 2Au(0) + 2X^- \quad (2)$$

$$2AuX_4^- \leftrightarrows 2Au(0) + 3X_2 + 2X^- \quad (3)$$

Our model hydroamination was between 1-octyne and aniline. To our delight, the alkyl corona of the ICRMs made Au$_n$@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,[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 ^{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$_n$@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_0 for the ICRMs.

Table 1. Hydroamination of 1-Octyne with Aniline Catalyzed by Au$_n$@ICRMs[a]



entry	ICRM	Au loading, %	W_0	yield (%)[b]
1	ICRM(**1**)	30	5	0[c]
2	ICRM(**1**)	50	5	0[c]
3	ICRM(**2**)	10	5	0
4	ICRM(**2**)	30	5	49
5	ICRM(**2**)	50	5	69
6	ICRM(**2**)	50	2	60
7	ICRM(**2**)	50	20	42
8	ICRM(**2**)	0	5	0[d]
9	$HAuCl_4$			20[c]

[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. [b]The reaction yield was determined by ^{1}H NMR spectroscopy. [c]Metal black precipitates formed during the reaction. [d]The reaction was carried out with the ICRMs only, without gold in the core.

The most surprising result was the drastically different performance of Au$_n$@ICRM(**1**) and Au$_n$@ICRM(**2**). Regardless of the gold loading in template synthesis, Au$_n$@ICRM(**1**) was completely inactive (Table 1, entries 1−2). In contrast, Au$_n$@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_0 = 2 or 20 for Au$_n$@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 $AuCl_4^-$ 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,[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$_n$@ICRMs. We noticed that gold black was formed in the case of Au$_n$@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$_n$@ICRMs are stable indefinitely in the absence of the reactants,[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_0.[8,10a,11] Generally, the size of the gold clusters formed could be determined by the emission wavelengths of the particles.[8,12] Our previous work indicates that, for ICRM(**1**) at W_0 = 5, 10% aurate loading in the template synthesis yielded mostly Au_{9-10} clusters in the ICRM core, with an emission wavelength of 487 nm.[10a] For Au$_n$@ICRM(**2**) with W_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_8 clusters emit at ~450 nm.)[13] Meanwhile, a minor emission peak at 640 nm gradually increased with the increase in the gold loading, corresponding to the formation of Au_{18} clusters.[13] However, because the increase of W_0 from 2 to 5 to 20 progressively enhanced the 640 nm peak (Figure S3) but Au$_n$@ICRM(**2**) with W_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 eq 3 when bromide was the counteranion in the ICRM core.[10a] It is known that Au(III) undergoes reduction readily under UV irradiation.[14] In our hands, because Au$_n$@ICRM(**2**) with and without UV treatment gave identical yields in the hydroamination (Table 2, entries 1–2), the gold catalysts should be in the reduced form, Au(0). We were not surprised by the result because aniline could reduce both Au(I) and Au(III).[15] Thus, even if a small amount of oxidized gold was present before the catalysis, it should be reduced by a large excess of aniline during the hydroamination.[16]

Table 2. Hydroamination of 1-Octyne with Aniline Catalyzed by Au$_n$@ICRM(2)^a

entry	counteranion	reducing agent	yield (%)
1	Br	none	69
2	Br	UV	69
3	Br	$NaBH_4$	6
4	Cl	none	9
5	Cl	UV	12
6	Cl	$NaBH_4$	<5

[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.

Reduction of the ICRM-encapsulated aurate by sodium borohydride has been shown to produce AuNPs instead of clusters.[8] The AuNPs, with a characteristic brown color from the surface plasmon absorption,[17] gave only 6% yield in the hydroamination, confirming the higher activity of the cluster-based catalysts.

In the literature, bromide has been shown to poison the catalytic properties of, at least, larger AuNPs.[18] Much to our surprise, bromide in the ICRM core turned out critical to the catalysis. As seen from Table 2 (entries 4–6), with chloride as the counteranion, Au$_n$@ICRM(**2**) showed poor activity, regardless of the reducing conditions. The stability of gold clusters is affected by both the intrinsic stability of the gold core and the surface ligands.[19] For halides, the binding affinity follows the order of $F^- < Cl^- < Br^- < I^-$.[20] Bromide adsorption on the gold surface is quite strong and has been used to control the growth of gold nanomaterials.[21] Our results suggest that bromide adsorption played important roles in the stability/activity of the gold clusters within ICRM(**2**).

