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Gold Supported on Nanocrystalline β-Ga_2O_3 as a Versatile Bifunctional Catalyst for Facile Oxidative Transformation of Alcohols, Aldehydes, and Acetals into Esters

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Esterification is one of the most fundamentally important reactions in organic synthesis.[1] Although a number of methods have been developed, the search for new, facile, cost-effective, and environmentally friendly procedures that avoid the use of large excess of reagents and expensive activators has attracted substantial interest.[2] An attractive alternative is the direct catalytic transformation of alcohols or aldehydes to esters, without the use of the corresponding acid or acid derivative.[3] In particular, the direct oxidative conversion of alcohols or aldehydes under mild conditions is an attractive goal. As opposed to the traditional esterification method, in which a two-step synthetic procedure first involving the synthesis of carboxylic acids or activated carboxylic acid derivatives, such as acid anhydrides or chlorides, is required,[4] the single-step nature of the oxidative esterification procedure has economic and environmental benefits in the synthesis of esters. However, relevant reports are limited to a few nonselective heterogeneous reactions or homogeneous systems, which utilize stoichiometric amount of oxygen donors and long reaction times.[5] In general, heterogeneous systems capable of catalyzing oxidative esterification of alcohols or aldehydes using molecular oxygen (O_2) as oxidant are relatively scarce.[6] One notable exception is the ethylene glycol to methyl glycolate (MGC) process based on a specific Au-based catalyst system with proprietary formulations recently developed by the company Nippon Shokubai;[6a–c] this result represents a milestone towards *greener* commercial process for clean and efficient production of carboxylic esters.

Solid catalysts based on supported gold nanoparticles[7] have attracted tremendous recent attention owing to their unique catalytic properties for a broad spectrum of organic transformations,[8] especially for aerobic oxidation of alcohols under mild conditions.[9] Over the last few years, our group,[10] Hutchings et al.,[11] Baiker et al.,[12] and Corma et al.[13] reported that gold nanoclusters deposited on TiO_2, CeO_2, and Cu-Mg-Al or Ga-Al mixed-metal oxides are highly effective for aerobic alcohol oxidation under solvent-free conditions. One critical issue associated with the gold-catalyzed primary-alcohol oxidation process is the selectivity toward aldehydes. Most recently, several studies have revealed that, depending on the substrate or acidic nature of the supports, the yielding of esters may severely reduce the selectivity toward target products of aldehyde,[14] with hemiacetal being identified as the key intermediate for ester formation. Taking into account that inorganic oxides contain some appropriate acid sites that are able to facilitate the hemiacetal formation,[13,14a] it appeared to us that a new concept of catalyst could be brought forward if the gold nanoparticles in the presence of these acidic sites can cooperatively work together by introducing a solid bifunctional catalyst that facilitates the generation and consecutive oxidation of the intermediate hemiacetals to the corresponding esters. To explore this possibility, we chose a solid catalyst formed by gold supported on nanocrystalline β-Ga_2O_3 (denoted as Au/β-Ga_2O_3). The reason for this choice is that gallium oxide has emerged as an exceptional catalytic or supporting material that is highly efficient for a wide range of acid-catalyzed reactions;[15] it is also known that significantly increased surface Lewis acidity can be achieved on nanocrystalline β-Ga_2O_3.[16]

The nanocrystalline β-Ga_2O_3 support was prepared by an alcoholic gel-precipitation method.[17] The X-ray diffraction (XRD) pattern of the as synthesized nanocrystalline support shows well-defined diffraction features characteristic of β-Ga_2O_3 (Figure S1 in the Supporting Information). Transmission electron microscopy (TEM) shows that the support is highly porous in nature; it consists of interconnected parti-

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cles with average crystallite size of 7–8 nm (Figure S2 in the Supporting Information). Owing to the nanocrystalline nature of the support, the BET (Brunner–Emmett–Teller) surface area of the as synthesized β-Ga_2O_3 is very high (84 $m^2 g^{-1}$). Surface acidity measurements by temperature-programmed desorption of NH_3 (NH_3-TPD) and pyridine adsorption coupled with FTIR measurements (for details in the Supporting Information, Table S1 and Figure S3) reveal an abundance of surface Lewis acidity of medium strength with a site density of ca. 0.60 mmol NH_3 $(g\,cat)^{-1}$ in the as synthesized β-Ga_2O_3 material, which is much higher than that previously reported for conventional calcination-derived β-Ga_2O_3 (~0.24 mmol NH_3 $(g\,cat^{-1})$).

