

Aerobic oxidation of alcohols catalyzed by gold nanoparticles supported on gallia polymorphs

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Abstract

Gold nanoparticles supported on polymorphs of gallia (α -, β -, and γ - Ga_2O_3) were evaluated for the solvent-free liquid phase oxidation of benzyl alcohol by molecular oxygen. High selectivity to benzaldehyde was obtained under the reaction conditions of 130 °C, 5 atm and 5 h in an autoclave. The Au/ γ - Ga_2O_3 catalyst was also evaluated for oxidation of a range of alcohols using mesitylene as solvent under flowing oxygen at atmospheric pressure and 90 °C. Under these conditions the conversion of benzyl alcohol reached 100% after 2 h and it was demonstrated that the catalyst can be recycled four times without significant loss of activity. The structural data (TEM, XPS and TPSR of 2-propanol adsorption) along with the catalytic results indicate that the unique dehydrogenation capabilities of the Au/ γ -gallia system are responsible for the enhanced activity achieved in the liquid phase oxidation of benzyl alcohol.

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1. Introduction

The selective oxidation of alcohols is one of the most important transformations in organic synthesis [1–4]. 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 toxic and expensive metal oxidants has attracted substantial interest [3]. An attractive alternative is the direct oxidation of alcohols catalyzed by reusable heterogeneous solid catalysts, using molecular oxygen (O_2) under solvent-free conditions [5,6]. To date, the catalysts suggested for aerobic alcohol oxidation are mainly based on supported noble metals such as palladium and platinum [7], which however generally suffer from a rapid deactivation at reaction conditions due to leaching as a consequence of over-oxidation of the metal active sites [8].

Supported gold nanoparticles have attracted considerable recent attention as new promising alcohol oxidation materials owing to their higher selectivity and less proneness to leaching compared to their conventional noble metal counterparts [9,10]. The gold particle size is considered to be of paramount importance for aerobic alcohol oxidation [11], but evidence indicates that, the support may also play key roles in determining the catalytic activity and selectivity of the reaction [8,12]. In the present study, we demonstrate that gallia polymorphs are new attractive supports applicable for fabrication of new gold nanocatalysts highly active for selective alcohol oxidation.

2. Experimental

2.1. Catalyst preparation

Three different polymorphs of gallium oxide were prepared using the solution-based procedures described in Ref. [13]. The gold precursor species were introduced on

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the gallia polymorphs using the homogeneous deposition–precipitation (HDP) method originally developed by Louis and coworkers [14]. Briefly, a 1.46×10^{-3} mol L⁻¹ solution of HAuCl₄ was prepared by dissolving 0.12 g HAuCl₄ · 3H₂O in 200 mL of deionized water. Urea (1.80 g) was added to the gold solution to achieve a concentration 100 times higher than the HAuCl₄ concentration. The gallium oxide (2.3 g) was then added, and the resulting suspension was stirred and heated to 90 °C over 4 h in a closed reactor kept away from light. The solid was filtered, washed thoroughly with distilled water to remove Cl⁻ remnant in the final products, dried at 100 °C for 12 h and finally calcined at 300 °C for 4 h. Reference support applied was CeO₂ ($S_{\text{BET}} = 78$ m² g⁻¹), purchased from Aldrich.

2.2. Catalyst characterization

The BET specific surface areas of the samples were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. The X-ray powder diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 20 mA. Transmission electron micrographs (TEM) were recorded digitally with a Gatan slow-scan charge-coupled device (CCD) camera on a JEOL 2011 electron microscope operating at 200 kV. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in acetone and applying a drop of very dilute suspension on carbon-coated grids. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Perkin–Elmer PHI 5000 C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K α , $h\nu = 1253.6$ eV) was used. The C 1 s line (284.6 eV) was used as the reference to calculate the binding energies (BE).

The TPSR (temperature programmed surface reaction) experiments were carried out as follows: After the catalyst was activated at 300 °C for 2 h, it was cooled down to room temperature and 2-propanol vapor was introduced for adsorption at RT for 0.5 h. After the catalyst was swept with He for 60 min, the temperature was increased linearly with rate of 10 °C min⁻¹ in He and the signals of H₂ ($M/e = 2$), acetone ($M/e = 43$ and $M/e = 58$), and propylene ($M/e = 41$) were recorded by the mass quadrupole spectrometer (Balzers OmniStar) simultaneously.

