Supporting Information for

Novel Au/La$_2$O$_3$ and Au/La$_2$O$_2$SO$_4$ Catalysts for the Water-Gas Shift Reaction Prepared via an Anion Adsorption Method

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In situ UV-Visible Spectroscopy Studies

The speciation of the gold precursor as a function of the solution temperature and pH value was followed *in situ* via a UV-Visible Spectrometer (Evolution 300 by Thermo Scientific) equipped with a heated cell. Typically, during preparation of 2 g of catalyst, the gold precursor solution (100mL, 1.0 mM) is added into 200 mL of support solution, resulting in an overall gold concentration of 0.4 mM. To simulate the actual preparation conditions as closely as possible, this gold concentration was used for the stock solution to be tested by UV-Vis. Approximately 3 mL of solution prepared in this manner (pH ~ 3.5) was added in a quartz cuvette with a path length of 1 cm and placed in the spectrometer cell. Several spectra were collected at RT prior to the ramping. The configuration of the instrument did not allow for setting of a specific ramping rate; however a heating rate of ~ 10 °C min^{-1} was typical for the temperature profile examined in our study. As shown in Figure S1, there is a blue shift in the characteristic gold ion absorption band[1] during the temperature ramp, suggesting speciation of the $[AuCl_4]^-$ to a more hydroxylated species $[AuCl_x(OH)_{4-x}]^-$. The effect of pH on the gold speciation was examined by adjusting the stock solution pH to 7 with the addition of small amounts of standard sodium hydroxide solution (0.05N, Alfa Aesar). At this neutral pH (Figure S1), gold is speciated to $[Au(OH)_4]^-$ as confirmed by the absence of any peak in the spectra. Taken together, these results indicate that at the preparation conditions, the predominant Au species in solution – and therefore available for adsorption to the support surface – is the $[Au(OH)_4]^-$ complex.

Figure S1. Speciation of $[Au(OH)_4]^-$ as measured by UV-Vis spectroscopy.
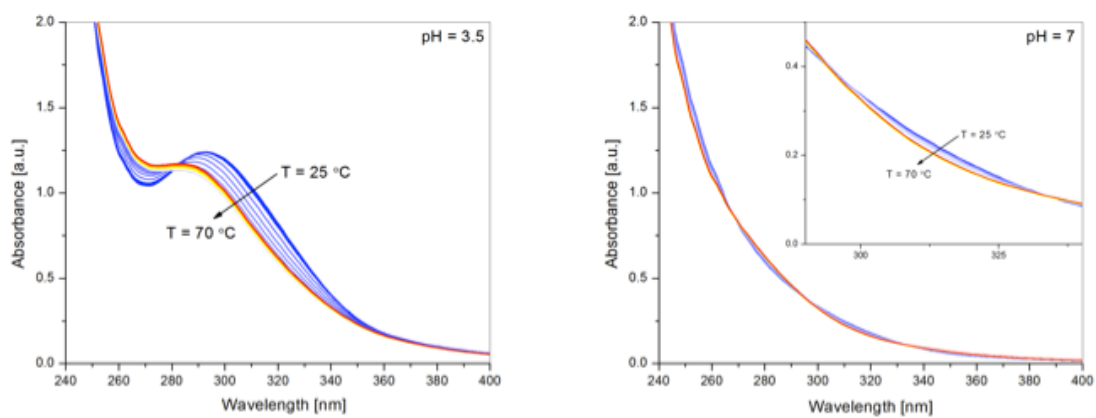
Silver Nitrate and Sodium Borohydride Tests

The supernatant (collected from filtration of the powder after gold deposition) and washing solutions collected during catalyst preparation were tested with silver nitrate and sodium borohydride to examine the successful speciation and deposition of the gold onto the surface of the support materials. Silver nitrate is a water-soluble salt known to react with chloride ions present in solution to form $AgCl_{(s)}$, a white crystalline solid of low solubility in water.

