MICROWAVE-ASSISTED CATALYTIC ACETYLATION OF ALCOHOLS BY GOLD-NANOPARTICLE–SUPPORTED GADOLINIUM COMPLEX

Tsao-Ching Chang and Shuchun Joyce Yu
Department of Chemistry and Biochemistry, National Chung Cheng University, Ming Hsüng, Chia Yi, Taiwan, China

GRAPHICAL ABSTRACT

Abstract A gold nanoparticle (AuNP)–supported gadolinium complex (RS-Au-L-Gd) catalyst was prepared through simple chelation of GdCl₃ to the surface-bound spacer, 1,4,7-tris(carboxymethyl)-10-(11-mercaptoundecyl)-1,4,7,10-tetraazacyclododecane (HSDO3A). This AuNP-supported Gd complex was found to be a highly effective catalyst for the acetylation of various alcohols and phenol in the presence of acetic anhydride. With a loading of 0.4 mol% of RS-Au-L-Gd, the almost complete transformation can be achieved in 60 s under microwave irradiation conditions. This hybrid catalyst was air stable, water soluble, dissolvable in many organic media, and precipitable. It can be readily recycled more than eight times without any significant loss of its catalytic activity.

Keywords Acetylation; gadolinium catalyst; gold nanoparticle supported catalyst

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Address correspondence to Shuchun Joyce Yu, Department of Chemistry and Biochemistry, National Chung Cheng University, Ming Hsüng, Chia Yi 621, Taiwan, ROC. E-mail: chejyy@ccu.edu.tw
INTRODUCTION

The preparation of complex and multifunctional organic molecules often demands protection and deprotection procedures to allow the survival of reactive functional groups before their transformation into the target molecules. Acetylation of alcohols is an important and routinely utilized protecting methods in organic chemistry.\textsuperscript{[1,2]} Since acetyl is one of the most common protecting groups used for the hydroxyl functionality because of its high stability\textsuperscript{[3]} in acidic conditions and ease of removal by mild alkaline hydrolysis.\textsuperscript{[4]} Many effective catalysts have been reported for acetylation of alcohols, such as organic acids and bases,\textsuperscript{[1b,5]} simple metal salts,\textsuperscript{[6]} metal triflates,\textsuperscript{[7]} and others.\textsuperscript{[8]} However, some of these catalysts are not fully satisfactory because of their toxicity, long reaction times, harsh reaction conditions, poor yields, time-consuming work-up procedures, and the production of corrosive chemical wastes. Furthermore, most of the metal triflates are relatively expensive and some need to be handled under critically anhydrous conditions for best results. To solve this problem, the strategy of immobilizing homogeneous transition-metal complexes to insoluble supports to prepare recoverable catalysts has been extensively applied in sustainable chemistry. This type of hybrid catalyst should be in principle congregating the advantages from both heterogeneous and homogeneous systems. A polymer-supported gadolinium triflate has been recently reported to be an effective heterogeneous catalyst for acetylation of alcohols.\textsuperscript{[7e]} This is a promising demonstration of a recyclable catalytic system. However, in many other cases, supported catalysts suffer a series of problems due to heterogenization and high costs.\textsuperscript{[9]} This has led to alternative liquid-phase methodologies to restore homogeneous reaction conditions. Hence soluble supports\textsuperscript{[10]} have been used to obtain detailed structures of the active catalysts, and much more fundamental knowledge about the catalyst modification, degradation, and at the interface would then become comprehensible.

