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Supporting Information

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Supported Gold Catalyzes Homocoupling of Phenylboronic Acid with High Conversion and Selectivity

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A BioRad spectrometer FTS-40A with a spectral resolution of 2 cm^{-1} was used to collect transmission infrared spectra of the solid catalysts. Samples were pressed (~ 2 ton/cm^2 for 5 minutes) into self-supporting wafers (10 mg cm^{-2})and loaded into a quartz cell with KRS-5 windows and connected to a vaccum/adsorption system, which allowed recording of the spectra while the treatment gas was adsorbed/desorbed from the samples during experiments. The catalysts were pretreated at 323 K in vacuum (10^{-2} Pa) for 1 h before adsorption experiments. Pulses of CO and O_2 were introduced at room temperature using a calibrated volume of 1.55 cm^3. In order to avoid O_2 and water

contamination during the CO adsorption experiments a cool trap (liquid nitrogen and isopropanol mixture) has been used. Each reported spectrum is the average of 64 scans.

Raman spectra were collected with a Renishaw inVia Raman spectrometer equipped with a Leica DMLM microscope and a 785-nm Ar^+ ion laser as an excitation source. Three fiber optics probes were used to focus the depolarized laser beam on a spot of about 3 μm in diameter and to monitor in situ the reaction media during catalysis experiments; using a laser power at the sample of 25 mW. The Raman scattering was collected with a CCD array detector and in the 100–4500 cm^{-1} spectral region with a resolution of 2 cm^{-1}. Each reported spectrum is the average of 20 scans with an exposure time each of 10 s.

XPS data were collected in a VG Escalab 210 spectrometer using monochromated Al Ka (*h?* = 1486.6 eV) X-ray radiation. To avoid photoreduction of ceria, the energy of the X-ray beam was limited to 100 W. Kinetic energies of photoelectrons were measured with a hemispherical electron analyzer working at constant pass energy of 50 eV. The pressure in the analyzing chamber was maintained at 750 × 10^{-6} Torr. The binding energy scales were corrected by setting the C1s transition at 284.5 eV.

Atomic Absorption Analysis (AAS) were carried out on a Varian Spectra AA–10 Plus using a hollow cathode lamp specific for gold. The sample introduction system consisted

of a PFA microflow nebuliser. After evaporation of the organic solvent the sample was dried 24 hours at 373 K to eliminate all possible traces of organic material. ***Aqua Regia*** was then added to re-dissolve the gold present, then the sample was diluted with H_2O MilliQ and analysed.

sample	B.E. Au $4f_{7/2}$ (eV)	assignment	B.E. Ce $3d_{5/2}$ (eV)	assignment
Au/CeO_2-nanocrystalline	86.2	Au^{3+}		
	84.7	Au^{+}		
			880.4	Ce^{3+}
			884.0	Ce^{4+}
Au/CeO_2	84.1	Au^{0}		
Au foil	84.0	Au^{0}		

Table 1: XPS results characterizing the gold supported on conventionally precipitated and nanocrystalline CeO_2 samples

