



Supporting Information

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Gold Nanoparticles Supported on Mesostructured Ga-Al Mixed Oxide with Enhanced Activity for Aerobic Alcohol Oxidation

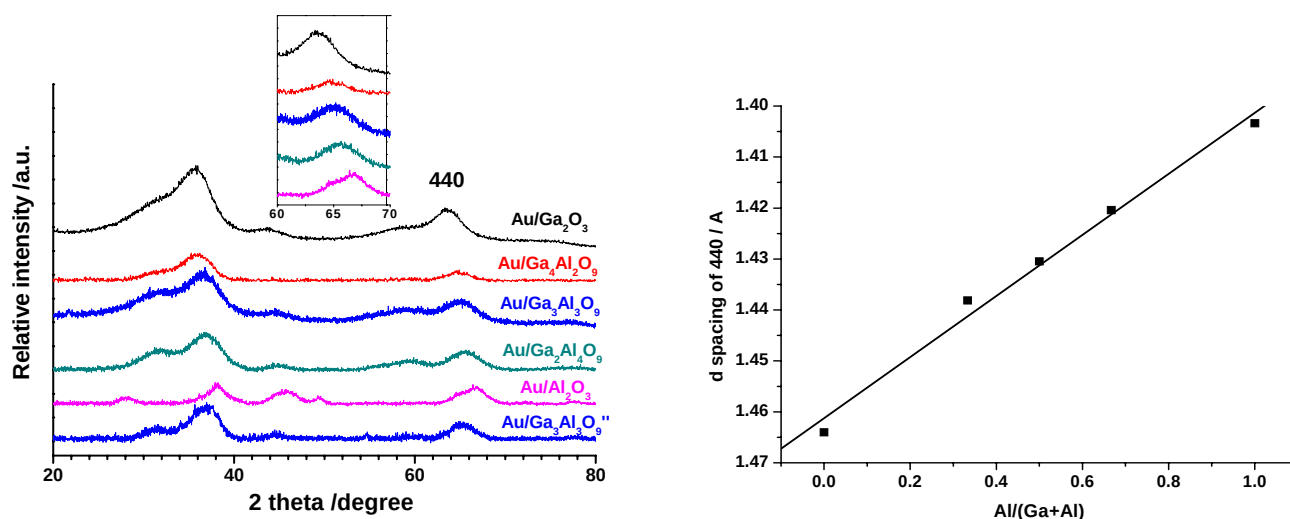
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I. Catalysts preparation

Mixed oxide supports including γ -Ga₂O₃-Al₂O₃, Ga₂O₃ and Al₂O₃ were prepared through an alcoholic sol-gel pathway.^[S1] In a typical synthesis, concentrated aqueous ammonia and ethanol (50:50 in volume) was added dropwise to the ethanol solution of gallium nitrate hydrate and aluminum nitrate hydrate with different Ga:Al molar ratio 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 500 °C for 6 h. The compositions (ratio of Ga/Al) of as-prepared powders were essentially identical to the charged ratio, determined by ICP-AES (see SI_Table 1). Gold nanoparticles were deposited onto these materials using the homogeneous deposition-precipitation (HDP) method using urea as the precipitation agent as developed by Louis and co-workers^[S2] and the gold content of the mixed oxide supported catalysts was 1 ± 0.02 wt% (ICP-AES).