Over the past few years, we have productively synthesized a series of gold-nanoparticle-supported metal complexes. Gold nanoparticles (AuNPs) are some of the most studied metal particles in the field of nanocatalysis. Alkanethiolate-protected AuNPs have been shown to present excellent solid surfaces similar to the (1 1 1) surface of bulk gold.\textsuperscript{[11]} These AuNPs also behave like soluble molecules, exhibiting both dissolvability and precipitability.\textsuperscript{[12]} Therefore, alkanethiolate-protected AuNPs are good candidates as supports for metal-complex catalysts, with the metal-nanoparticle catalyst combining the advantages of both supported and homogeneous catalysts. Several recent reports by our group and others have demonstrated the successful use of AuNP-supported metal-complex catalysts for various organic transformations.\textsuperscript{[13]}

In extension of our continuing studies on gold-nanoparticle-supported catalysts for sustainable and efficient synthetic procedures,\textsuperscript{[13a–c]} it is found that AuNP-supported Gd complex is an air-stable, water-soluble, mild, and efficient recyclable hybrid catalyst for the acetylation of various alcohols and phenol (Scheme 1). In addition, the rates of these catalytic acetylation reactions can be further accelerated under microwave (MW) irradiation conditions. Also, this AuNP-supported hybrid catalyst can be successively reused many times and its catalytic activity remains nearly unchanged even after eight cycles.
RESULTS AND DISCUSSION

Our design for the preparation of AuNP-supported Gd-complex catalyst is illustrated in Fig.1. Immobilization of complexes with use of covalent tethering techniques is, at present, the most favorable approach to design stable hybrid catalysts. \[10a\] The compound \([1,4,7\text{-tris(carboxymethyl)-10-(11-mercaptoundecyl)-1,4,7,10-tetraazacyclododecane (DO3ASH, 1)}\] was synthesized to be used as the tethering linker because the thiol end and the DO3A end have been demonstrated to readily bind surface Au and Gd\(^{3+}\), \[14\] respectively. The AuNPs surfaces were functionalized with use of the place-exchange method\[15\] by treating 155 mg of dodecanethiolate-covered AuNPs\[15c,16\] (Au-SR, 2.9 ± 0.9 nm) with various quantities of 1 (100–150 mg)
Table 1. Molecular Gd-DO3A (4)-catalyzed acetylation of alcohols

| Entry | Substrate        | Product | NMR yield $^c$ (isolated yield)$^d$ (%) |
|-------|------------------|---------|----------------------------------------|
| 1$^a$ | CH$_3$(CH$_2$)$_6$OH | $\text{H}_3\text{C}(\text{H}_2\text{C})_6\text{O}\text{OCH}_3$ | 65$^e$ 93$^e$ |
| 2$^a$ | CH$_3$(CH$_2$)$_{11}$OH | $\text{H}_3\text{C}(\text{H}_2\text{C})_{11}\text{O}\text{OCH}_3$ | 68 (65) 96 (95) |
| 3$^a$ | | | 64$^e$ 96$^e$ |
| 4$^a$ | | | 61 (60) 99 (98) |
| 5$^a$ | | | 51 (47) 92 (90) |
| 6$^a$ | | | 49 (46) 94 (90) |
| 7$^b$ | | | 41 (37) 78 (75) |
| 8$^b$ | | | 36 (32) 76 (75) |
| 9$^b$ | | | 14$^e$ 86 (85) |
| 10$^b$ | | | 13$^e$ 72 (70) |
| 11$^a$ | | | 22$^e$ 55$^e$ |

(Continued)
in CHCl₃ at ambient temperature for 24 h. The resulting mixed thiolates-covered AuNPs, RS-Au-L (2), have diameters of 2.5–3.6 nm. Because these surface functionalized AuNPs typically obtained under our reaction conditions are soluble in many organic solvents we could therefore use simple solution ¹H NMR spectroscopy to determine the average thiolate coverage and the amount of spacer linker loading. Molar ratios of L/RS ranging from 1:0.4 to 1:0.6, where RS = dodecanethiolate and L = DO₃ASH (see the Supplemental Material), can be obtained under our reaction conditions. Further treatment of 2 with GdCl₃ would make the molecular Gd-complex tethered onto AuNPs via direct binding with surface DO₃ASH. The resulting Gd-functionalized AuNPs, RS-Au-L-Gd (3), have average core sizes of 3.8–5.3 nm with the Gd loading levels of 0.35–0.37 mmol/g, which were determined by transmission electron microscopy (TEM) and inductively coupled plasma–atomic emission spectrometry (ICP-AES), respectively (see the Supplemental Material). The AuNP-supported form was also confirmed by energy-dispersive x-ray spectroscopy (EDX) and FT-IR spectroscopy. Meanwhile, as for the control study, the molecular Gd-complex (Gd-DO₃A, 4) was prepared according to the reported procedures.[17]

