

## Transient and steady-state reactions on structurally characterized Au nanoparticles supported on SiO<sub>2</sub> and TiO<sub>2</sub>

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### Introduction

Nature of the support is well known to affect the stability and activity of Au catalysts [1]. In SiO<sub>2</sub> especially the activity is found to vary considerably depending upon preparation method, presence of water, time-on-stream and factors which are not well understood. Unusual lightoff curves with minima in conversion and strong effects of water are reported [2] Catalysts made by different methods with Au particles in the active size range of 2 to 5 nm have been reported to exhibit poor activity[3]or high activity and stability[4]depending upon preparation method. In order to better understand the causes of variation in performance of silica supported catalysts we have performed several types of experiments to relate particle size under *in situ* conditions

### Materials and Methods

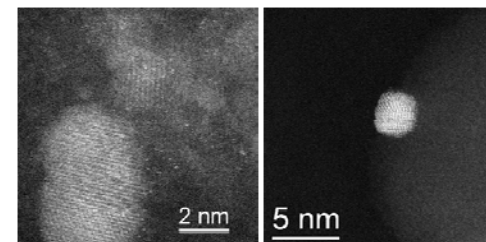
Catalysts were prepared from DP at pH 10 using Au(en)<sub>2</sub>Cl<sub>3</sub> precursor species. This cationic Au species permitted DP on silica (Cabosil) to be performed at pH 10 and can lead to highly active catalysts [4]. Following DP the samples were filtered and dried in a vacuum oven at 50°C to yield the “as-synthesized” catalyst form. Catalytic CO oxidation was assessed in an Altamira AMI-200 operated as a plug-flow reactor or in a transient reactor with FTIR analysis of surface species. STEM was performed on a JEOL-2200FS with CEOS aberration corrector. XRD was performed on a 2-circle diffractometer under a program of variable temperatures under reaction conditions. EXAFS measurements were performed at the X-19a beamline under operando conditions.

### Results and Discussion

Catalytic measurements indicate that the activity of the silica catalysts varied widely depending upon details of how they were treated. High activity was achieved when the as-synthesized material was reduced at 150°C in flowing 10% H<sub>2</sub>/He for three hours followed by ramp and hold to 500°C in flowing O<sub>2</sub>/He. One portion of as-synthesized catalyst treated by this procedure was initially highly active, but deactivated following several days on stream at variable conditions. Calcination of the as-synthesized material in a furnace in ambient atmosphere at 300°C and then 500°C for 1 hour led to a material that was inactive.

Surface CO and CO<sub>2</sub> surface species were probed on an active catalyst during transient gas switching and compared with similar experiments performed previously on TiO<sub>2</sub> supported Au catalysts [5]. CO adsorbed on Au is observed under reaction conditions but its desorption rate is faster for the SiO<sub>2</sub> supported catalysts than for reference TiO<sub>2</sub> supported catalysts indicating weak adsorption. CO<sub>2</sub> desorption is also fast and absence of carbonate buildup on catalyst leads to rapid removal of CO<sub>2</sub> from the reactor[5]. Water has little observable effect on CO, CO<sub>2</sub> or carbonate species under any conditions, but steady state CO conversion is affected.

STEM of the active catalyst exhibited irregularly shaped, thin Au particles 2-5 nm in diameter but also many individual atoms of Au. Analysis of the XRD for the active catalyst indicated 3 nm particle size in good agreement. STEM from the deactivated catalyst showed rounder, thicker Au particles in the range of 2-5 nm. The inactive catalyst had much lower particle densities with spherically shaped particles, some as large as 15 nm. Individual Au atoms were not found on the deactivated or inactive catalysts. EXAFS determination of the Au mean coordination numbers and simultaneous measurements of the catalytic activity were performed following thermal treatments and in the presence or absence of water in the reaction mix. Variations in CO conversion by up to a factor of 10 were observed with no detectable change in Au mean coordination number.



**Figure. 1** Micrographs of active (left) and deactivated (right) Au/SiO<sub>2</sub> catalysts. Individual atoms are apparent on the active catalyst, but not seen on the deactivated catalyst.

### Significance

Results support the conclusion that measurable particle diameter does not correlate well with variations in activity observed for Au/SiO<sub>2</sub>, although large, spherical particles are inactive. Weak CO adsorption and low CO coverages under reaction condition suggest that availability of CO may vary sensitively with particle shape changes.

### References

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