Aerobic Oxidation

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Ga–Al Mixed-Oxide-Supported Gold Nanoparticles with Enhanced Activity for Aerobic Alcohol Oxidation**

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The selective oxidation of alcohols is one of the most challenging reactions in green chemistry.[1] Although a number of methods have been developed, the search for new, facile, cost-effective, and environmentally benign procedures that avoid the use of a large excess of toxic and expensive stoichiometric metal oxidants has attracted substantial interest.[2,3] An attractive method is the direct oxidation of alcohols—promoted by reusable heterogeneous catalysts—using air or molecular oxygen (O_2) under solvent-free conditions or (in the case of solid alcohols) in green organic solvents.[4] Ideally, the reaction should also be performed under mild conditions (preferably at room temperature) for the synthesis of complex, thermolabile compounds, which are typical in fine chemistry. Satisfactory results were attained in only very few cases, in which a large excess of base additives was required, and this was usually achieved at the expense of selectivity.[5,6] Therefore, the development of excellent reusable catalysts for liquid-phase aerobic oxidation of alcohols under mild conditions would constitute a breakthrough in both green chemistry and organic synthesis.

Recently, supported gold nanoparticles have attracted considerable attention because of their extraordinarily high activity and selectivity.[7] The outstanding catalytic ability of gold is related to the size and shape of the nanoparticles, the degree of coordinative unsaturation of the gold atoms, and the interactions between gold and the oxide support.[8,9] Although several gold systems have been reported for the catalysis of alcohol oxidation reactions, in most cases they have been applied at temperatures above 100 °C.[10] Dehydrogenation is known to be the rate-limiting step in the oxidation of alcohols on various noble metals.[11–13] Therefore, the combination of gold nanoparticles with a suitable support (characterized by an exceptional alcohol-dehydrogenation activity) may allow the fabrication of new, versatile gold catalysts that could be used for liquid-phase organic synthesis under mild conditions. Herein, we demonstrate for the first time that mesostructured Ga–Al mixed-oxide solid solutions are highly promising supports for the fabrication of exceptionally effective gold catalysts for aerobic alcohol oxidation under mild conditions.

A series of binary mesostructured Ga–Al mixed-oxide supports (denoted as $Ga_xAl_{6-x}O_9$; $x=2, 3, 4$), along with unitary oxides of γ-Ga_2O_3 and γ-Al_2O_3, was prepared through an alcoholic sol–gel pathway.[14] The X-ray diffraction (XRD) patterns of all as-synthesized binary substrates are characteristic of γ-Ga_2O_3/Al_2O_3 solid solutions with a spinel-type structure. When gold nanoparticles were deposited onto these high-surface-area materials, no gold diffraction line was detected, and the pattern showed no significant differences relative to that of the support, thus indicating that the structure of the catalyst was maintained.[15] A representative transmission electron microscopy (TEM) image of the Au/$Ga_xAl_{6-x}O_9$ sample confirms that the gold particles were evenly deposited on the Ga–Al mixed-oxide support, with most particles being smaller than about 6 nm (see the Supporting Information for TEM and XRD data).

To check the possible alcohol-dehydrogenation capability of the Au/$Ga_xAl_{6-x}O_9$ materials, we adsorbed 2-propanol on their surface and performed temperature-programmed surface reaction (TPSR) measurements of the desorbed H_2 molecules (see the Supporting Information). Ga-containing mixed-oxide supports were found to be indispensable for attaining highly active alcohol-dehydrogenation materials (Figure 1 A). Furthermore, the dehydrogenation activity of the catalysts was observed to be strongly dependent on the composition of these supports. A strongly enhanced hydrogen signal was identified in the case of a $Ga_3Al_3O_9$ solid solution containing a Ga/Al molar ratio of 1:1—in sharp contrast to what was observed for the reference gold catalysts Au/TiO_2 and Au/Fe_2O_3 (provided by the World Gold Council), where no H_2 species were detected. These results can be rationalized by assuming that the formation of Ga–Al mixed-oxide solid solutions may favor the creation of specific dehydrogenation sites as a consequence of the presence of Ga atoms at the surface atomic sites (T_d and O_h) of Al_2O_3 and highly dispersed GaO_4 tetrahedra in the surface spinels.[16] These sites are responsible for the considerably enhanced dehydrogenation activity observed for the Ga–Al mixed-oxide-supported Au catalysts.