As for sustainability concern, MW radiation has been an alternative to conventional heating in organic synthesis for transforming electromagnetic energy into heat though highly dielectric media such as dimethylsulfoxide (DMSO), ROH (R = Me, Et, and Pr), and ethylene glycol for very rapidly heating.[18] However, because of the nature of most organic substrates, many reactions preferably proceed in less polar solvent systems which have substantially low dielectric constants.[19] In the current study, we have introduced AuNP not only as the catalyst support but also as a high MW-absorbing material that will couple MW effectively and get heated to high temperatures[20] very rapidly. Therefore, even with a heterogeneous system in a

| Entry | Substrate | Product | NMR yield° (isolated yield)° (%)| Thermal (60°C/4 h) | MW (300 W/60 s) |
|---|---|---|---|---|---|
| 12⁻ | | | | 0 | 18⁶ |

Note: Reaction conditions: solvent = DMF/H₂O = 4:1.

°Alcohol = 2 mmol, acetic anhydride = 6 mmol, catalyst 4 = 0.01 mmol (0.5 mol%).

⁻Alcohol = 0.5 mmol, acetic anhydride = 5 mmol, catalyst 4 = 0.01 mmol (2 mol %).

°NMR yield was determined by ¹H NMR spectroscopy analysis. The NMR signals of the α-CH₃ protons of the starting ROH and the α-CH₃ protons of acetate products were integrated against the OCH₃ protons (δ = 3.74 ppm) of a 0.045 M internal standard 4-idoanisole.

°Isolated yields were obtained either by column chromatography on silica gel (EA/hexane, 1/70) or by the extraction with CH₂Cl₂ (3 mL). The organic layer was then washed with DI water (3 × 5 mL), dried with Na₂SO₄, and evaporated under vacuum to afford the desired acetate products.

⁶Only the NMR yield was given, due to either the low conversion or the high volatility of the product.
Table 2. MW-assisted acetylation of alcohols and phenol catalyzed by RS-Au-L-Gd (3)

| Entry | Substrate      | Product         | NMR yield<sup>a</sup> (isolated yield<sup>b</sup> (%) |
|-------|----------------|-----------------|-----------------------------------------------|
|       |                |                 | No cat. Cat. 3                               |
| 1     | CH₃(CH₂)₆OH    | CH₃C₆H₄OCH₂CH₃ | 6 >99                                         |
| 2     | CH₃(CH₂)₁₁OH   | CH₃C₆H₄OCH₂CH₃ | 8 >99 (96)                                    |
| 3     | HO-<br>CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂      | 8 >99<sup>c</sup> | |
| 4     | Phenol         | Phenol          | 0 98 (94)                                      |
| 5     | Phenol         | Phenol          | 4 91 (90)                                      |
| 6     | Phenol         | Phenol          | 5 99 (98)                                      |
| 7     | Phenol         | Phenol          | 9 99 (97)                                      |
| 8     | Phenol         | Phenol          | 4 96 (93)                                      |
| 9     | Phenol         | Phenol          | 3 99 (96)                                      |
| 10    | Phenol         | Phenol          | 4 80 (77)                                      |