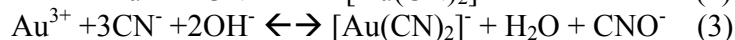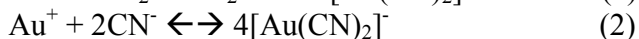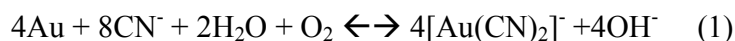$$AgNO_{3(aq)} + Cl^- \rightarrow AgCl_{(s)} + NO_3^-$$
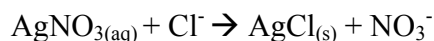
Sodium borohydride on the other hand, is a strong reducing agent that would cause rapid reduction of residual gold ions present in solution into metallic gold of colloidal size; the presence of the latter is confirmed by the change in the color solution from transparent to deep purple.

Based on the chemistry described above, these two tests offer a quick qualitative tool to test for presence of chlorides and residual gold ions in solution. The supernatant solution is rich in chlorides, hence indicating successful gold speciation to the hydroxide species. No gold was evident in this solution. Subsequent washing solutions were free of chloride and gold ions. ICP measurements confirm the absence of Au in the supernatant and washing solutions.

Since the ICP instrument is not equipped for chloride analysis, hot H_2O and aq. NH_3 washes were used in isolated tests to examine whether any residual chlorides were present. After these washes, the filtrates were tested with $AgNO_3$ and $NaBH_4$. Neither chlorides nor Au were seen in the solutions upon visual inspection. These results, while only qualitative, suggest that a strong, chloride-free interaction between the Au and the support surface.

NaCN Leaching – Procedure Details

Gold removal by NaCN leaching is an established process in metallurgy to dissolve metallic gold away from ores[2]. Cyanide leaching was performed by suspending the as-prepared fresh catalyst (both before and after calcination) in a 2 wt. % solution of NaCN in aqueous NaOH (pH > 12). The cyanidation reactions of gold (metallic or ionic) are as follows:

$$4Au + 8CN^- + 2H_2O + O_2 \leftrightarrow 4[Au(CN)_2]^- + 4OH^- \quad (1)$$
$$Au^+ + 2CN^- \leftrightarrow 4[Au(CN)_2]^- \quad (2)$$
$$Au^{3+} + 3CN^- + 2OH^- \leftrightarrow [Au(CN)_2]^- + H_2O + CNO^- \quad (3)$$

The equilibrium constant (K_{sp}) for the formation of the gold cyanide complex is $10^{38.3}$ [3], suggesting an extremely favorable and stable complex. Nevertheless, the gold speciates and deposits on the support surface as a hydroxide, and therefore for the cyanidation of ionic gold (reactions 2 and 3) to occur, the gold hydroxide dissociation reaction needs to occur first:

$$Au(OH)_3 \leftrightarrow Au^{3+} + 3OH^- \quad (4)$$

The equilibrium constant for this reaction is $10^{-45.26}$ [3] suggesting that the gold present on the support before calcination is a hydroxylated species and will not be removed by cyanide leaching. This is not the case for metallic gold species. ICP measurement of the fresh uncalcined catalysts and the corresponding leached sample showed the same amounts of gold. Absence of gold in the leachate solution also confirmed that hydroxylated species are not removed by cyanide.

Similar results were obtained when the calcined materials where leached. This suggests that the gold is strongly interacting with the support surface and it is not in a metallic state (metallic gold can be easily removed by cyanide)[4].

BET surface areas

The BET surface areas of the bare supports and Au-containing catalysts were measured by single-point N_2 adsorption/desorption cycles using a Micromeritics model AutoChem II 2920 apparatus. Elemental analysis of each catalyst powder was performed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Leeman Labs Prodigy). Surface composition and Au oxidation state were determined by X-Ray Photoelectron Spectroscopy (XPS) (Kratos AXIS Ultra) using a pass energy of 20 eV and aligned using the C 1s at 284.5 eV. The evolution of the gold speciation in solution, as a function of temperature and pH, was followed *in situ via* a UV-Visible Spectrometer (Evolution 300 by Thermo Scientific) equipped with a heated cell. Temperature programmed surface reaction (TPSR) studies were performed on a Micromeritics model Autochem II 2920. Following the calcination, the catalysts were exposed to 10% CO – 3% H2O – He (30 mL min^{-1}). Once the RGA signal had stabilized, the temperature was ramped from ambient to 400 °C at a rate of 10 °C min^{-1}, cooling to ambient temperature after each reaction cycle was performed in He. Feed and product gas composition was measured by online mass spectrometry (SRS Residual Gas Analyzer).

References

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