Our initial aerobic-oxidation studies focused on the case of benzyl alcohol (Figure 1 B), with the aim to understand the effect of the composition of the support on the catalytic performance of the gold catalysts. The reactions were performed in a magnetically stirred glass batch reactor in the presence of a solvent (at 90 °C) under O_2 and at

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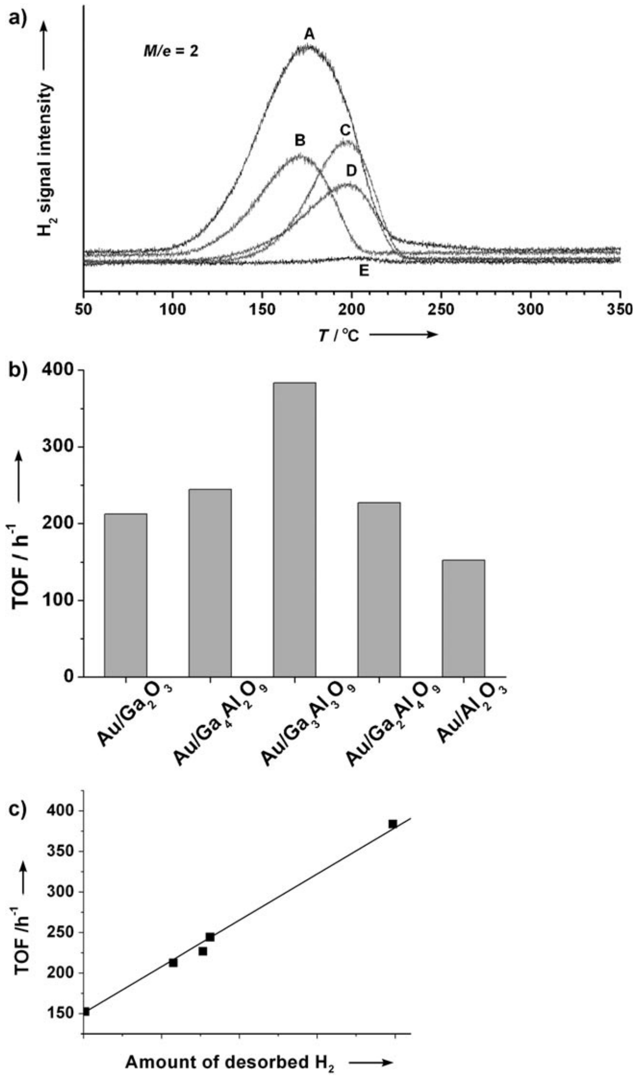


Figure 1. a) TPSR diagram of 2-propanol on various gold catalysts (H_2 mass intensity): Au/$Ga_3Al_3O_9$ (A), Au/$Ga_4Al_2O_9$ (B), Au/$Ga_2Al_4O_9$ (C), Au/Ga_2O_3 (D), and Au/Al_2O_3 (E); the mass/charge ratio(M/e) = 2. b) TOF for the aerobic oxidation of benzyl alcohol using gold supported on different mixed oxides, $Ga_xAl_{6-x}O_9$ ($x = 0, 2, 3, 4, 6$), as catalysts (measured at $t = 1$ h). Conditions: 90°C, catalyst (100 mg), benzyl alcohol (3.85 mmol), O_2 bubbling rate: 20 mL min^{-1}. Trace amounts of byproducts were detected. c) Correlation between the amount of desorbed H_2 and the specific oxidation rate of benzyl alcohol using Au/$Ga_xAl_{6-x}O_9$ ($x = 0, 2, 3, 4, 6$) catalysts. The amount of desorbed H_2 was determined from the relative peak area of the H_2 mass signal.

atmospheric pressure. The maximum benzaldehyde formation rate was observed for the Au/$Ga_3Al_3O_9$ samples with the molar ratio Ga/Al = 1:1, which indicates that the specific nature of the solid solution contributes to the enhanced activity. Note that the reaction also proceeded with the unitary Ga_2O_3 and Al_2O_3 supports, but at much lower reaction rates. On the other hand, if we compare the reaction rates with the H_2 signals from the TPSR measurements, we obtain an excellent linear correlation (Figure 1 C). Therefore, the fact that the Ga–Al mixed-oxide support may substantially facilitate the crucial alcohol-dehydrogenation step appears to be a key factor for achieving a high activity in the aerobic oxidation of alcohols.