When gold nanoparticles were deposited onto the nanocrystalline β-Ga_2O_3 (see Supporting Information for the detailed preparation procedure),[18] the XPS spectrum of the Au $4f_{7/2}$ core level shows a contribution from Au^0 at a binding energy of 83.1 eV (Figure S4 in the Supporting Information). This value is significantly lower than the reported value (84.0 eV) for a bulk gold metal, suggesting the presence of a strong metal–support interaction in the Au/β-Ga_2O_3 system. The sole presence of metallic gold was also confirmed by the IR band of adsorbed CO (Figure S5 in the Supporting Information). An almost identical XRD pattern was obtained for Au/β-Ga_2O_3 relative to β-Ga_2O_3, indicating that the crystal structure of the nanocrystalline support is maintained. TEM analysis of the Au/β-Ga_2O_3 catalyst reveals randomly dispersed particles, and energy-dispersive X-ray (EDX) analyses confirmed that the particles corresponded to gold with an average diameter of about 2–4 nm. It should be noted that, upon the introduction of gold nanoparticles, similar NH_3-TPD results were obtained for the Au/β-Ga_2O_3 catalyst (Table S1), thus revealing that the surface acidity of β-Ga_2O_3 was largely retained after deposition of gold nanoparticles.

The gold nanoparticles supported on nanocrystalline β-Ga_2O_3 were initially tested as a catalyst for the selective oxidation of 1-phenylethanol with O_2 as the oxidant in the absence of solvent (see Supporting Information for experimental details). The Au/β-Ga_2O_3 catalyst is found to be highly effective for alcohol oxidation, with very high turnover frequencies (~15,000 h^{-1}) achievable for the exclusive synthesis of acetophenone. Subsequent experiments exploring the oxidative esterification of benzyl alcohol in the presence of methanol have shown that the Au/β-Ga_2O_3 catalyst was highly active and selective for the facile oxidative transformation of benzyl alcohol into methyl benzoate.[19] The benefit of using nanocrystalline β-Ga_2O_3 as a bifunctional support for gold catalysts is evident when comparing the catalytic activity of Au supported on conventional β-Ga_2O_3 (Au/β-Ga_2O_3-c), γ-Ga_2O_3 (Au/γ-Ga_2O_3) and gold reference catalysts (Au/TiO_2, Au/Fe_2O_3 and Au/C) supplied by the World Gold Council (Table 1). A clear advantage of the Au/β-Ga_2O_3 catalyst over Au/$Ga_3Al_3O_9$ was also noticed when the reaction was conducted by using Au/$Ga_3Al_3O_9$ under otherwise identical conditions. Among various Au catalysts tested, the Au/β-Ga_2O_3 catalyst showed the highest catalytic activity for the oxidative esterification of benzyl alcohol. Note that Au/C showed only very little activity under present additive-free conditions.

Table 1. Oxidative esterification of benzyl alcohol in the presence of methanol over various gold catalysts.[a]

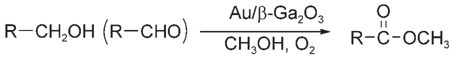
Entry	Catalysts	Conv. [%]	Selectivity [%] Ester	Aldehyde	Acetal
1	Au/β-Ga_2O_3	90	93.3	4.1	1.2
2	Au/β-Ga_2O_3-c	71	22.6	32.1	43.4
3	Au/γ-Ga_2O_3	77.4	81.6	14.9	2.5
4	Au/$Ga_3Al_3O_9$	97	85	9.2	4.4
5	Au/TiO_2	70	64.5	20.7	13.1
6	Au/Fe_2O_3	36.8	45	27.1	26.3
7	Au/C	5.5	12	31.2	54.2
8[b]	Au/β-Ga_2O_3	88	93.9	3.7	2.1

[a] Reaction conditions: benzyl alcohol (3.5 mmol) and Au catalysts (0.29 mol%) in methanol (10 mL) at 90°C, 5 atm O_2, time = 2 h; conversion (conv.) and selectivity were determined by GC by using *n*-nonane as the external standard. [b] Results for the fifth run.

