

CHEMISTRY 
A EUROPEAN JOURNAL

Supporting Information

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Gold Supported on Nanocrystalline β -Ga₂O₃ as Versatile Bifunctional Catalyst for Facile Oxidative Transformation of Alcohols, Aldehydes and Acetals into Esters

Fang-Zheng Su, Ji Ni, Hao Sun, Yong Cao*,^[a] He-Yong He, Kang-Nian Fan

[a] Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials

Fudan University, Shanghai 200433, P. R. China

I. Catalysts preparation

Nanocrystalline β -Ga₂O₃ was prepared through an alcoholic gel-precipitation pathway. In a typical synthesis, concentrated aqueous ammonia and ethanol (50:50 in volume) was added dropwise to the ethanol solution of gallium nitrate hydrate until no more precipitation occurred. The resulting gel was quickly filtered and washed by ethanol, and dried at 100 °C for overnight, and finally calcined at 600 °C for 5 h. Conventional β -Ga₂O₃ was prepared by direct calcinations of the commercial gallium oxide (Aldrich, product no. 215066) at 800 °C for 6 h. Gold nanoparticles were deposited onto these materials using the homogeneous deposition-precipitation (HDP) method using urea as the precipitation agent and the gold content of the catalysts was 1.5 wt% (ICP-AES).

II. Procedure for catalytic oxidation

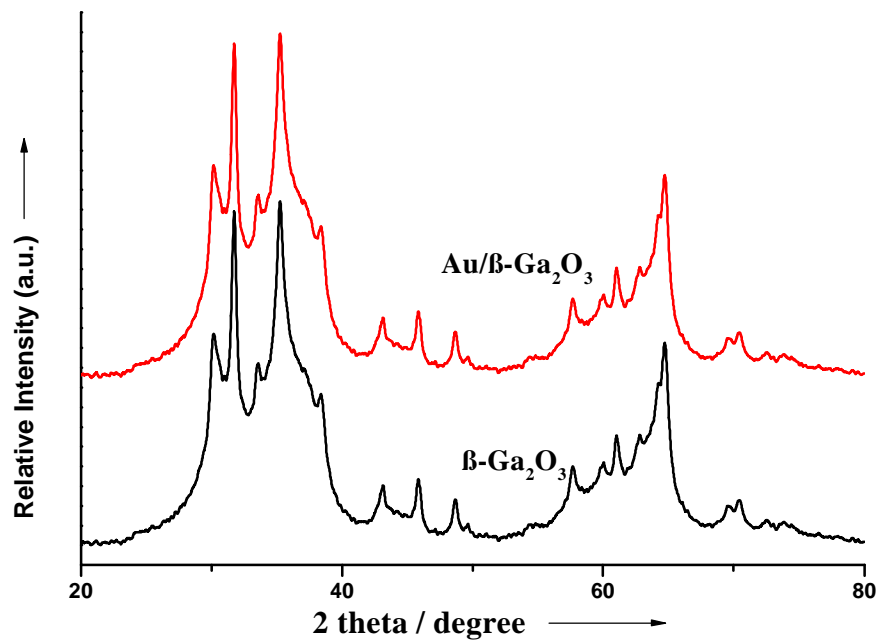
The oxidation reactions were carried out in a stirred autoclave reactor (Dalian Tongchan Co. Ltd., Capacity: 50 ml) using molecular oxygen as the oxidant under 5 atm pressure and at 90 °C. The stirring speed was set at 1000 rpm and reaction mixtures from the reactor were taken periodically via a sampling 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), using n-nonane as the external standard. The identification of the products was done in a GC-MS spectrometer comparing with commercially pure products.