The scope of the Au/$Ga_3Al_3O_9$ catalyst was investigated using a range of substrates and conditions (Table 1). In the initial experiments, which were conducted at 80°C in the presence of a solvent (Table 1, entries 1 to 4), the activity of the Au/$Ga_3Al_3O_9$ catalyst was compared with that of other Au- and Pd-based reference catalysts. The Ga–Al mixed-oxide-supported catalyst exhibited an activity toward benzyl alcohol oxidation similar to that of a hydroxyapatite-supported palladium (PdHAP) catalyst, which has been reported to be one of the most active catalysts for alcohol oxidation.[12] Note that the highly active Au/CeO_2 catalyst, which is based on the method developed by Abad et al.,[17] can only afford a moderate benzyl alcohol conversion of about 78 % within 2 h at 80°C (see Table 1, entry 3). Using an Au/TiO_2 reference catalyst provided by the World Gold Council, we found that about 42 % of benzyl alcohol was oxidized to benzaldehyde under the same conditions (see Table 1, entry 4). These results clearly indicate that the binary solid-solution-supported Au catalyst is much more active than other conventional oxide-supported systems, and that the collaborative interaction between gold and the mixed-oxide support is essential for alcohol oxidation.

We note that Au/$Ga_3Al_3O_9$ was highly active and extremely selective for the aerobic oxidation of all substrates, thus indicating a high versatility of the solid-solution-supported gold catalyst. Substituted benzyl alcohol compounds containing electron-donating groups (such as, CH_3 or OCH_3; see Table 1, entries 6 and 7) are more easily oxidized than those containing electron-withdrawing groups (Table 1, entries 8 and 9). In the latter case, the reaction rate was even slower than that of unsubstituted benzyl alcohol. Note that Au/$Ga_3Al_3O_9$ also displays a high activity for the oxidation of allylic alcohols; for example, cinnamyl alcohol was selectively oxidized to cinnamyl aldehyde (with 95 % conversion in 2.5 h; see Table 1, entry 10). On the other hand, the catalytic activity for most aliphatic alcohols was found to be significantly low. Secondary aliphatic alcohols showed a higher activity than their primary counterparts, with surprisingly high activities for 2-octanol and cyclohexanol (Table 1, entries 11, 12, and 15). This trend is markedly different from that observed in Pd-containing catalysts, such as Au-Pd/TiO_2[10c] and PdHAP.[12] Indeed, when the PdHAP catalyst was used, only 10.5 % of 2-octanol was selectively oxidized to 2-octanone within 3 h (at 80°C; see Table 1, entry 14). Furthermore, alcohols containing a hetero atom, such as N (which is considered to coordinate strongly to the gold nanoparticles), could also be smoothly oxidized to the corresponding aldehyde compounds, thereby obtaining a high yield (Table 1, entry 16).

The Au/$Ga_3Al_3O_9$ catalyst was so active that it was able to catalyze the aerobic oxidation of benzyl alcohol and 1-phenylethanol at ambient temperature (Table 1, entries 17–20). Both substrates were smoothly oxidized into their corresponding aldehyde and ketone compounds in the absence of water or base. Note that under these conditions, the reaction did not proceed at all when the (highly active)

Table 1: Aerobic oxidation of various alcohols, catalyzed by Au/$Ga_3Al_3O_9$.[a]

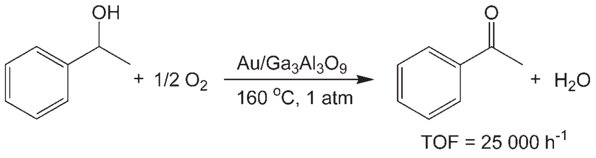
Entry	Substrate	Product	Conversion [%]	Selectivity [%]	*t* [h]
1	benzyl alcohol	benzaldehyde	98	>99	2
2[b]	benzyl alcohol	benzaldehyde	42	>99	2
3[c]	benzyl alcohol	benzaldehyde	78	>99	2
4[d]	benzyl alcohol	benzaldehyde	98	99	2
5	1-phenylethanol	acetophenone	>99	>99	1
6	4-methyl benzyl alcohol	4-methyl benzaldehyde	97	>99	1.5
7	4-methoxy benzyl alcohol	4-methoxy benzaldehyde	99	99	1.75
8[e]	4-chloro benzyl alcohol	4-chloro benzaldehyde	98	99	1
9[e]	4-nitro benzyl alcohol	4-nitro benzaldehyde	88	99	2.5
10	cinnamyl alcohol	cinnamaldehyde	95	99	2.5
11[e]	cyclohexanol	cyclohexanone	67	>99	3
12[e]	2-octanol	2-octanone	90	99	4
13	2-octanol	2-octanone	58	99	3
14[d]	2-octanol	2-octanone	10.5	99	3
15[e]	1-octanol	octanal	28	99	3
16[e]	2-pyridinemethanol	2-pyridinecarboxaldehyde	96	99	4
17[f]	benzyl alcohol	benzaldehyde	80	95	12
18[f]	benzyl alcohol	benzaldehyde	>99	90	30
19[f]	1-phenylethanol	acetophenone	>99	>99	15
20[f][g]	1-phenylethanol	acetophenone	>99	>99	40
21[h]	benzyl alcohol	benzaldehyde	96	>99	2