After the catalytic oxidative esterification of benzyl alcohol was completed under the conditions in Table 1, the reaction mixture was filtered to remove the Au/β-Ga_2O_3. It was confirmed that no gold was present in the filtrate by inductively coupled plasma atomic emission spectroscopy (ICP-AES; detection limit of 2.5 ppb). In addition, the oxidation process was terminated by the removal of Au/β-Ga_2O_3 from the reaction solution (Figure S6 in the Supporting Information). These results indicate that any contribution to the observed catalysis from gold species that leached into the reaction solution can be ruled out and that the observed catalysis is truly heterogeneous. The Au/β-Ga_2O_3 catalyst could be reused after aerobic oxidation, and both the catalytic activity and selectivity toward the oxidative esterification reactions were retained (entry 8 in Table 1).

Oxidative esterifications of other primary alcohols were examined by using the Au/β-Ga_2O_3-catalyzed protocol, and the results are depicted in Table 2. A family of aromatic and aliphatic primary alcohols, including benzyl alcohol, cinnamyl alcohol, and 1-octanol, can be converted into their corresponding methyl, ethyl, or propyl esters with essentially complete conversion and high selectivities (Table 2, entries 1, 4, 5, 9, and 10), although longer reaction times are required for the aliphatic alcohols. The results in Table 2 also indicate that the benzyl alcohols substituted with an electron-donating group ($-OCH_3$) tend to be oxidized more easily than those with electron-withdrawing substituents, the reaction rate for which was also slower than unsubstituted benzyl alcohol (entries 2 and 3). Furthermore, it was established that oxidative esterification of heteroaromatic primary alcohols such as furfuryl alcohol under the Au/β-Ga_2O_3-catalyzed conditions also proceeded efficiently, and the ester products were produced in good yields (>75%, Table 2 entry 6). In contrast, only moderate selectivities to the corresponding methyl esters was obtained for allylic primary alcohols such as crotonyl alcohol and allyl alcohol under the same condition as described above (Table 2, entries 7 and 8). The lower selectivity obtained for the oxida-

Table 2. Au/β-Ga_2O_3-catalyzed oxidative esterification of alcohols (aldehydes).[a]



$$R{-}CH_2OH\ (R{-}CHO)\ \xrightarrow[CH_3OH,\ O_2]{Au/\beta\text{-}Ga_2O_3}\ R{-}\overset{O}{\overset{\|}{C}}{-}OCH_3$$

Entry	Substrate	Product	*t* [h]	Conv. [%]	Select. [%][e]
1	benzyl alcohol (benzaldehyde)	methyl benzoate	2.5 (1)	98 (>99)	96.5 (94.3)
2	anisalcohol (anisaldehyde)	methyl anisate	2 (1)	97 (96.5)	98 (94.8)
3	4-nitro benzyl alcohol (4-nitro benzaldehyde)	methyl 4-nitro benzoate	4 (2.5)	83 (90)	97 (80.9)
4	cinnamyl alcohol (cinnamaldehyde)	methyl cinnamate	4.5 (2.5)	>99 (93.4)	94 (97.5)
5	1-octanol[b] (octanal)	methyl octanoate	6 (1)	81 (93)	94.7 (91)
6	furfuryl alcohol (furfural)	methyl pyromucate	8 (4)	89 (91)	84.4 (92.3)
7	crotyl alcohol (crotonaldehyde)	methyl crotonate	4 (3)	92.5 (98)	73.5 (81.7)
8	allyl alcohol (acrolein)	methyl acrylate	5.5 (2)	>99 (>99)	65.5 (84)
9[c]	benzyl alcohol (benzaldehyde)	ethyl benzoate	3.5 (3)	94 (92)	95.5 (95)
10[d]	benzyl alcohol (benzaldehyde)	*n*-propyl benzoate	3.5 (2)	93 (95)	94.3 (95.8)

[a] Reaction conditions: 2.5 mmol alcohol (or aldehyde) and Au catalysts (0.62 mmol%) in methanol (10 mL) at 90°C, 5 atm O_2; conversion (conv.) and selectivity (select.) were determined by GC with *n*-nonane as the external standard. [b] Alcohol (1 mmol). [c] Ethanol (10 mL) instead of methanol. [d] *n*-Propanol (10 mL) instead of methanol. [e] Selectivity of the ester was measured based on substrate (alcohol or aldehyde) conversion. As noted by Hayashi et al.,[6c] the excess methanol (ethanol or propanol) as a solvent may also undergo the oxidative esterification reaction, leading to undesired formation of appreciable amount of self-esterification products, that is, methyl formate, ethyl acetate, or propyl propanoate. We confirmed, however, that the yield of the self-esterification products is always less than 2% in the present reactions.

tive esterification of allylic primary alcohols is probably due to an undesired formation of oligomers of allyl acrylate, since there is no other low-molecular products detected by GC and GC-MS.