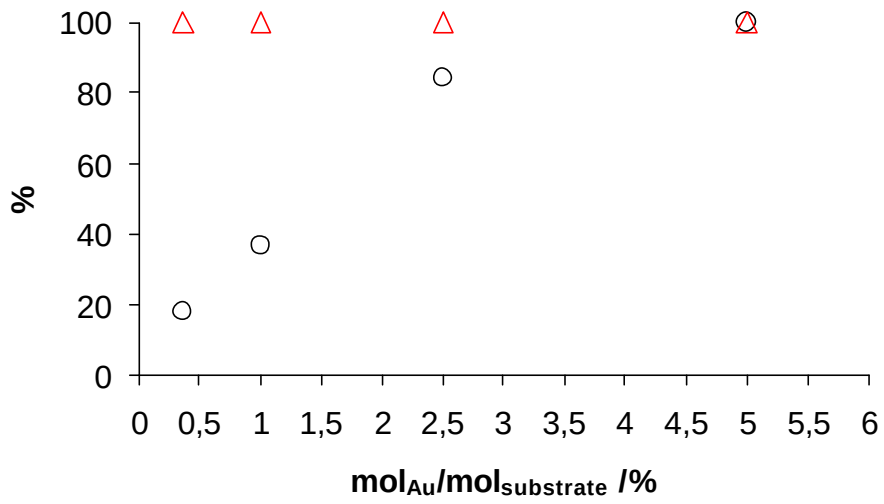

Figure 1: Homocoupling of phenylboronic acid on 2.25% Au/CeO_2, 0.3 mmol phenylboronic acid, 0.4 mmol K_2CO_3, 5 ml toluene, T = 333K, 15 hrs. (O) Boronic acid conversion; (△) Selectivity to Biphenyl.