II. Characterization methods

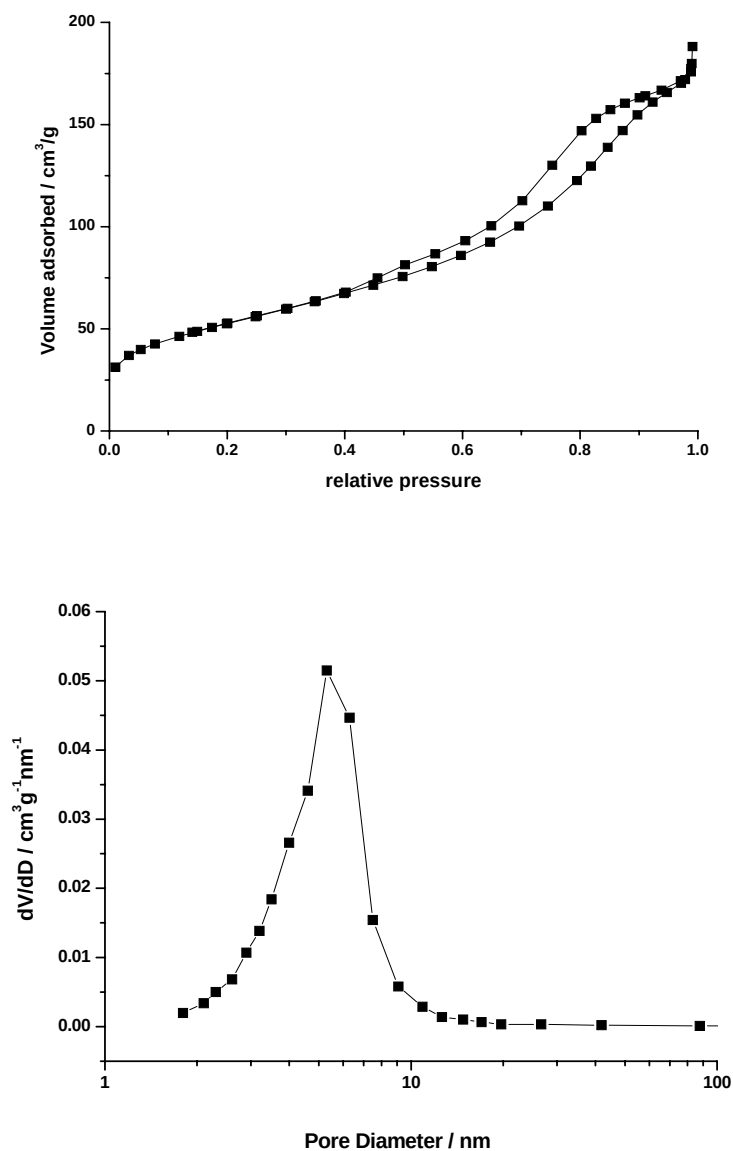
The BET specific surface areas of the samples were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. The X-ray powder diffraction (XRD) of the catalysts was carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered Cu K α radiation at 40 kV and 20 mA. 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 samples were dissolved in a mixture of concentrated HCl and HNO₃ with volumetric ratio of 3/1 prior to the analysis. The temperature programmed surface reaction (TPSR) experiments were carried out as follows: After the catalyst (50 mg) was activated at 300 °C for 2 h under He stream (20 ml·min⁻¹), 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.



SI_Figure 1. XRD patterns (left) of various oxides supported gold catalysts, the inset shows the reflected peaks assigned to (440) of oxides (the bottom plot depicts the Au/Ga₃Al₃O₉ sample after reaction). The linear correlation (right) between d₍₄₄₀₎ spacing and molar ratio of Al/(Ga + Al) for the Ga-Al solid solution.

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

catalysts	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{pore} (nm)	Ga/Al ratio from ICP-AES
Au/Ga ₂ O ₃	120	0.22	5.7	/
Au/Ga ₄ Al ₂ O ₉	123	0.15	4.2	2.06
Au/Ga ₃ Al ₃ O ₉	190	0.30	6.0	0.994
Au/Ga ₂ Al ₄ O ₉	254	0.22	4.4	0.52
Au/Al ₂ O ₃	175	0.30	4.9	/