Another issue from Table 2 worth noting is the high substrate selectivity of Au/β-Ga_2O_3 to promote the oxidative transformation of various primary alcohols to their corresponding esters. In contrast, it has been reported that under these conditions the excess methanol as a solvent may also undergo the oxidation reaction.[6c] Particularly relevant is the undesired formation of appreciable amount of methyl formate by competitive oxidative esterification. To make a straightforward comparison of the substrate selectivity as reported by Hayashi et al.,[6c] we examined the oxidative esterification using *n*-propanol and *n*-butanol as the sole reaction substrates (Table S2 in the Supporting Information). We found that under identical conditions both alcohols are oxidized at higher rates than the Au/TiO_2 or Au/ZrO_2 catalysts used by Hayashi et al.,[6a–c] with selectivities to *n*-propyl propanoate or *n*-butyl butanoate always being higher than 90%. Moreover, by decreasing the catalyst loading it is possible to achieve a low conversion of these substrates within a short time-frame. This result, together with the intrinsically more active substrate relative to the excess solvent (i.e., methanol, ethanol or *n*-propanol),[10,19] may account for the high substrate selectivity of present Au/β-Ga_2O_3 for alcohol oxidative esterification.

Further to oxidative transformation of aldehydes, we examined the catalytic activity of Au/β-Ga_2O_3 for the oxidative esterification of aldehydes, which is also a synthetically useful transformation. In general, the oxidation of the aldehydes proceeded towards esters much more efficiently than the corresponding alcohols (results are given in parentheses in Table 2 under the same reaction conditions), indicating that the first step of oxidation of alcohols to corresponding aldehydes may play an important role in the whole catalytic process. The aromatic aldehydes tend to be more easily oxidized than the aliphatic and allylic ones (entries 1, 5, and 8). Similarly, less active allylic aldehydes such as crotonaldehyde and acrolein also afford good yields of around 80% for the corresponding esters (entries 6 and 7). Notice that these values constitute a significantly higher selectivity compared with their alcohol counterparts. Additionally, the catalytic system efficiently oxidizes aliphatic aldehydes to the corresponding ester compounds: for the oxidation of octanal, methyl octanoate was produced in a 91% yield in 1 h (entry 8, Table 2). This observation is in contrast to the oxidative esterification of 1-octanol, for which a much longer reaction time is required to complete the reaction

The present Au/β-Ga_2O_3 catalyst also has high catalytic activity for the direct conversion of acetals to the corresponding esters with molecular oxygen. With benzaldehyde dimethyl acetal as the model substrate, the results obtained for the conversion into methyl benzoate with various gold catalysts (compared in Figure 1) showed a high versatility of the β-Ga_2O_3-supported gold catalyst. The Au/β-Ga_2O_3 system is found to be highly active and selective for the aerobic oxidation; in most cases benzaldehyde was obtained as the sole byproduct. Using Au/TiO_2, Au/Fe_2O_3 or Au/C reference samples provided by the World Gold Council as the catalysts, we found that less than 56% of the benzaldehyde dimethyl acetal was oxidized to methyl benzoate within 2 h at 90°C. It should be mentioned that under the same reaction conditions, benzaldehyde was obtained as the major product over the least active Au/C catalyst, presumably due to the presence of excess amount of water in the as-received WGC sample.[20] These results clearly indicate that bifunctional Au/β-Ga_2O_3 catalyst is much more active and selective than conventional oxide-supported Au catalysts and that the collaborative interaction between gold and the nanocrystalline β-Ga_2O_3 support are essential for the oxidative esterification of acetals.

