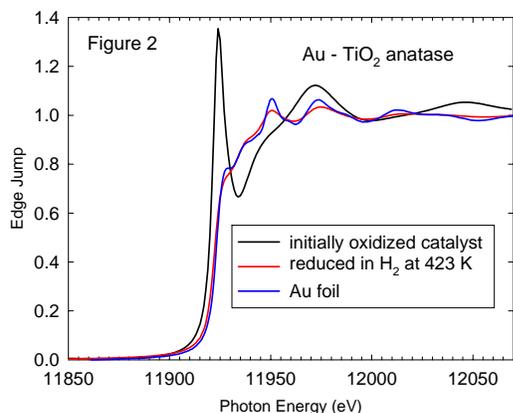
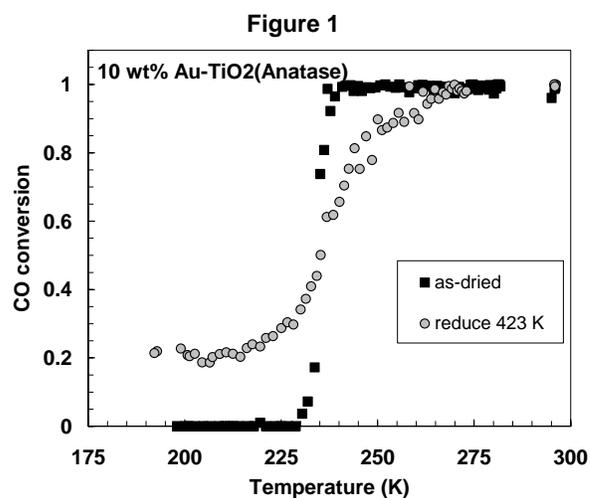


Mechanisms of oxidation by Au catalysts supported on allotropic titanium oxide supports

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Both the exceedingly high activity of Au nanoparticles for catalyzing the CO oxidation reaction and the extreme sensitivity of this activity to preparation techniques have been a subject of great scientific interest in the catalysis community. It is known that Au particle size and the nature of the support strongly affect activity. For the first time, researchers at ORNL have examined the activity of identically prepared Au catalysts on four different titanium oxides allotropes. They have demonstrated that the crystallographic differences are unimportant as a predictor of catalytic activity. Further, they find that oxidized Au is not required for high activity, supporting a mechanism in which redox exchange processes occur on the titania support.

ORNL researchers used advanced synthesis techniques to prepare pure titania of different structures and morphology. Besides commercially available high surface area P-25 titania, single phase nanocrystalline supports of brookite, rutile or anatase allotropes were obtained using sonochemical and hydrothermal synthesis methodologies. Mesoporous titania was synthesized using templating techniques. In each case, Au was post-deposited using an identical deposition-precipitation procedure. The resulting catalysts were extremely active both in the as-synthesized state and following treatments in hydrogen at 423 K to complete reduction of the Au particles, as shown for the anatase supported catalyst in Figure 1. Complete oxidation of CO is achieved at temperatures well below room temperature. Interestingly, catalysts exhibited nearly identical activities for each titania support, indicating that the crystallographic structure and crystallite morphology of the titania support is not responsible for the wide variations in catalyst activity, frequently observed for Au catalysts. However, subsequent aging and thermal treatments revealed differences in stability of the Au catalysts which could be related to differences in growth of the Au nanoparticles on the



different supports. The oxidation state of the Au was probed by x-ray absorption spectroscopy under conditions which precisely match those used in the reaction studies. In the as-synthesized initial state, Au is oxidized, as indicated by the prominent white line peak (black curve Figure 2). Following H₂ treatment, a pre-treatment which yields high activity, the Au particles were >98% reduced (red curve). This result suggests that the Bond-Thompson model¹, thought to describe catalytic activity on alumina and iron oxide, is not applicable to the case of Au on titania. Instead, the results indicate a mechanism in which the redox exchange occurs on the titania (presumably adjacent to reduced Au), rather than on the Au particles.

¹ Bond, G.C. and Thompson, D. T. Gold Bulletin, 2000 (3), 2000, 41-51