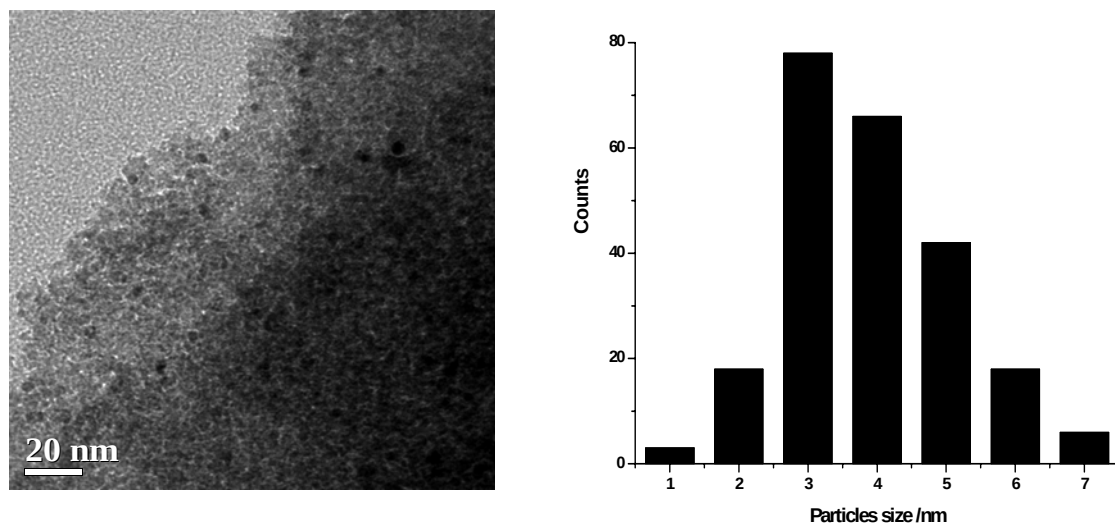


SI_Figure 2. Nitrogen adsorption-desorption isotherm (up) of Au/Ga₃Al₃O₉, and the corresponding pore size distribution curve (bottom) via BJH method.

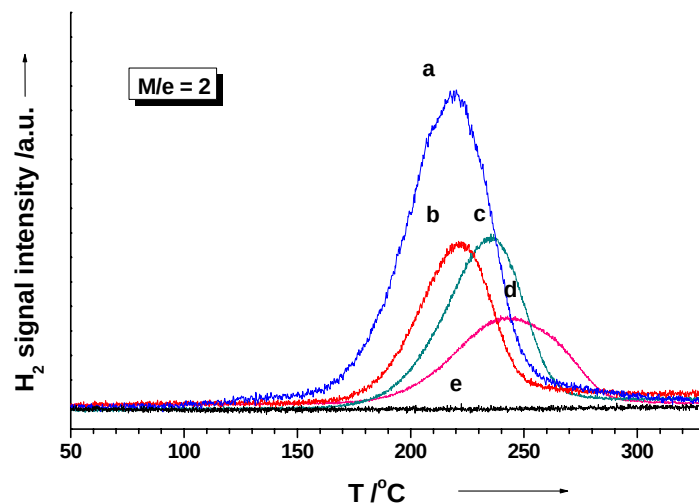
SI_Table 2. Comparison of the specific reaction rate (TOF) for aerobic oxidation of benzyl alcohol over various Au- or Pd-based catalysts.

Catalysts ^a	Con. (%)	Sel. (%)	Time (h)	TOF ^b (h ⁻¹)
Au/Ga ₃ Al ₃ O ₉	60	>99	0.5	237
Au/CeO ₂	54	>99	0.5	90
PdHAP	30	99	0.5	592
Au/TiO ₂	26	>99	0.5	65

[a] Catalysts see Table 1. [b] TOF was measure at t = 0.5 h, under reaction condition: benzyl alcohol (1 mmol), catalyst (0.1 g), toluene as solvent (10 ml), 80 °C, O₂ bubbling (20 ml·min⁻¹).



SI_Figure 3. Representative TEM image (left) and size distribution (right) of Au/Ga₃Al₃O₉.



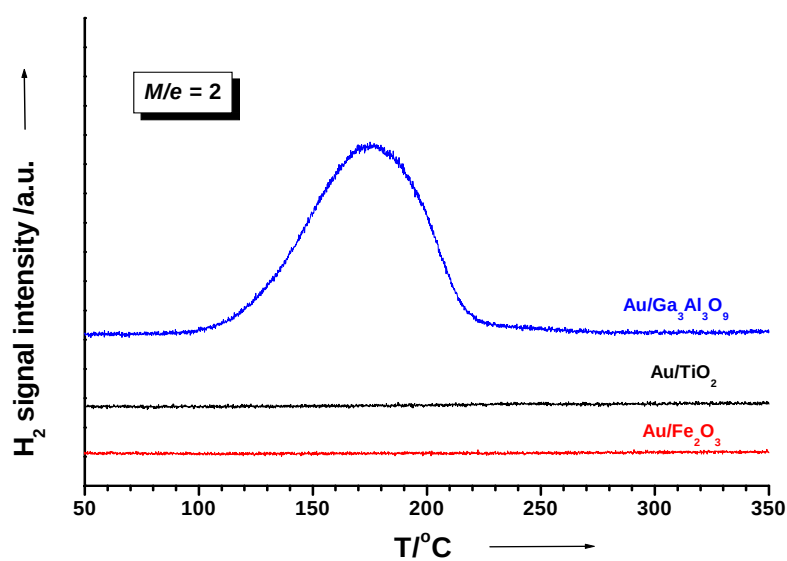
SI_Figure 4. TPSR diagram of 2-propanol on various supports for H₂ mass intensity.