Based on the reaction pathway for alcohol oxidation as proposed by Hayashi et al.,[6c] a possible mechanism for the

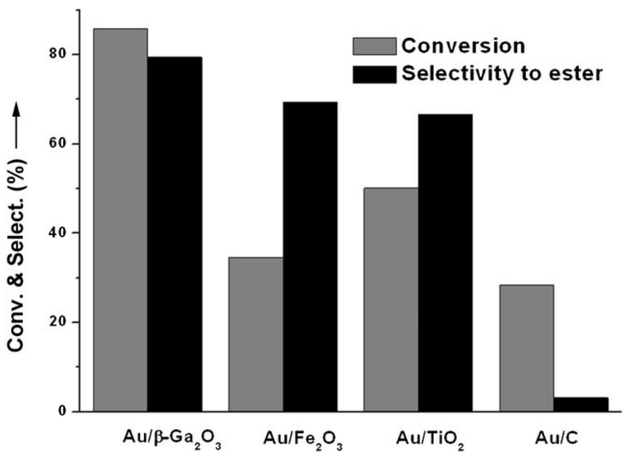
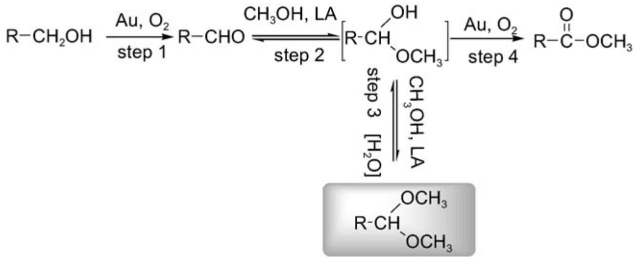


Figure 1. Oxidative esterification of benzaldehyde dimethyl acetal over various gold catalysts. Reaction conditions: substrate (2.5 mmol), 1 equiv H_2O and Au catalysts (0.47 mol %) in methanol (10 mL) at 90 °C, 5 atm O_2, time = 2 h; Conversion and selectivity were determined by GC using *n*-nonane as the external standards.



Scheme 1. A proposed mechanisms for Au/β-Ga_2O_3-catalyzed oxidative esterification (LA = Lewis acid).

Au/β-Ga_2O_3-catalyzed oxidative esterification of primary alcohols, aldehydes, and acetals is illustrated in Scheme 1. The one-pot aerobic conversion of primary alcohols into methyl esters involves three steps: Initially, selective oxidation of the primary alcohols in the presence of gold catalyst proceeds to form aldehydes (step 1). Kinetic studies revealed that step 1 is the rate-determining step (Figure S7 in the Supporting Information), probably in the abstraction of β-H from alcohol.[10,21] Then, the condensation reaction between aldehyde and alcohol takes place, leading to the formation of hemiacetal species[6a,14,22] (step 2). Ester products are directly formed by the direct oxidation of hemiacetals (step 3). It is worth noting that hemiacetal formation from aldehydes and alcohols, in general, is a facile reaction due to the good electrophilic properties of aldehydes and nucleophilic properties of alcohols, and may not require a catalyst. However, in the presence of factors that decrease electrophilicity/nucleophilicity of the aldehyde/alcohol, a catalyst may be required for the transformation. In this sense, the fact that the Au/β-Ga_2O_3 can function as a bifunctional catalyst to catalyze both oxidation and hemiacetal formation in a single procedure under mild conditions is also important for step 4, as indicated by the significantly higher efficiency of the Au/β-Ga_2O_3 catalysts for the oxidative esterification of acetals as compared with that of other Au-based reference catalysts. Indeed, we have seen that the introduction of nanocrystalline β-Ga_2O_3, which acts as an effective heterogeneous Lewis acid for step 2 or 4, into the reaction mixture greatly facilitates the oxidative transformation of aldehydes or acetals over the less effective Au/TiO_2 catalyst (Figure S8 in the Supporting Information).

In conclusion, we have shown that the combination of gold nanoparticles and nanocrystalline β-Ga_2O_3 can allow the devise of new versatile gold catalyst for greener organic synthesis under mild conditions. Catalyst design has resulted in the novel bifunctional catalyst that is an outstanding material for the additive-free direct catalytic transformation of primary alcohols, aldehyde,s or acetals to esters under mild, neutral conditions, providing an environmentally benign protocol for the direct synthesis of carboxylic esters.

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Keywords: esterification · gallium oxide · gold · heterogeneous catalysis · Lewis acids

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