Supporting Information

Structure-Activity Relationship of Au/ZrO$_2$ Catalyst on Formation of Hydroxyl Groups and Its Influence on CO Oxidation

Christopher J.Karwacki[1], P. Ganesh[2], Paul R. C. Kent[2,3], Wesley O. Gordon[1],

Gregory W. Peterson[1], Jun Jie Niu[4], and Yury Gogotsi[4]

[1] Edgewood Chemical Biological Center, 5183 Blackhawk Rd., APG, Maryland 21010-5424, United States

[2] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[3] Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[4] Department of Materials Science and Engineering and A. J. Drexel Nanotechnology Institute, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104

Corresponding author: christopher.j.karwacki.civ@mail.mil

Phone: (410) 436-5704. Fax: (410) 436-5513

Supporting information includes adsorption equilibrium, textural properties of titania supports, TEM images of gold particles on zirconia prepared at pH 3.0 and 9.0, catalyst activity at pH 3.0 – 9.0 and description of test apparatus.
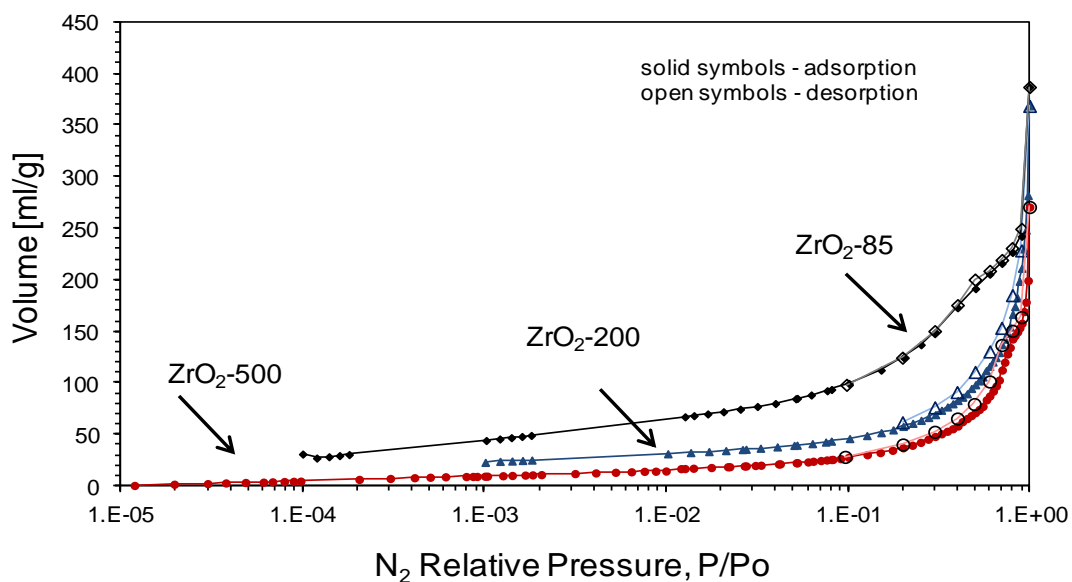

Figure S1. Nitrogen isotherms on ZrO_2 with thermal treatment at 85, 200, 500 ^{o}C.

Instrument: Quantachrome Autosorb-1
Adsorbate: nitrogen
Relative Pressure Range 1e-5 to 1
Number of points: 64
Software: version 1.55
Sample Outgassing Temperature: 85 ^{o}C for 24 hrs under vacuum
Sample Weight: 0.03 to 0.05 g, post-outgassing

Table S1. Textural properties of titania samples.