2.3. Activity test

For solvent-free oxidation of benzyl alcohol, the reaction was carried out in a stirred autoclave reactor (Dalian Tongchan Co. Ltd., capacity: 100 mL) using molecular oxygen as the oxidant under pressurized conditions (reaction mixture = 20 mL benzyl alcohol + 200 mg catalyst, temperature = 110–160 °C, oxygen pressure = 2–8 atm, and reaction time = 1–10 h). The pressure was maintained

constant throughout the experiment and so as the oxygen was consumed in the reaction it was replenished. The stirring speed was set at 1000 rpm and reaction mixtures from the reactor were taken periodically via a sampling pipe. The products were analyzed by gas chromatography (Trace GC Ultra) fitted with a HP-5 capillary column (25 m × 0.32 mm) and flame ionization detector (FID).

For atmospheric pressure oxidation of alcohols under oxygen flow, catalytic tests were performed at 90 °C, in a two necked batch reactor fitted with a reflux condenser, oil bath, thermocouple and magnetic stirrer. A mixture of 200 mg Au/ γ -Ga₂O₃ in mesitylene (20 mL) was prepared in a round-bottom flask. The alcohols with specific amount of 1 or 0.25 mmol were then added into the solution and the resulting mixture was stirred at 90 °C with a stirring speed of 1000 rpm. Oxygen (100 mL min⁻¹) was bubbled through the vigorously stirred liquid at atmospheric pressure. The flow was regulated by a mass flow controller. Samples were taken periodically for subsequent gas chromatography analysis (Trace GC Ultra using a HP-5 capillary column and a flame ionization detector).

3. Results and discussion

The X-ray diffraction (XRD) patterns of the as synthesized gallia support (not shown) show well-defined diffraction features characteristics of α -, β -, and γ -Ga₂O₃ [15]. After gold nanoparticles (~2.5 wt% by ICP-AES) were deposited onto the Ga₂O₃ supports, an almost identical XRD pattern as shown in Fig. 1 (Top) was obtained for all corresponding Au-containing catalysts, indicating well maintaining of the crystal structure of the gallia supports. The XRD was unable to detect the diffraction peaks from the gold catalyst particles, which is a good indication of a well-dispersed catalyst. Representative TEM image of the structure of the Au/ γ -Ga₂O₃ catalyst is shown in Fig. 1 (bottom). It is evident that the support exhibited a narrow particle size distribution with primary particle sizes in the 5–10 nm range. The histogram of the particle size distribution shows that the gold particles were evenly deposited on the γ -Ga₂O₃ support, with most particles smaller than 6 nm. The XPS spectrum of the Au 4f_{7/2} core level shows a contribution from Au⁰ at a binding energy of 83.1–83.4 eV (not shown). 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/Ga₂O₃ systems [16].

For the gallia supported gold catalysts, our initial studies focused on the oxidation of benzyl alcohol because this reaction is often employed as a model reaction for alcohol oxidation [17]. Furthermore, this molecule was chosen because of its relatively high reactivity and because the main product is a non-enolizable aldehyde thus reducing the number of possible side products [18]. The catalytic results obtained in the solvent-free liquid phase oxidation of benzyl alcohol to benzaldehyde by molecular oxygen at 130 °C over nanosize gold supported over different gallia