III. Characterization methods

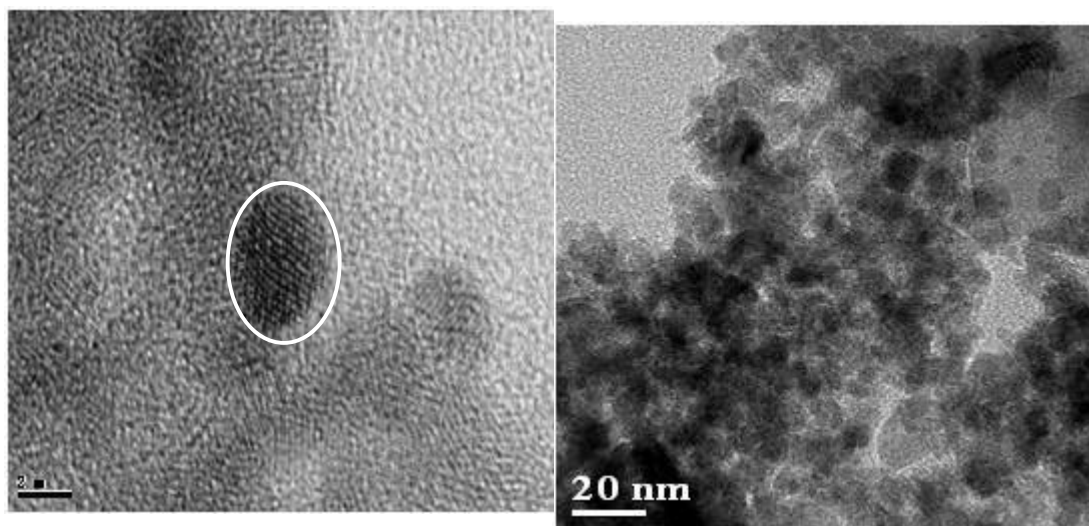
The BET specific surface areas of the samples were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. The X-ray powder diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Perkin Elmer PHI 5000C 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 1s line (284.6 eV) was used as the reference to calculate the binding energies (BE). 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 ethanol and applying a drop of very dilute suspension on carbon-coated grids. Elemental analysis was performed using ion-coupled plasma (ICP) atomic emission spectroscopy on a Thermo Electron IRIS Intrepid II XSP spectrometer. The sample was dissolved in a mixture of concentrated HCl and HNO₃ with volumetric ratio of 3/1 prior to the analysis.

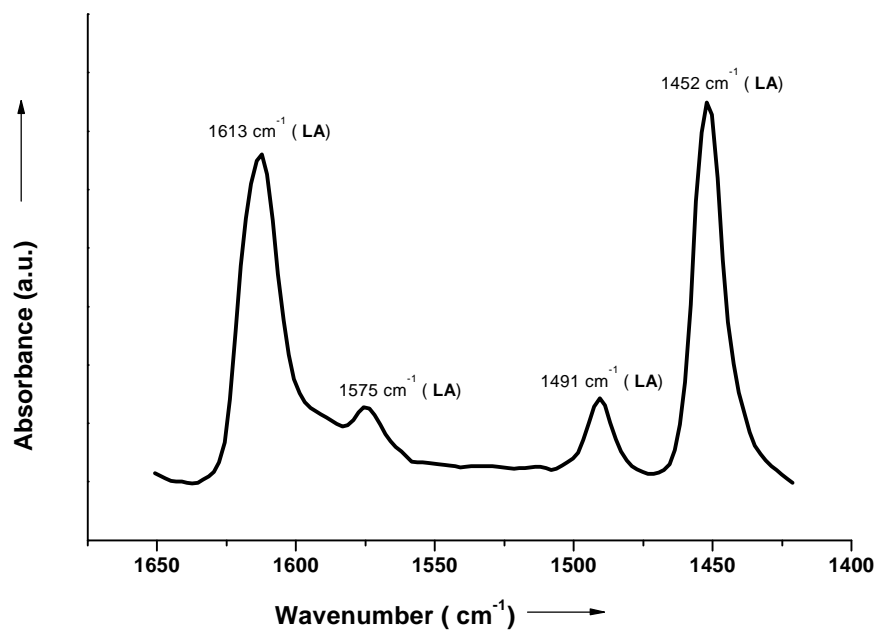
The amount surface acidity was measured by NH₃ temperature-programmed desorption (NH₃-TPD) in a flow-type fixed-bed reactor at ambient pressure. The sample (100 mg) was pretreated at 500 °C for 2 h and cooled to 120 °C in flowing He. At this temperature, sufficient pulses of NH₃ were injected until adsorption saturation, followed by purging with He for about 2 h. The temperature was then raised from 120 to 600 °C at a rate of 10 °C/min to desorb NH₃. The NH₃ desorbed was collected in a liquid N₂ trap and detected by on-line gas chromatography. Fourier transform infrared spectroscopy was used to study surface acidity, by means of pyridine adsorbed at room temperature. For these measurements, thin self-supported wafers of each sample were prepared and activated (outgassed) for 2 h at 300 °C under flowing He. After pyridine was allowed to equilibrate with the wafer for 30 min, gaseous and physically adsorbed pyridine was evacuated and a spectrum was collected at 200 °C. For the CO FT-IR, the sample was pretreated for 1 h at 200 °C under flowing He and then cooled to room temperature (25 °C). CO adsorption (CO/He = 5:95 in volume) was carried out at room temperature for 10 min and the IR spectra was collected using Nicolet 760.