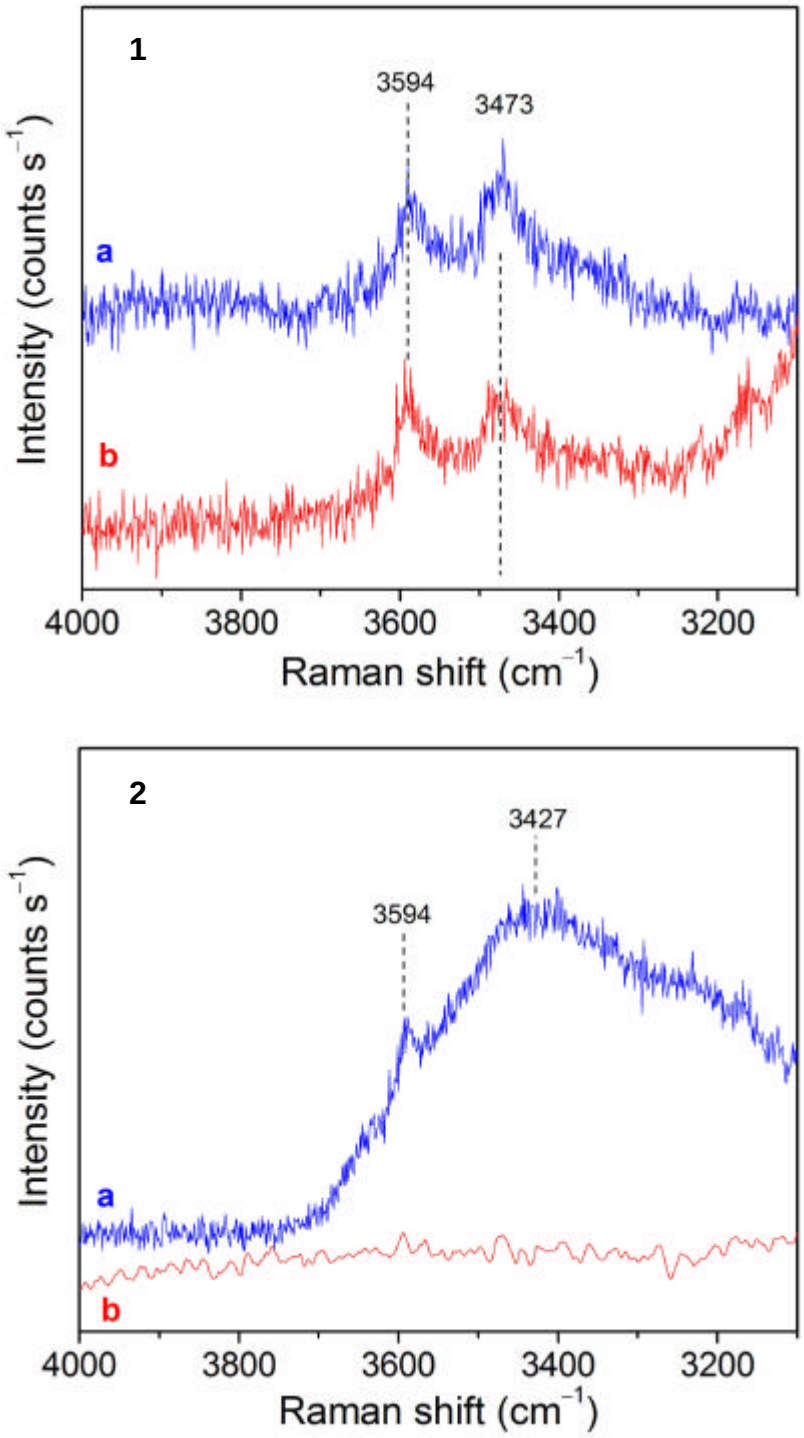

Figure 2: Raman Spectra of: 1) CeO_2 after addition of water (blue, a) and after addition of water and $PhB(OH)_2$ (red, b); 2) Au/CeO_2 after addition of water (blue, a) and after addition of water and $PhB(OH)_2$ (red, b).

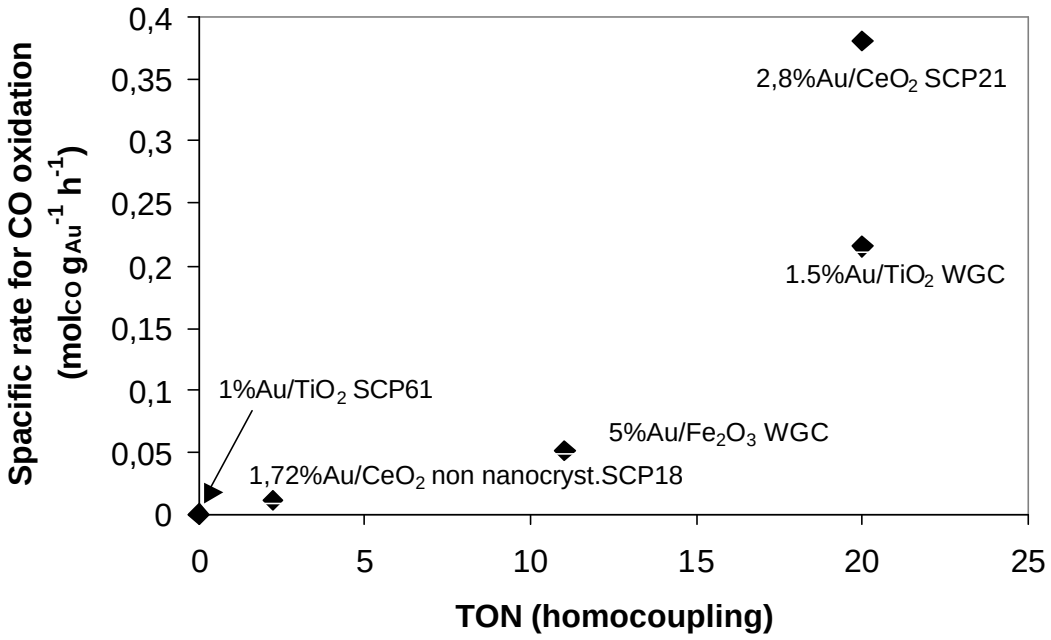

Figure 3: Specific rate (mol_{CO} g_{Au}^{-1} h^{-1}) for CO oxidation on supported gold catalysts compared with TON for homocoupling of phenylboronic acid. 1.5%Au/TiO_2 and 5%Au/Fe_2O_3 catalysts have been supplied by the World Gold Council. CO oxidation: CO-Air-He molar ratio of 0.2-19.8-80; contact time, W/F, of 94 (g_{cat} h mol_{CO}^{-1}); reaction temperature = 278 K. Homocoupling reaction: 5 ml toluene; 5% mol of Au; T = 333K; 15 hours; yield determined by GC-MS. (WGC: World Gold Council).