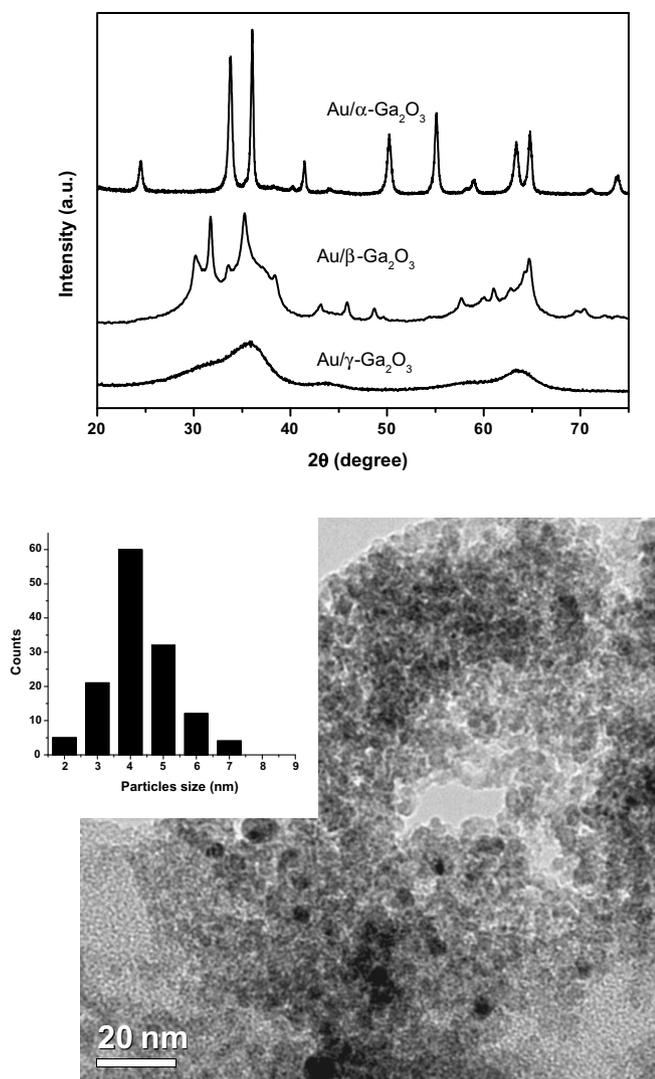


Fig. 1. Top: XRD patterns of gold nanocatalyst supported on various gallia polymorphs. Bottom: TEM images of the Au/ γ -Ga₂O₃ catalyst used for benzyl alcohol oxidation. The inset shows the histogram of particle size distribution.

polymorphs are presented in Table 1. In the absence of catalyst or when using the support in the absence of gold no oxidation was observed, confirming that the presence of

gold was essential to obtain catalytic oxidation [19]. It is observed that the gallia supported gold nanoparticles are highly active and selective for the oxidation of benzyl alcohol, with the order of the catalysts for the yielding of benzaldehyde being Au/ γ -Ga₂O₃ > Au/ β -Ga₂O₃ > Au/ α -Ga₂O₃. With the Au/ γ -Ga₂O₃ catalyst, a conversion of $\sim 40\%$ was observed which corresponded to a TOF_{t=5 h} of 606 h⁻¹, while the selectivity to benzaldehyde was always higher than 97%. Comparing the catalytic performance with the Au/CeO₂ catalyst based on a commercially available CeO₂ as well as the reference Au/TiO₂ and Au/Fe₂O₃ catalysts provided by World Gold Council confirms the high activity of these new materials.

Fig. 2 depicts the influence of reaction time on the conversion of benzyl alcohol and selectivity to benzaldehyde over catalyst Au/ γ -Ga₂O₃. At the initial stage of the reaction, a rapid increase in the benzyl alcohol conversion is observed. With extended reaction, significant conversion up to 50% could readily be achieved over a course of 10 h reaction. The fact that a continuous accumulation of benzyl benzoate occurs with extended reaction time may be due to the presence of a competitive oxidative pathway involving the consecutive oxidation of the intermediate hemiacetals leading to formation of benzyl benzoate as suggested respectively by Corma and Hutchings et al. [20,21]. With extended reaction time up to 10 h, benzaldehyde selectivities higher than 94% could be obtained, in sharp contrast to the yielding of substantial amount of benzyl benzoate (5–30%) in previous studies using gold nanocrystals supported on conventional oxide supports for solvent-free benzyl alcohol oxidation [22]. The catalytic activities of the Au/ γ -Ga₂O₃ sample were also found to be strongly dependent on the reaction temperature and oxygen pressure (see Fig. 3). In all cases, benzaldehyde was obtained as the major product, and only small amounts of other product, viz., benzyl benzoate, was observed. It is interesting to note that benzoic acid was not detected by GC for all Au/Ga₂O₃ samples, inferring that it reacted immediately with benzyl alcohol as it was formed, which however may also contribute to some extent to the formation of benzyl benzoate as mentioned above [22].