It is well-known that catalytic properties of metal particles on metal oxide support are strongly affected by the support.[22] A unique feature of Au$_n$@ICRMs 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,[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[24] relative to the surfactant to a chloroform solution of Au$_n$@ICRM(**2**). A chloroform-soluble, hydrolyzable metal oxide precursor—e.g., $Si(OMe)_4$ for SiO_2, $SnCl_4$ for SnO_2, $(s\text{-}BuO)_3Al$ for Al_2O_3, and $Ti(OiPr)_4$ for TiO_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_2) at room temperature and shown to be complete by the released alcohol side product monitored by ^1H NMR spectroscopy. The metal oxide-modified Au$_n$@ICRM(**2**) in all cases was completely soluble in chloroform. In contrast, the same sol–gel synthesis in the absence of Au$_n$@ICRM(**2**) yielded precipitate in the chloroform solution.

Table 3 shows that hydroamination was strongly influenced by the metal oxide around Au$_n$@ICRM(**2**). In the absence of metal oxide, the hydroamination catalyzed by Au$_n$@ICRM(**2**) gave 83% yield (with 2 mol % gold to substrate). SiO_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$_n$@ICRM(**2**) and SiO_2@ICRM(**2**), showed no improvement in the reaction yield (data not shown). SiO_2@ICRM(**2**) itself showed no activity (entry 6). Our study also showed that SnO_2 had little impact, and Al_2O_3 lowered the yield slightly. The most unusual result was TiO_2. In heterogeneous catalysis, TiO_2 is known to interact with AuNPs strongly to help the latter's deposition and stability.[25] In our hands, the small amount of TiO_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_2.[26] Our Au$_n$–SiO_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.[5]

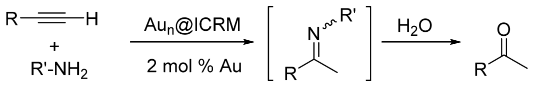
Table 3. Hydroamination of 1-Octyne with Aniline Catalyzed by Au$_n$–M_xO_y@ICRM(2)^a

entry	M_xO_y	yield (%)
1	None	83
2	SiO_2	>95
3	SnO_2	81
4	Al_2O_3	75
5	TiO_2	0^b
6	SiO_2	0^c

[a] Reaction conditions: 0.25 mmol of 1-octyne, 0.50 mmol of aniline, and 2 mol % of catalyst at room temperature for 24 h. [b] Metal black precipitates formed during the reaction. [c] The reaction was carried out with SiO_2–ICRM(**2**) without gold in the core

In summary, gold clusters encapsulated within ICRMs were found to be efficient catalyst systems for intermolecular

Table 4. Hydroamination of Alkynes Catalyzed by Au$_n$–SiO_2@ICRM(2)^a



entry	R	R′	yield (%)
1	n-C_6H_{13}	Ph	>95
2	n-$C_{10}H_{21}$	Ph	94
3	Ph	Ph	86
4	n-C_6H_{13}	4-Br-Ph	>95^b
5	n-C_6H_{13}	2-Br, 4-CH_3–Ph	>95
6	n-C_6H_{13}	3-Cl-Ph	>95

[a] Reaction conditions: 0.25 mmol of 1-octyne, 0.50 mmol of aniline, and 2 mol % of catalyst at room temperature for 24 h. The reaction yield was determined by ^1H NMR spectroscopy on the basis of the spectroscopic data of the known ketone end products. [b] Chloroform (0.1 mL) was added to the reaction mixture to dissolve 4-bromophenylaniline, which was a solid at room temperature.

hydroamination of alkynes 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).[26] Given the large tunability of metal-encapsulated ICRMs,[8−10] these metal cluster−ICRM composites may open new possibilities in catalyst design and applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, UV and fluorescence spectra for Au$_n$@ICRMs, 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.

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