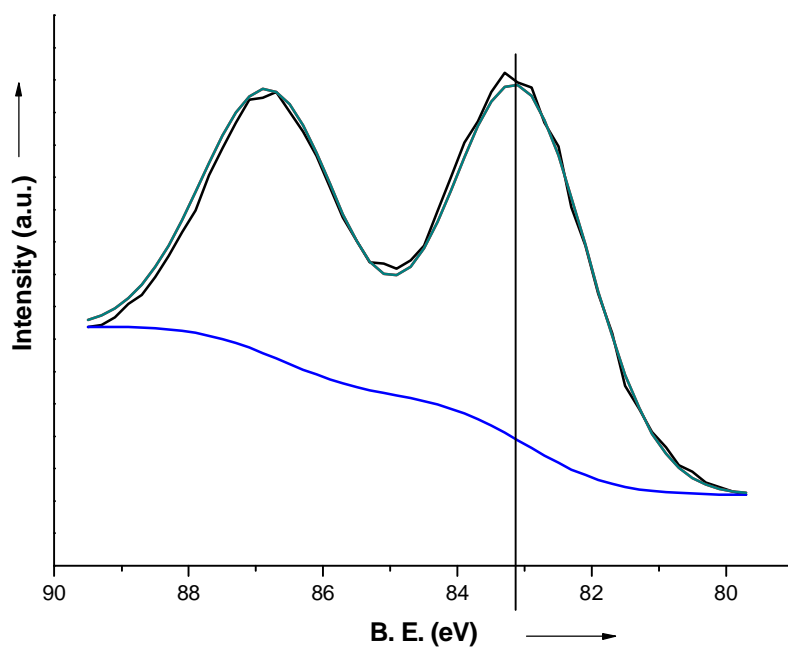
SI_Figure 1. XRD patterns of Au/β-Ga₂O₃ and β-Ga₂O₃.



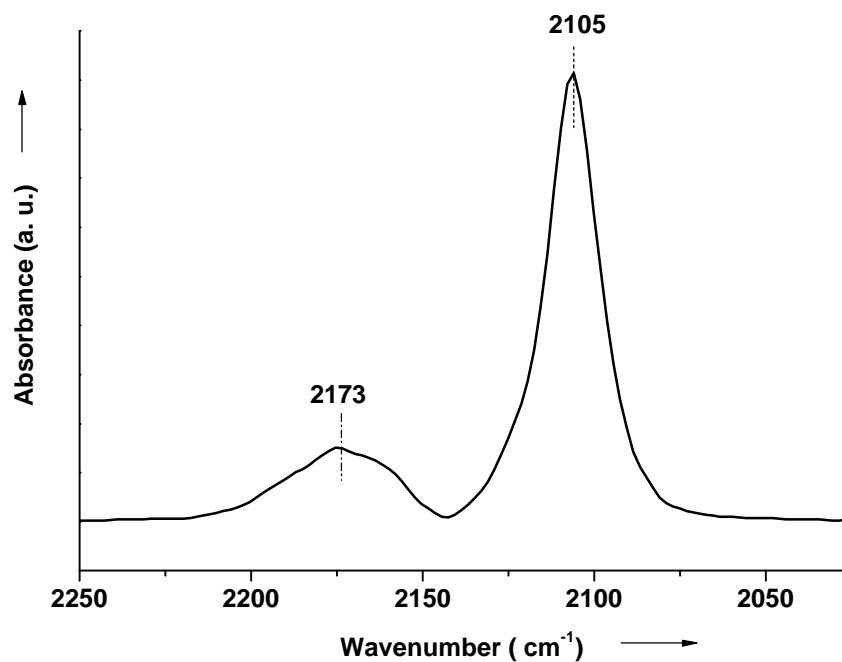
SI_Figure 2. Representative TEM image of Au/β-Ga₂O₃.



SI_Figure 3. FTIR spectra of pyridine adsorbed and then evaluated at 200 °C of Au/ β -Ga₂O₃.



SI_Figure 4. XPS spectra of Au 4f core level line of Au/ β -Ga₂O₃.