Table 1

Properties of gold catalysts and results of solvent-free oxidation of benzyl alcohol over various gold catalysts^a

Gold catalysts	S _{BET} (m ² g ⁻¹)	Content of Au (wt%)	Conversion (%)	Selectivity (%)			Benzaldehyde Yield (%)	TOFs (h ⁻¹)	TOFs (mol g ⁻¹ _(Au) h ⁻¹)
				Benzaldehyde	Benzyl benzoate	Benzoic acid			
Au/ α -Ga ₂ O ₃	40	2.3	7.60	99.4	0.6	–	7.6	125	0.63
Au/ β -Ga ₂ O ₃	71	2.4	23.2	97.8	2.2	–	22.7	366	1.86
Au/ γ -Ga ₂ O ₃	133	2.5	40.0	97.7	2.3	–	39.1	606	3.08
Au/CeO ₂ ^b	76	2.5	16.5	95.1	1.5	3.4	15.7	250	1.27
Au/TiO ₂ ^c	48	1.4	6.0	93.2	2.3	4.5	5.6	162	0.82
Au/Fe ₂ O ₃ ^d	35	4.4	2.1	89.9	4.1	6.0	1.9	18	0.10

^a Reaction condition: benzyl alcohol: 20 mL, catalyst: 0.2 g, temperature: 130 °C, oxygen pressure: 5 atm, reaction time: 5 h, average TOF values based on 5 h reaction.

^b Gold catalyst supported on commercial ceria purchased from Aldrich.

^c Gold reference catalyst, Type A, Lot no. Au/TiO₂ # 02–1.

^d Gold reference catalyst, Type C, Lot no. Au/Fe₂O₃ # 02–5.

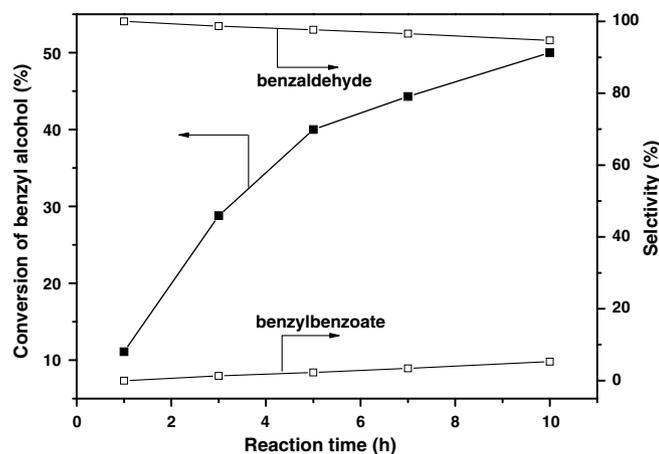


Fig. 2. Performance of 200 mg Au/ γ -Ga₂O₃ catalyst in the solvent-free oxidation of 20 mL of benzyl alcohol with O₂ at 130 °C and 5 atm.

Since the Au/ γ -Ga₂O₃ showed the highest activity for the solvent-free oxidation of benzyl alcohol, it was chosen for the atmospheric pressure oxidation. The results for various structurally different alcohols are summarized in Table 2, indicating a high versatility of the γ -Ga₂O₃-supported gold catalyst. Electron-withdrawing groups like chloro-groups led to a decrease in activity, whereas electron-donating groups like methyl-, and methoxy-groups afforded higher activities. The oxidation of aliphatic alcohol was also studied but the catalyst activity for which was one order of magnitude lower compared with aromatic alcohols. All the alcohols could be highly selectively (>98%) oxidized to their corresponding ketones and aldehydes. Recycling experiments were examined for the atmospheric pressure aerobic oxidation of benzyl alcohol. It is remarkable that the Au/ γ -Ga₂O₃ sample maintained its high catalytic activity affording a high benzyl alcohol conversion above 99% even after four recyclings and reuse of the catalyst. In addition, the oxidation of benzyl alcohol stopped by the removal of Au/ γ -Ga₂O₃ from the reaction solution as shown in Fig. 4. The Au concentration in the filtrate is less than 2.5 ppb as found by ICP. Therefore, we conclude that Au leaching was negligible and the nature of the observed catalysis is truly heterogeneous.