[a] Alcohol (1 mmol), 1 wt% Au/$Ga_3Al_3O_9$ (0.1 g), toluene as solvent (10 mL), 80 °C, O_2 bubbling rate (20 mL min^{-1}). [b] 1.6 wt% Au/TiO_2 (0.1 g). [c] 2.4 wt% Au/CeO_2 (0.1 g) prepared following the procedure described in ref. [17]. [d] 0.2 wt% PdHAP (0.1 g) prepared following the procedure described in ref. [12]. [e] Alcohol (0.25 mmol). [f] Alcohol (0.5 mmol), 1 wt% Au/$Ga_3Al_3O_9$ (0.3 g), toluene (10 mL), ambient temperature, O_2 bubbling rate (20 mL min^{-1}). [g] Air was used as the oxidant instead of O_2. [h] Oxidation results for the fifth run.

polystyrene-based copolymer-microencapsulated gold nanocatalysts (PI/Au) developed by Kabayashi and co-workers were used.[18] In the presence of Au/$Ga_3Al_3O_9$, benzyl alcohol was selectively oxidized to benzaldehyde (with an 80% conversion within 12 h, see Table 1, entry 17). After 30 h, the reaction was essentially complete—with a selectivity of over 90% for benzaldehyde (Table 1, entry 18). Relative to benzyl alcohol, 1-phenylethanol was found to be more reactive toward oxidation by Au/$Ga_3Al_3O_9$. This alcohol was smoothly oxidized to acetophenone, thereby undergoing complete conversion within 15 h (see Table 1, entry 19). The Au/$Ga_3Al_3O_9$ catalyst showed a high activity, even when the reaction was carried out using air instead of pure O_2 (although in this case a longer reaction time was required, see Table 1, entry 20).

Furthermore, Au/$Ga_3Al_3O_9$ is stable and can be reused after aerobic oxidation. After reaction with benzyl alcohol, the catalyst was separated from the reaction mixture by centrifugation, thoroughly washed with acetone, and then reused in the next run under the same conditions. The catalytic results indicate that there is no difference in either activity or selectivity between the first and fifth runs (Table 1, entries 1 and 21). Gold leaching was negligible during subsequent cycles. The concentration of the metal in the filtrate was less than 2.5 ppb, as found by inductively coupled plasma (ICP) measurements. The XRD patterns indicated that the crystallinity of the recycled Au/$Ga_3Al_3O_9$ sample (see Supporting Information) was the same as that of the fresh sample, which shows that the spinel structure is retained during the oxidation process.

Interestingly, the Au/$Ga_3Al_3O_9$ catalyst is also highly effective for the aerobic oxidation of alcohols under solvent- and base-free conditions. Kabayashi and co-workers recently reported PI/Au nanocatalysts as being the most active Au catalysts in the current literature, with a very high turnover frequency (TOF) of 20000 h^{-1} for the conversion of 1-phenylethanol to acetophenone (at 160 °C).[18] Under these conditions, our Au/$Ga_3Al_3O_9$ catalyst gave an exceptionally high TOF of 25000 h^{-1}, thus showing a great potential for practical applications (Scheme 1).



Scheme 1. Solvent-free aerobic oxidation of (±)1-phenylethanol using an Au/$Ga_3Al_3O_9$ catalyst. Turnover frequency given for the following conditions: measuring time *t* = 30 min, (±)-1-phenylethanol (165.7 mmol), Au (4.0×10^{-4} mol%).

In summary, we have successfully demonstrated that mesostructured Ga–Al mixed-oxide solid solutions, which are characterized by unique dehydrogenation properties, may be used as new attractive supports for the fabrication of exceptionally active gold catalysts for the liquid-phase aerobic oxidation of alcohols under mild conditions. These catalysts can even efficiently catalyze the aerobic oxidation of several alcohols under ambient conditions in the absence of water or base. Further extension of these catalysts to other oxidation processes, as well as studies to clarify other factors that control oxidation, are currently in progress.

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