<sup>a</sup>NMR yield.<br><sup>b</sup>Isolated yield.<br><sup>c</sup>Continued.
low-MW-absorbing organic solvent, these AuNP-supported metal complex catalysts can still provide compatible catalytic activity to that of the corresponding homogeneous system.\[13a\] As shown in both Tables 1 and 2, the MW heating method provided significant rate acceleration as compared to the conventional thermal heating method. With a catalyst loading of 0.5–2 mol%, the MW-assisted, \(\text{4}\)-catalyzed reactions of primary alcohols and phenol offered 72–99% yields with final temperatures of 120–140 °C in 60 s (entries 1–10, Table 1), whereas the same catalyses gave much worse yields after 4 h under thermal conditions. Even with the less reactive, secondary alcohols such as L-menthol, the reaction under MW gave 18% yield in 60 s, while the same mixture at 60 °C for 4 h provided 0% conversion (entry 12, Table 1).

However, the Gd complex immobilized at the interphase, in a form of RS-Au-L-Gd (3), was found to be a very active catalyst for acetylation of alcohols and phenol under MW irradiation conditions. As shown in Table 2, with a catalyst loading of 0.4 mol%, the MW-assisted, \(\text{3}\)-catalyzed acetylation of primary alcohols and phenol were carried out heterogeneously in dimethylformamide (DMF)\[21\] to offer 91–99% yields of acetate products in 60 s (entries 1–9, Table 2). Even for bulky alcohols and less reactive alcohols, the AuNP-supported \(\text{3}\) (0.4 mol%) still offered 49–80% yields of products in 60 s, while the homogeneous reactions gave 18–72% yields when using molecular \(\text{4}\) (0.5–2 mol%) as the catalyst (entries 10–12 in Tables 1 and 2). Furthermore, similar MW-assisted reactions without the presence of Gd catalysts were carried out for the control study. It was found that the product conversions of 0–9% (Table 2) with final temperatures of 75–94 °C were obtained, while the MW-assisted, RS-Au-L-Gd (3)–catalyzed reactions gave 49–99% yields

### Table 2. Continued

| Entry | Substrate | Product | NMR yield\(a\) (isolated yield\(b\)) (%) |
|-------|-----------|---------|---------------------------------------|
|       |           |         | No cat.  | Cat. 3 |
| 11    |           | 3       | 75\(c\) |
| 12    |           | 0       | 52 (48) |

**Note**: Reaction conditions: alcohol = 0.5 mmol, acetic anhydride = 5 mmol, catalyst 3 = \(2 \times 10^{-3}\) mmol (0.4 mol%), solvent = DMF (80 µL).

\(a\)NMR yield was determined by \(^1\)H NMR spectroscopy analysis. The NMR signals of the \(\alpha\)-CH\(_2\) protons of the starting ROH, the \(\alpha\)-CH\(_2\) protons of acetate products were integrated against the OCH\(_3\) protons (\(\delta = 3.74\) ppm) of a 0.045 M internal standard 4-idoanisole.

\(b\)Isolated yields were obtained either by column chromatography on silica gel (EA/hexane, 1/70) or by the extraction with CH\(_2\)Cl\(_2\) (3 mL). The organic layer was then washed with DI water (3 × 5 mL), dried with Na\(_2\)SO\(_4\), and evaporated under vacuum to afford the desired acetate products.

\(c\)Only the NMR yield was given due to the high volatility of the product.

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of acetate products and final temperatures of 110–130 °C. These results suggested that AuNPs-containing reactions mixtures are indeed absorbing MW much more effectively to provide higher temperatures.[22]

Because the AuNP surface-bound Gd-complex catalysts in our study can be heterogeneously suspended in most organic solvents, they can be easily separated and quantitatively recovered from the reaction mixture through simple filtration. A series of catalyst recycling experiments were readily accomplished in the system containing 0.5 mol of phenol, 5 mmol of acetic anhydride, and 2 × 10⁻³ mol of RS-Au-L-Gd (3) (0.4 mol%) in DMF (80 µL) under 300 W MW radiation for 60 s. As shown in Table 3, the catalytic system can be effectively recycled with reactivity remaining at ≥94% yield throughout eight cycles.