Table 2

Aerobic oxidation of alcohol to the corresponding aldehydes/ketones catalyzed by Au/ γ -Ga₂O₃^a

Entry	Substrate	Time (h)	Conversion (%)	Selectivity (%)
1	PhCH ₂ OH	2	>99	99
2 ^b	PhCH ₂ OH	2	98	97
3 ^c	PhCH ₂ OH	2	98	96
4	PhCHOHCH ₃	0.5	>99	>99
5	PhCH=CHCH ₂ OH	2	98	99
6	4-CH ₃ OPhCH ₂ OH	1.5	99	98
7	4-CH ₃ PhCH ₂ OH	1.5	97	99
8	4-ClPhCH ₂ OH	4	93	>99
9 ^d	1-Octanol	2.5	45	99

^a Conditions: 90 °C, 100 mL min⁻¹ O₂, 200 mg catalyst, 1 mmol substrate, 20 mL mesitylene.

^b The second use of the catalyst.

^c The fourth use of the catalyst.

^d 0.25 mmol Substrate.

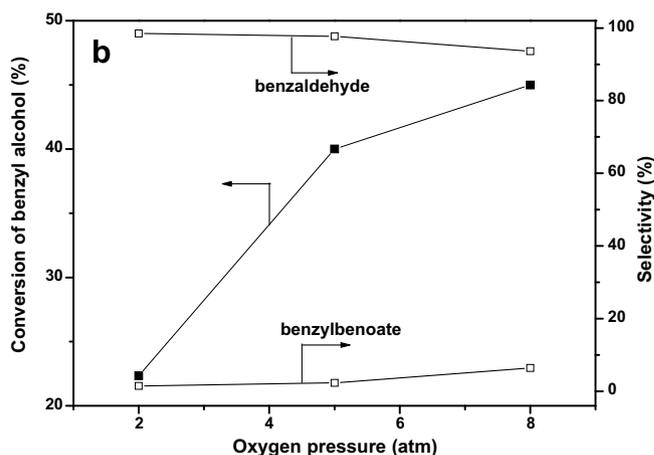
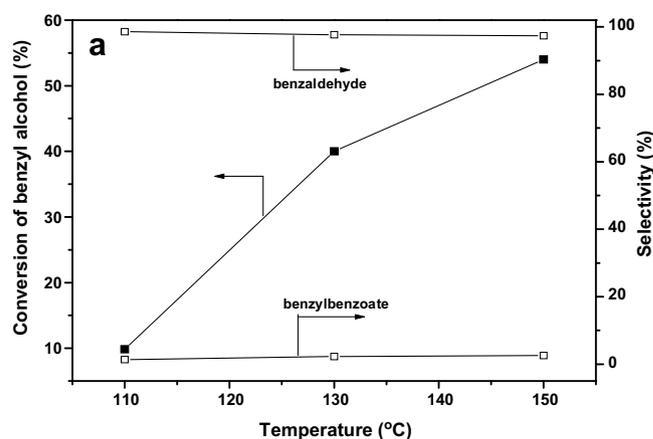


Fig. 3. Benzyl alcohol conversion and selectivity to benzaldehyde with 20 mL of benzyl alcohol after 5 h in the presence of 200 mg of Au/ γ -Ga₂O₃ catalyst. Top: temperatures of 110–150 °C and O₂ pressure of 5 atm. Bottom: pressures of 2–8 atm and a temperature of 130 °C.

Attempting to gain insight into the origin of the enhanced activity achieved by using gallia polymorphs as supports is important. It has been shown that the rate-limiting step for the oxidation of alcohols on various noble metals is a dehydrogenation step [5,23]. A recent spectroscopic investigation by Baiker et al. has confirmed that the basicity of the support is important to facilitate the

