



Supporting Information

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Catalysis by Gold: Isolated Surface Au³⁺ Ions are Active Sites in the Hydrogenation of 1,3-Butadiene over Au/ZrO₂ Catalysts

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Details of experiments and data analysis

Catalyst Preparation: ZrO₂ powders were prepared by conventionally method as described earlier.^[24] The BET surface area of ZrO₂ powders is 120 m²/g (ASAP2010C measurement) after being caclined in air at 400 °C for 5 h. Au/ZrO₂ catalysts were prepared by deposition-precipitation method by mixing ZrO₂ powders (2 g) with appropriate amounts of aqueous solutions of chloroauric acid (HAuCl₄) at a fixed pH (9.0 ± 0.1) adjusting with 0.2 M NH₄OH solution. The aqueous dispersion was stirred for 6 h and aged for 2 h, and then suction filtered. Extensive washing with deionized water was then followed until it was free of chloride ions (i.e. until conductance of the washed solution in the final wash was less than 10⁻⁵ Sm⁻¹). The samples was dried at 110 °C for 12 h, and calcined at 200 °C for 5 h in flowing air (60 mL/min). The concentration of gold was adjusted to yield catalysts containing 0.76, 0.23, 0.05 and 0.01% Au by weight (ICP-AES analysis). The calcination temperatures were changed, i.e. 200, 300 and 500 °C for 0.76% Au/ZrO₂ catalysts.

Treatment with KCN solution: The catalyst was treated with aqueous solutions of KCN using a process similar to that reported by Fu et al. 1.0 g of the 0.76% Au/ZrO₂ catalyst (calcination temperature: 200 °C) was added to 20 mL of a 2 wt% KCN (A. R.) aqueous solution adjusted to pH >12 with a few drop of a 1 M NaOH solution. This mixture was stirred for 70 min at room temperature, and then suction filtered. The resulting material was extensively washed with deionized H₂O. The sample was dried at 110 °C for 12 h, and calcined at 200 °C for 5 h in flowing air (60 mL/min). ICP-AES

measurement shows the loading of gold of this sample is 0.08% and no K and Na are detected.

Hydrogenation of 1,3-butadiene Catalysis: Hydrogenation of 1,3-butadiene was performed in a fixed-bed stainless steel reactor (i.d.= 4 mm) at atmospheric pressure and 120 °C. The reactant of 2.15 vol% 1,3-butadiene in H₂ was introduced to the catalyst at a flow rate of 13.5 mLmin⁻¹. Before reaction all samples (0.1 g diluted with 0.45 g quartz powder) were pretreated in situ in 30 mLmin⁻¹ Ar at 200 °C for 2 h. The reactor effluent was one-line analyzed using gas chromatograph.

ICP-AES and BET analysis: Inductively coupled plasma analysis was performed on a Leeman Prodigy spectrometer, using 100 mg of sample dissolved in about 15 mL of aqua regia at 75 °C for 12 h. BET measurements were carried out with nitrogen adsorption at 196 °C on a Micromeritics ASAP 2010C instrument. The samples were dehydrated under vacuum at 200 °C for 5 h before the adsorption measurement.

Temperature-Programmed Reduction (TPR) study: Quantitative TPR measurement of the Au/ZrO₂ catalysts was conducted from 20 to 780 °C on a homemade TPR apparatus equipped a thermal conductivity detector (TCD) with 5% H₂/Ar as the reductant. The temperature ramp was 10 °C/min. Water, which is the only volatile product of the reduction reaction, was removed from the exit gas with a cold trap at - 114 °C to avoid its interference into the TCD detector. Before the reduction, the sample was pretreated at 200 °C for 30 min in the flowing pure Ar. The H₂ consumption was calculated by integrating the area under the TCD signal and on the basis of the calibrations determining TCD responses at various weight of pure CuO.

X-ray Photoelectron Spectra: X-ray photoelectron spectra (Au 4f) of the catalysts were recorded with a PHI-5300 ESCA spectrometer equipped with Mg Ka radiation. The residual pressure in the analytical chamber was maintained below 10⁻¹⁰ Torr

during data acquisition. The binding energies of Au 4f were corrected for surface charging by referencing them to the energy of C 1s peak of contaminant carbon at 285.0 eV.

TEM characterization: TEM and high-resolution transmission electron microscopy (HRTEM) characterizations were performed on JEM-2010F (200 kV). The samples were dispersed in ethanol using an ultrasonic bath, and then deposited on a polymer coated copper grids. EDS was combined to differentiate the gold particles from zirconia particles (figure is not shown here). About 200 particles were chosen to determine the average size of Au particles according to equation $d = \sum n_i d_i / n_i$.