CONCLUSION

In summary, we have developed a hybrid catalyst system by immobilizing molecular gadolinium(III) complex onto the surface of AuNPs. The resulting colloidal particles are air stable, water soluble, dissolvable in many organic media, and precipitable. We have also demonstrated a greener and highly efficient methodology for the acetylation of various alcohols and phenols by using this AuNP-bound interphase Gd catalyst under MW irradiation conditions. As compared to their corresponding unbound free form the AuNP-bound Gd complex was shown to be a more effective catalyst and provides significant reactivity enhancement. In addition, this hybrid catalyst can be successfully recycled more than eight times without any significant loss of its catalytic activity.

As demonstrated herein, hybrid catalysts of this type combine the advantages from both heterogeneous and homogeneous systems. It is expected that many sustainable and applicable catalysts of this form can be made by tethering a wide range of metal complexes or even organocatalysts to a variety of metal nanosurfaces.
and they may be useful for promoting many types of chemical reactions in a greener fashion.

EXPERIMENTAL

All chemicals were used as supplied without further purification. $^1$H NMR spectra were recorded in CDCl$_3$ and methanol-$d_4$ on a 400-MHz spectrometer (Bruker DPX-400), and coupling constants are reported in hertz. Chemical shifts are given in parts per million (ppm) relative to TMS. All MW irradiation experiments described herein were performed with a single-mode Discover Labmate System from CEM Corporation, using either a standard cylindrical Pyrex vessel for sealed vessel processing (capacity 10 mL) or a 10-mL Pyrex round-bottomed flask for open-vessel reflux chemistry.

Synthesis of AuNP-Supported Gd Complex (RS-Au-L-Gd, 3)$^{[23]}$

Aqueous NaOH (1 M, 2 mL) was added to a solution of AuNPs (2, 167 mg) and GdCl$_3$·6H$_2$O (154 mg, 0.20 mmol) in H$_2$O (3 mL) to maintain its pH at 6–8. After stirring for 24 h at room temperature, the reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in minimal H$_2$O (1 mL) and acetone (15 mL) was added to allow the precipitation of RS-Au-L-Gd (3), yield = 80 mg.

General Procedures for the (4)-Catalyzed Acetylation of Alcohols Under Thermal Conditions

A mixture of molecular 4 (1.0 × 10$^{-2}$ mmol of Gd), alcohol (2.0 mmol for liquid substrate and 0.5 mmol for solid substrate), and acetic anhydride (1.5 mmol for liquid substrate and 5 mmol for solid substrate) in DMF/H$_2$O (400 µL, DMF/H$_2$O = 4:1) was allowed to stir for 4 h at 60 °C. After the reaction, the resulting mixture was used directly for $^1$H NMR analysis for the analytic yield.

MW-Assisted RS-Au-L-Gd (3)-Catalyzed Acetylation of Alcohols

A mixture of colloidal AuNP-surface-bound Gd catalyst RS-Au-L-Gd (3) (2.0 × 10$^{-3}$ mmol Gd), alcohol (0.5 mmol), and acetic anhydride (5 mmol) in DMF (80 µL) was placed in the reaction vessel under 300 W MW (CEM single-mode Discover Labmate System) for 60 s. After the reaction, the resulting mixture was used directly for $^1$H NMR analysis for the analytic yield.

MW-Assisted, (4)-Catalyzed Acetylation of Alcohols

A mixture of molecular 4 (1.0 × 10$^{-2}$ mmol Gd), alcohol (2.0 mmol for liquid substrate and 0.5 mmol for solid substrate), and acetic anhydride (1.5 mmol for liquid substrate and 5 mmol for solid substrate) in DMF (400 µL) was placed in the reaction vessel under 300 W MW for 60 s. After the reaction, the resulting mixture was used directly for $^1$H NMR analysis for the analytic yield.
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SUPPORTING INFORMATION
Supplemental data for this article can be accessed on the publisher’s website.

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