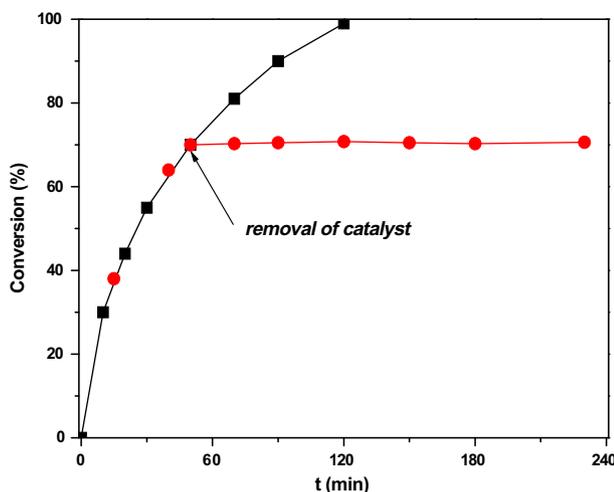


Fig. 4. Effect of removal of Au/ γ -Ga₂O₃ on the aerobic oxidation of benzyl alcohol. Reaction condition is the same as those in Table 2. Without removal of Au/ γ -Ga₂O₃ (■); the arrow indicates the removal of Au/ γ -Ga₂O₃ (●).

dehydrogenation step, thus leading to strong enhancement of activity for deposited gold nanoparticles in aerobic alcohol oxidations [24]. It is therefore worthwhile to make a comparison of the dehydrogenation activity of the present gold catalysts as measured by surface adsorption with 2-propanol [25]. As shown in Fig. 5, two weak hydrogen peaks centered around 190 and 350 °C were identified for the Au/CeO₂ sample, being the second more intense. Interestingly, no hydrogen signals could be detected for reference Au/TiO₂ and Au/Fe₂O₃ catalysts. When TPSR experiments were carried out by adsorbing 2-propanol on γ -Ga₂O₃, two hydrogen peaks at ca. 222 and 368 °C appeared. Notice that the adsorption of 2-propanol on Au/ γ -Ga₂O₃ produces a single hydrogen peak with pronounced intensity at much lower temperature of 198 °C,

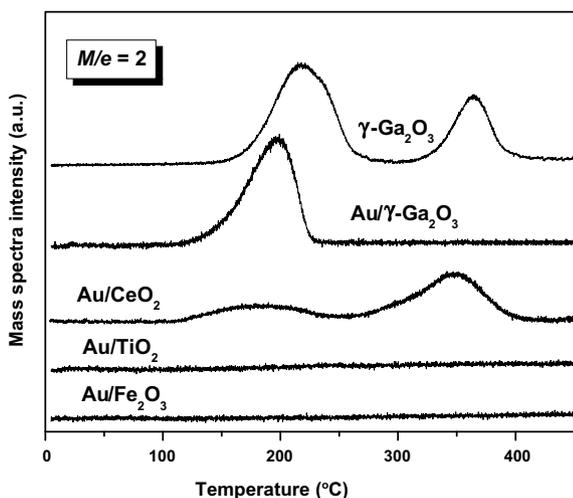


Fig. 5. TPSR spectra of 2-propanol on Au/ γ -Ga₂O₃, Au/CeO₂, Au/TiO₂ and Au/Fe₂O₃ catalysts for H₂ mass intensity. For comparison, the spectrum recorded for parent γ -Ga₂O₃ is also included. 2-Propanol adsorption at TR, 10 °C min⁻¹ heating rate.

inferring the presence of gold can greatly facilitate the dehydrogenation process of the adsorbed 2-propanol over the gallia supports. This allows confirming the presence of a significantly higher dehydrogenation capability and a strong metal-support interaction in the Au/ γ -Ga₂O₃ system, which could be the main reasons for its markedly enhanced alcohol oxidation activity.

4. Conclusion

In summary, we have successfully demonstrated that the combination of gold nanoparticles and gallia allows for the favourable generation of new type of gold catalysts highly effective for solvent-free liquid phase aerobic oxidation of benzyl alcohol by molecular oxygen. Benzaldehyde was obtained with high selectivity under the reaction conditions of 130 °C, 5 atm and 5 h. The Au/ γ -Ga₂O₃ catalyst was also very active for atmospheric pressure aerobic oxidation of benzyl alcohol, being stable under the reaction conditions and the conversion for 2 h reaction was still better than 98% after recycling four times. The significantly enhanced activity achievable over the Au/ γ -Ga₂O₃ catalyst as compared to its corresponding analogues supported on conventional supports has been attributed to the significantly enhanced dehydrogenation capabilities as well as a strong interaction between gold nanoparticles and the γ -Ga₂O₃ material.

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