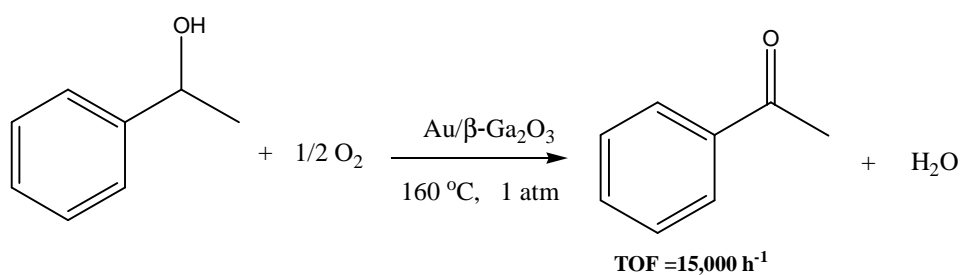


SI_Figure 5. FTIR spectra of CO adsorbed on Au/ β -Ga₂O₃ at room temperature. (The broad band around 2180 cm⁻¹ was characteristic of ambient gas CO.)

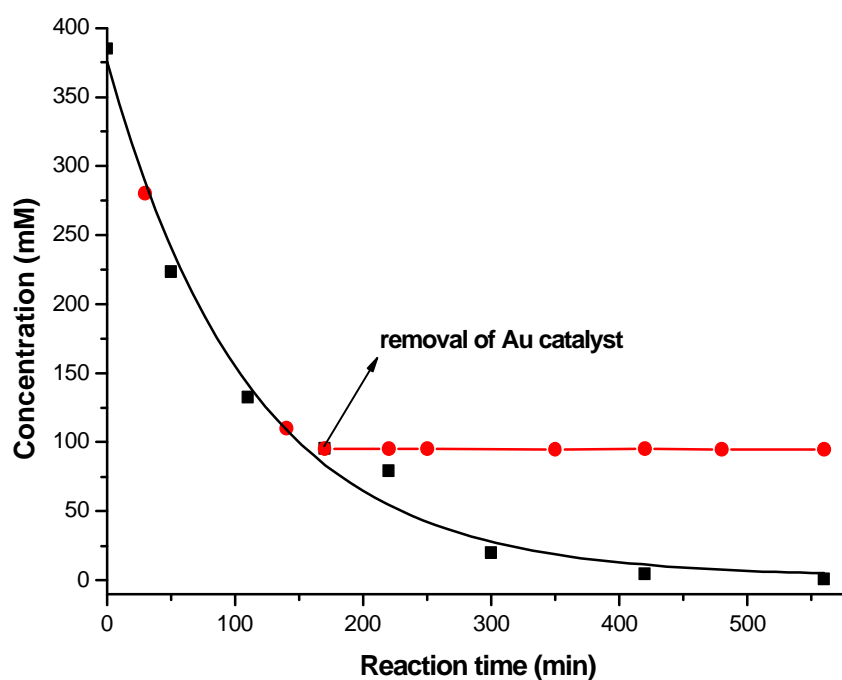
SI_Table 1. Physicochemical properties of gold catalysts supported on various oxides.

Catalysts	S _{BET} (m ² /g)	NH ₃ desorbed (mmol/g _{cat})
Au/ β -Ga ₂ O ₃	82.3	0.58
β -Ga ₂ O ₃	84	0.60
Au/Ga ₂ O ₃ -c	12	0.24
Au/?-Ga ₂ O ₃	120	0.35

Au/Ga ₃ Al ₃ O ₉	190	0.48
Au/TiO ₂	48.3	0.20
Au/Fe ₂ O ₃	35.1	0.25
Au/C	625.3	0.02



SI_Scheme 1. Turnover frequencies for solvent-free aerobic oxidation of (±)-1-phenylethanol based on Au/β-Ga₂O₃ measured at t = 20 min under the following conditions: (±)-1-phenylethanol (165.7 mmol), 3.0×10⁻⁴ mol % Au.



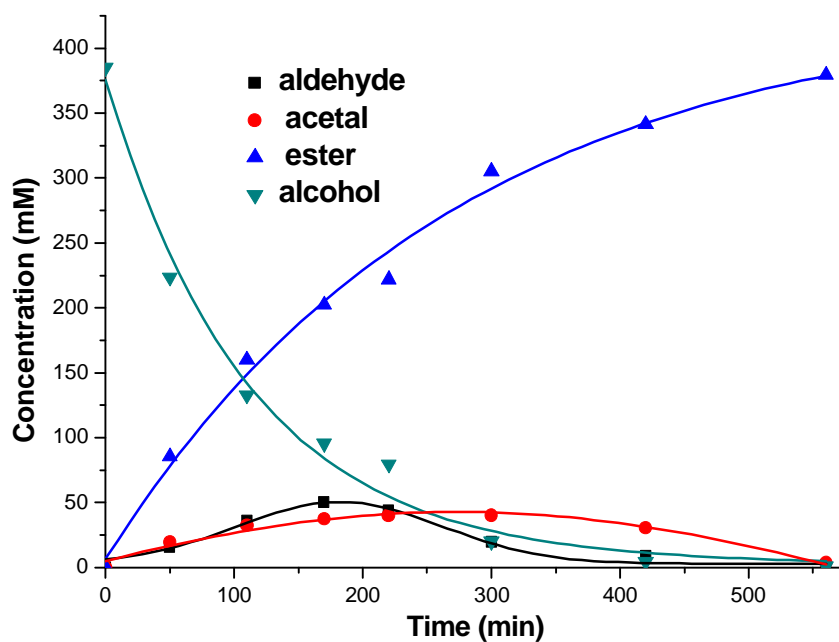
SI Figure 6. Effect of removal of Au catalyst on the oxidative esterification of benzyl alcohol over Au/ β -Ga₂O₃. Reaction condition: 5.78mmol benzyl alcohol and Au catalyst (0.2 mol%) in methanol (15ml), 90 °C, 5atm O₂.