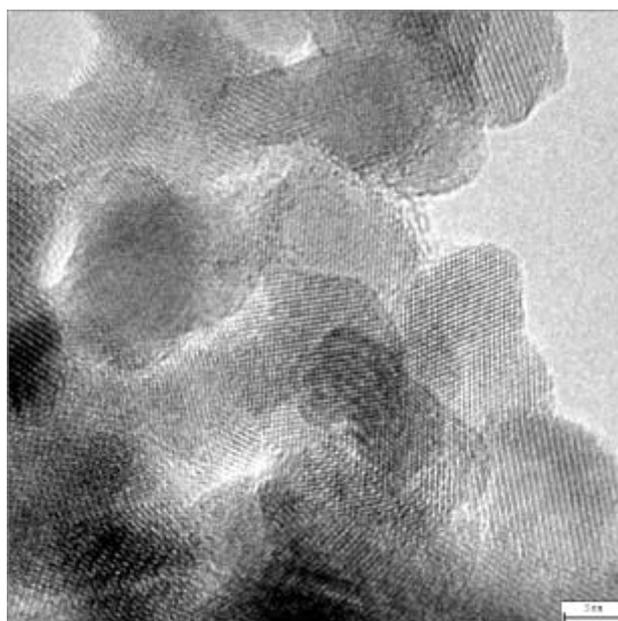


Figure S1. High resolution TEM image of the 0.08% Au/ZrO₂ catalyst. Au/ZrO₂ catalysts containing 0.01% and 0.05% Au, and also the bare ZrO₂ support showed similar TEM images.

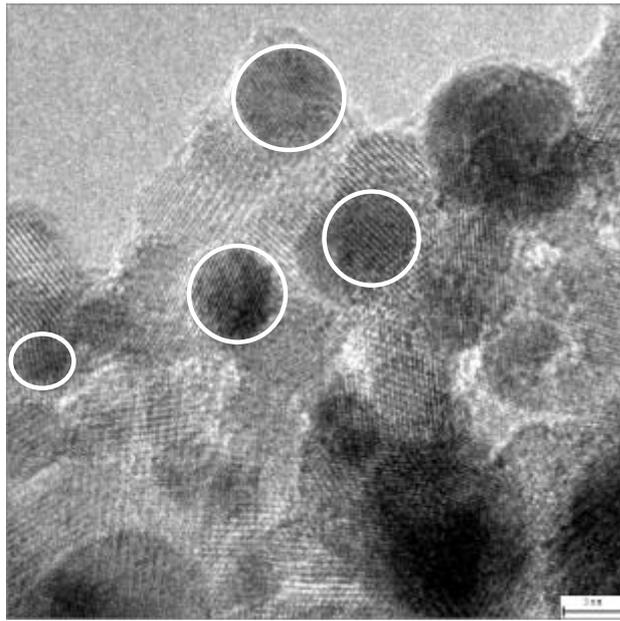


Figure S2. TEM image of 0.76% Au/ZrO₂ sample calcined at 200 °C

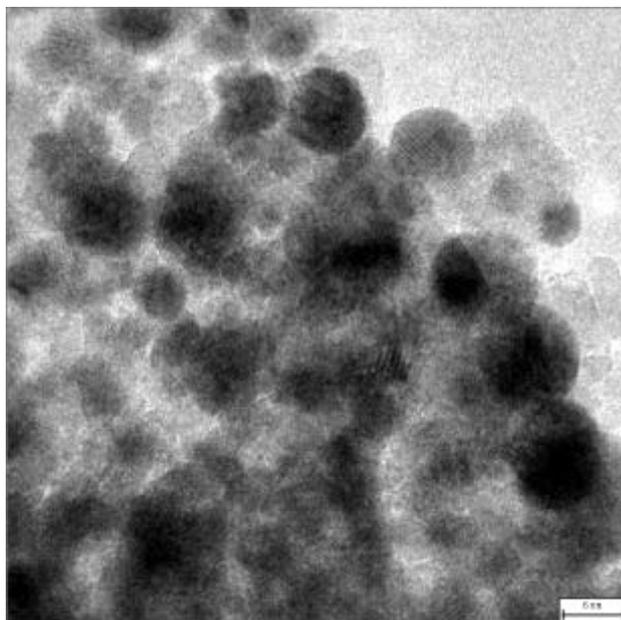


Figure S3. TEM image of 0.76% Au/ZrO₂ sample calcined at 300 °C

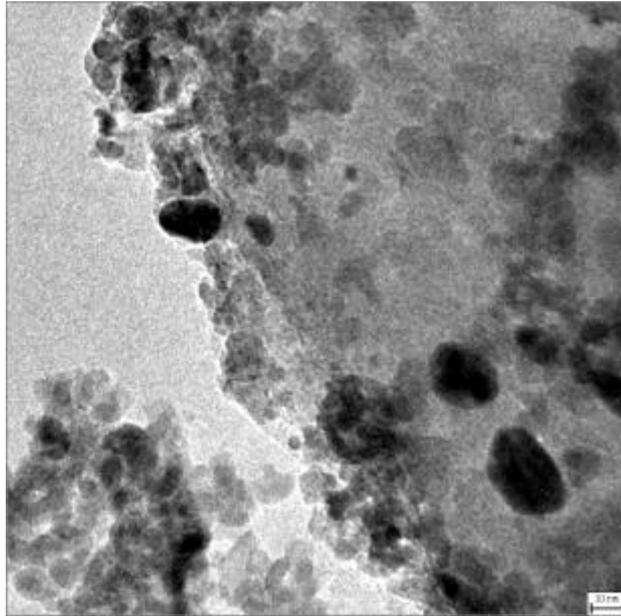


Figure S4. TEM image of 0.76% Au/ZrO₂ sample calcined at 500 °C