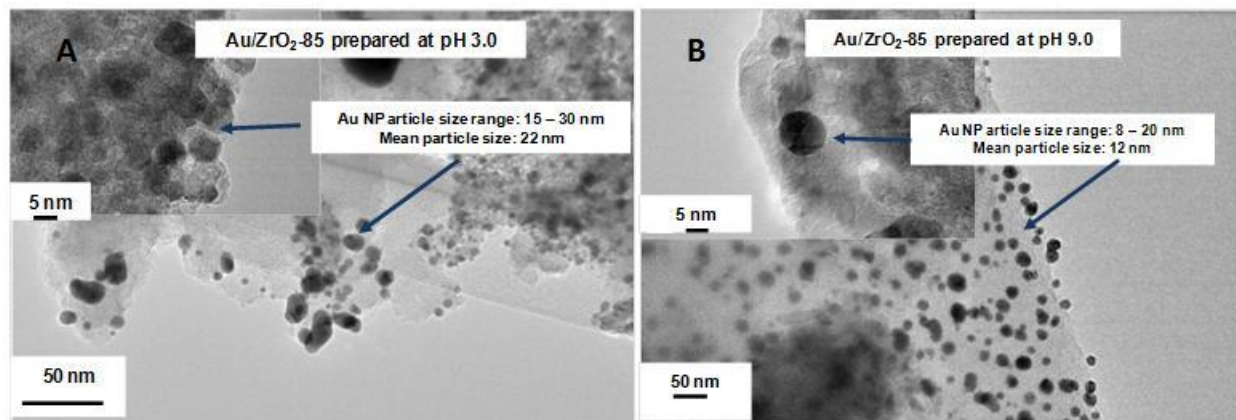| Sample	BET Surface Area (m^2/g)	Pore Width[a] (nm)	V_{micro} (ml/g)
Ti-anatase-85	206	2.5	0.077
Ti-isopropoxide-85	577	1.6	0.19
a. pore diameter calculated by NLDFT silica-equilibrium adsorption kernel			

Figure S2. TEM images of gold particles dispersed on zirconia support (Au/ZrO$_2$-85) prepared at pH 3.0 (panel A: pH 3.0 range 15-30 nm, mean = 22 nm) and 9.0 (panel B: pH 9.0 range 8-20 nm, mean = 12 nm). Note the increased size of the gold particles compared to the preparations at pH 6.4 (mean size 3.6 nm, see TEM Fig. 1D and histogram Fig. 1G)
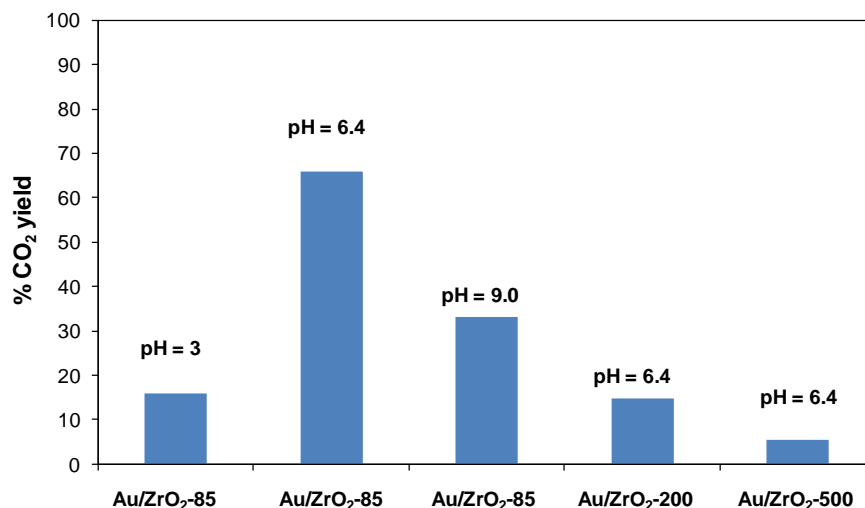
Figure S3. Plotted data shows the effect of pH of dispersed solution in preparation of Au/ZrO_2 catalyst

Figure S3 shows the $\%CO_2$ yield for zirconia catalysts, prepared at different pH and temperature treatments, exposed to a CO/air/water mixture. For the catalyst activity measurements, each catalyst sample was run at a bed temperature of 100 °C, with a CO feed concentration of 1000 ppm, 25% RH, at a flow rate of 100 ml/min (25,400 hr^{-1}) under single pass plug-flow conditions. The data for the Au/ZrO_2-85 indicates the maximum yield (66.1%, avg. n=5) occurs at about pH 6.4, followed by 33% and 16% at pH 9 and 3, respectively. For comparison, catalyst activities for the 200 and 500 °C thermal treatments are provided in Figure S2. Both of these supports (ZrO_2-200 and ZrO_2-500) were prepared with gold under pH 6.4 conditions. The effect of pH treatment on catalyst activity is likely related to the ratio and chemical state of cations and anions in solution (Cl^-, Na^+, OH^-, PVA, and water) containing Au NP and charge on the surface of the metal oxide.