SI Table 2. Control experiments for solvent-free oxidation of alcohols over Au catalysts.^[a]

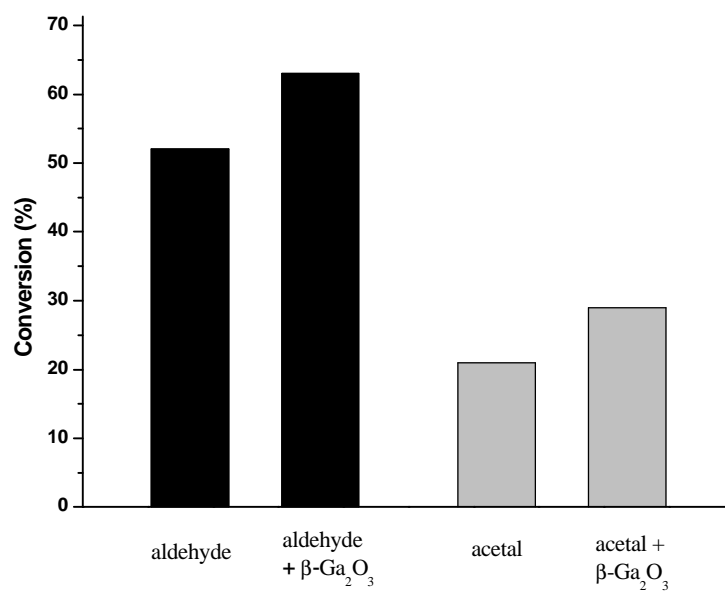
Substrate	Catalyst	Au/Sub (mol/mol)	Temp. (°C)	Time (h)	Product	Con. (%)	Sel. (%)
<i>n</i> -Propanol	Au/ β -Ga ₂ O ₃	5.96×10^{-4}	80	5	<i>n</i> -Propyl propionate	30	93
<i>n</i> -Propanol	Au/TiO ₂ ^[b]	5.96×10^{-4}	80	5	<i>n</i> -Propyl propionate	23	81
<i>n</i> -Propanol	Au/ β -Ga ₂ O ₃	5.96×10^{-5}	80	2	<i>n</i> -Propyl propionate	1.2	95
<i>n</i> -Butanol	Au/ β -Ga ₂ O ₃	6.8×10^{-4}	90	5	<i>n</i> -Butyl Butanoate	36	92
<i>n</i> -Butanol	Au/ZrO ₂ ^[b]	6.8×10^{-4}	90	5	<i>n</i> -Butyl Butanoate	28	79
<i>n</i> -Butanol	Au/ β -Ga ₂ O ₃	6.8×10^{-5}	90	2	<i>n</i> -Butyl Butanoate	1.4	93

[a] Reaction condition: substrate (15 ml) under 3 atm O₂. As suggested by the referee, the product analysis has been performed by quenching the reactor in an ice bath before depressurizing and sampling.

[b] Results from Hayashi's work of "Catal. Today, **2006**, *117*, 210".



SI_Figure 7. Kinetic study of the oxidative esterification of benzyl alcohol over Au/ β -Ga₂O₃. Reaction condition: 5.78 mmol benzyl alcohol and Au catalyst (0.2 mol%) in methanol (15 ml), 90 °C, 5 atm O₂.



SI_Figure 8. Influence of Lewis acid β -Ga₂O₃ additive on the oxidative esterification of benzaldehyde and benzaldehyde ethylene acetal over Au/TiO₂. Reaction condition: 4 mmol substrate, 50 mg β -Ga₂O₃ additive (5 mol%) and Au catalyst (0.078 mol%) in methanol (10 ml), 90 °C, 5 atm O₂, t = 0.5 h.