

# Low temperature CO oxidation kinetics by dendrimer templated supported Au catalysts

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## Introduction

Despite its relative bulk inertness, gold has remarkable chemical properties; particularly surprising is the catalytic activity of gold clusters supported on various metal oxides. It has been known for more than 85 years that highly dispersed gold may catalyze oxidation reactions [1]. In the past 15 years it has been shown that small gold particles supported on metal oxides can be highly active, low temperature CO oxidation catalysts [2,3].

The dearth of reliable, detailed and reproducible kinetic data has been cited as a deficiency in the field of gold catalysis [4] and has contributed to the proposal of several different reaction mechanisms for carbon monoxide oxidation on gold surfaces. Further, a detailed kinetic characterization directly probes the catalytic active site and can provide a means of comparing and contrasting catalysts prepared by different methods. The aim of this study is develop such a detailed kinetic characterization of Au catalysts and to compare various systems to a reference catalyst provided by the World Gold Council.

## Materials and Methods

The reference catalyst was diluted 1250:1 using SiC. Activation at 523 K under N<sub>2</sub> was followed by a thirty minute 20/20/60 H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> treatment. During activity measurements, CO, O<sub>2</sub> and He were flowed at 27 mL min<sup>-1</sup> through a single pass plug-flow microreactor using automated mass flow controllers. Steady state conversion data was collected over three hours for each rate measurement. Temperatures evaluated fell between 268 and 293 K.

Au monolayer protected clusters (MPCs) were prepared from poly(amidoamine) PAMAM dendrimer templates as previously reported [5]. Briefly, HAuCl<sub>4</sub> was stirred with a solution of hydroxy-terminated generation 5 PAMAM (G5OH) in nanopure water in a ratio of 147 Au:G5OH for three minutes. A solution of NaBH<sub>4</sub> in NaOH was then added to produce the DENs. The Au nanoparticles were extracted as MPCs using a 100 fold molar excess of C10SH in toluene. The Au MPCs were then purified by precipitation/centrifugation and deposited onto TiO<sub>2</sub> (p-25 Degussa) via incipient wetness. The new catalysts were kinetically characterized as described above. Additional characterization methods included IR spectroscopy, chemisorption and TPD.

## Results and Discussion

In a detailed kinetic characterization of the WGC Au/TiO<sub>2</sub> test catalyst, we measured changes in CO oxidation activity as a function of temperature as well as CO and O<sub>2</sub> pressure. Conversions were kept low (<2%) in order to maintain differential reactor conditions and to ensure that intrinsic steady state activities were measured. The reaction showed a consistent zero order dependence on CO pressure from 0.2 to 1.0% CO.

The oxygen dependence was more complicated, showing saturation kinetics. Interestingly, the reactions shows near second order oxygen dependence until  $\approx 12\%$  O<sub>2</sub> in the feed, at which point the reaction rapidly switches to a zero order dependence (see Figure 1). This behavior was highly reproducible, including the kinetic oxygen saturation, which was observed over the entire temperature range studied. The saturation kinetics suggest that, at lower oxygen concentrations the activation of O<sub>2</sub>, (which is frequently achieved by a cleavage of the O-O bond resulting in the formation of chemisorbed oxygen atoms) is likely to be involved in the rate determining step.

The temperature-dependence of the reaction was evaluated using the saturated catalytic rate ( $v_{max}$ ) in the range of 268-293 K (Figure 2). The Arrhenius plot showed a strong linear correlation with an apparent activation energy of 45.5 kJ/mol. Apparent activation energies at lower oxygen concentrations were similar. This value (45.5 kJ/mol) is slightly higher than most reported activation energies for CO oxidation ( $\approx 30$  kJ/mol) [4]. These differences are likely attributable to the measurements at higher conversions measuring additional changes with temperature beyond the intrinsic activities (e.g. local catalyst heating).

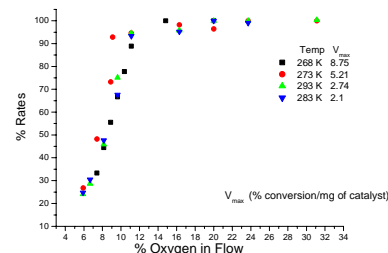


Figure 1. CO Oxidation O<sub>2</sub> Dependence

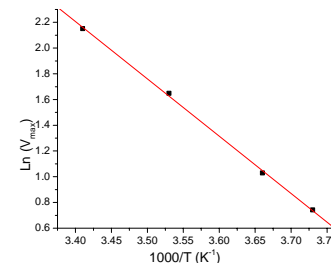


Figure 2. Temperature-dependence of rate

Using the kinetic characterization of the WGC catalyst as a baseline, we compare and contrast this system to dendrimer templated supported nanoparticle catalysts with the goal of providing a kinetic description of each system's active site with respect to the reference catalyst. Because the dendrimer templated nanoparticles are deposited with surface thiols, appropriate pretreatment conditions are crucial for activating these catalysts. The optimum activation treatment consisted of N<sub>2</sub>/H<sub>2</sub> flow at 523 K for sixteen hours to remove the thiols, followed by the WGC treatment protocol.

These two catalysts, although prepared by substantially different routes, show very comparable activities. Since the dendrimer templated nanoparticles are prepared through known and reproducible syntheses, this method and analysis has the potential to provide a reliable basis for the kinetic characterization of gold catalysis which Bond, Thompson, and Lewis report has been missing until now [4]. Additionally, the preparation route used for the dendrimer templated nanoparticles may shed some light onto the polarized debate regarding the nature of the active site (Au<sup>0</sup> vs. Au<sup>1</sup>). This kinetic characterization is also extended to bimetallic Au-Ni and Au-Co nanoparticles to evaluate the effects of incorporating heterometals into Au nanoparticles.

## Significance

Our work is directed towards developing a kinetic characterization and better understanding of the CO oxidation active sites in gold catalysts. We provide a kinetic characterization of the active sites of catalysts prepared via vastly different methodologies, and can extend this characterization to evaluate the effects of heterometal incorporation.

## References

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