The effect of pH on catalyst activity during preparation of the gold solution and zirconia support was performed. The pH of the gold solution and surface of the support are known to influence the structure of the ionic species and the deposition and stability of gold on the support surface. At low pH, the equilibrium favors stabilization of the $AuCl_4^-$, and under acidic conditions the chloride is difficult to remove. With increasing pH, the chloride dissociates substituting OH onto gold, forming $Au(OH)Cl_3$, $Au(OH)_2Cl_2$, and $Au(OH)_3Cl$. During catalyst preparations at low pH, the chloride ion reduces the deposition of gold onto the metal oxide support and facilitates agglomeration of the gold colloid and reduced metal clusters. The acidic environment favors retention of chloride and interferes with CO oxidation. At mid-range pH (6–9), there is an increase in $Au(OH)_3$ formation with enhanced deposition onto the support. However, the ionic nature of the support, that is its pH and IEP, can promote or diminish

absorption of gold ions. With increasing pH (>9) and difference in the support's IEP, the deposition of gold can decrease.

The pH values ranged from 3 to 9 and were adjusted in both the gold solution and support when dispersed in water. pH 6.4 was selected since this value is equivalent to the point of zero charge (pzc) for ZrO_2. Under these conditions the surface environment was ionic neutral, thus reducing competitive effects between surface and solution ions. The addition of $NaBH_4$ decreased the pH, which required further addition of NaOH to increase the pH to 6.4. Similarly, the pH of the support dispersed in water (usually 100 ml) was adjusted to the value of the gold solution. Typically as the solution was stirred, the pH decreased slightly, likely due to the release of chloride ions, and was readjusted with the addition of NaOH. A similar process was used for the pH 3 and 9 preparations.
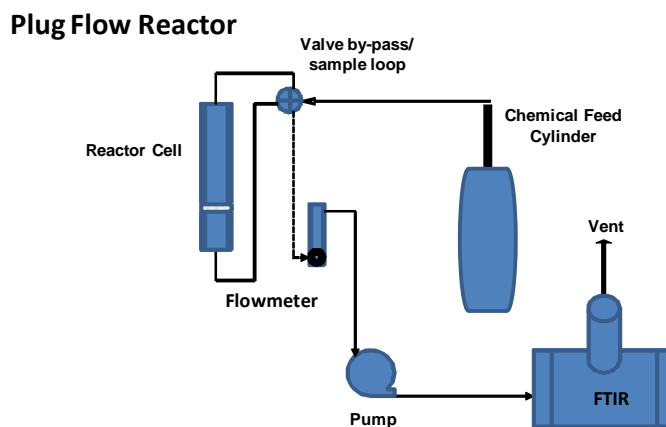

Figure S4. Schematic of test apparatus for measuring catalyst activity.

Description of Operation

Test system is a single-pass plug flow design consisting of a sample tube for supporting catalyst, rotometer for flow control, pump, mixing ballast, stream selection valve, and infrared detector. The sample tube consists of a 15 cm long tube with a 10 mm inside diameter and 15 mm outside diameter. The ends of the glass sample tube contain 3/8 inch metal couplings fused to each end of the glass tube. The metal couplings are fitted with a Swagelok 3/8 inch nut and ferrule for connection to sample lines. The sample tube is temperature controlled by resistance heating wrap. A thermocouple is placed between the heat wrap and the glass tube to monitor the temperature. Located in the glass sample tube is a quartz frit to support the catalyst sample. The frit is porous and allows gas mixture to pass through the catalyst sample bed. The direction of flow is downward to prevent the catalyst sample from fluidizing. Gas flow

rate through the tube is regulated by a rotometer and a bellows pump containing stainless steel reed valves. The flow rate is typically 100 ml/min during activity measurements but can be adjusted from zero to about 300 ml/min. A stream selection valve upstream of the sample tube directs the flow of gas into the sample tube or around the sample. The by-pass allows the gas mixture concentration to be established before its exposure to the sample catalyst. The gas mixture concentration is based on the mass of chemical injected into the chemical feed cylinder, the volume of air in the cylinder at total pressure.