a: Ga₃Al₃O₉, b: Ga₄Al₂O₉, c: Ga₂Al₄O₉, d: Ga₂O₃, e: Al₂O₃.

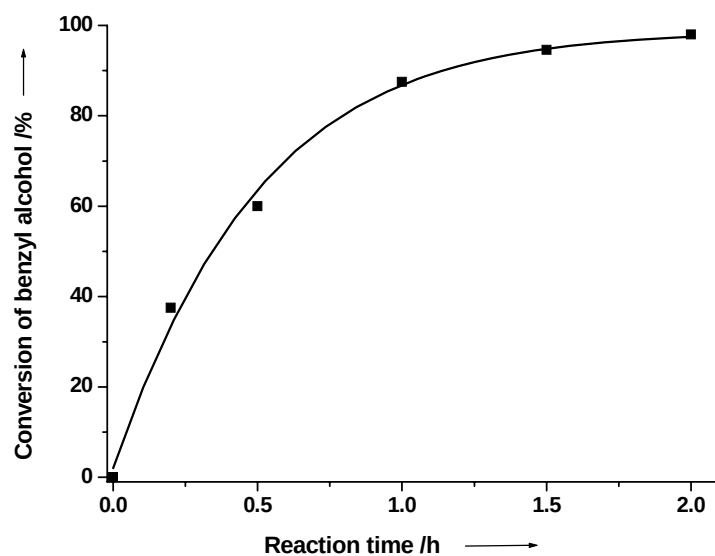
SI_Table 3. TPSR results of various Ga-Al mixed oxides as well as their corresponding gold catalysts.^[a]

Catalyst	T_M (°C)	Relative H ₂ Intensity (%) ^[b]	Support ^[c]	T_M (°C)	Relative H ₂ Intensity (%) ^[b]
Au/Ga ₂ O ₃	199	29	Ga ₂ O ₃	245	25
Au/Ga ₄ Al ₂ O ₉	172	39	Ga ₄ Al ₂ O ₉	222	36
Au/Ga ₃ Al ₃ O ₉	175	100	Ga ₃ Al ₃ O ₉	220	79
Au/Ga ₂ Al ₄ O ₉	198	36	Ga ₂ Al ₄ O ₉	238	33
Au/Al ₂ O ₃	208	0.6	Al ₂ O ₃	/	/

[a] Experimental conditions: 50 mg sample, 2-propanol adsorption at RT, 10 °C·min⁻¹ heating rate. [b] The normalized relative peak intensity based on H₂ mass signal. [c] In the absence of catalyst or when using the support in the absence of gold no alcohol oxidation was observed, confirming that the presence of gold was essential to obtain catalytic oxidation [S3].



SI_Figure 5. TPSR diagram of 2-propanol on $\text{Au/Ga}_3\text{Al}_3\text{O}_9$, Au/TiO_2 and $\text{Au/Fe}_2\text{O}_3$ catalysts for H_2 mass intensity.



SI_Figure 6. Conversion of benzyl alcohol as a function of time. Reaction condition: benzyl alcohol (1 mmol), 1 wt% $\text{Au/Ga}_3\text{Al}_3\text{O}_9$ (0.1 g), toluene as solvent (10 ml), 80°C , O_2 bubbling ($20\text{ ml}\cdot\text{min}^{-1}$).

References

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- [S2] R. Zanella, S. Giorgio, C. R. Henry and C. Louis, *J. Phys. Chem. B*, **2002**, 106, 7634.
- [S3] D. I. Enache, J. K. Edwards, P. Landon, B. Solsna-Espriu, A. F. Carely, A. A. herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, 311, 362.