

Characterization of Au-based Catalysts Using Novel Cerium Oxide Supports

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Gold dispersed on various oxide supports has been shown to exhibit high activity in a variety of important catalytic reactions, the most widely investigated of which remains the low-temperature oxidation of CO to CO₂ [1]. The nature of the oxide support can have a profound effect on the activity of the catalysts, and Au-catalysts utilizing nanocrystalline oxide supports such as CeO₂ and Y₂O₃ have been found to possess a significantly greater activity than those dispersed on larger support particles [2]. In the present study, a novel synthesis method involving the use of supercritical CO₂ as an anti-solvent was devised to prepare CeO₂ (scCeO₂) support particles. The rapidity of precipitation using this method makes possible the formation of structures that are not available with traditional precipitation methods. This process has previously been used to produce vanadium phosphate catalysts with unusual morphologies and improved activity [3].

With this in mind, a systematic series of scCeO₂ supports was synthesized using scCO₂ as an anti-solvent under varying conditions of temperature and pressure [4]. These were used to create Au-based catalysts via deposition precipitation. Subsequent catalytic testing showed that, regardless of the different synthesis conditions, all the scCeO₂ samples exhibited a marked improvement in CO conversion relative to the untreated Au/CeO₂ (unCeO₂) catalysts. The level of the increase in activity of the Au/scCeO₂ samples depended upon the specific supercritical conditions (temperature and pressure) of the scCO₂ anti-solvent. XPS analysis revealed no clear difference in the Au electronic structure of any of the scCeO₂ catalysts.

All of the samples were then studied using a spherical aberration corrected VG HB603 STEM in addition to a JEOL 2000FX TEM operating at 300 and 200 keV, respectively. Bright-field (BF) and high-angle annular dark-field (HAADF) imaging indicated that the scCeO₂ supports consisted of spherical, polycrystalline agglomerates (Figure 1). In addition, the contrast at the perimeter of the spheres is much stronger than that at the center, suggesting that the spheres were in fact hollow. This morphology is a result of densification in the absence of particle growth that occurs upon crystallization inwards from the exterior surface of the amorphous precursor during calcination. STEM-XEDS analysis also confirmed the hollow nature of the agglomerates.

STEM-XEDS spectrum imaging revealed the origin of the variation in CO oxidation activity with scCO₂ synthesis conditions. As shown in Figure 2, the best catalyst in terms of CO conversion exhibited no distinct gold particles; instead the Au-L_α x-ray signal indicates that the gold is highly (perhaps atomically) dispersed over the spherical scCeO₂ support. In contrast, the catalyst with the lowest CO conversion performance was found to contain distinct 5-10 nm gold crystallites. The catalysts that had intermediate CO conversion exhibited dispersions that were a mixture of particulate and highly dispersed Au. In all cases, the dispersion on the scCeO₂ supports was higher than that in the unCeO₂, thus explaining the origin of their improved performance. These techniques were also applied to characterizing changes to the Au dispersion which occurred under reaction conditions, and a decrease in Au dispersion was observed.

A similar investigation of Au-Pd alloy particles supported on scCeO_2 was also carried out, because previous investigations [5] suggested that such materials would be good candidates for catalyzing the selective oxidation of primary alcohols to aldehydes. A comparable improvement in catalytic performance was observed with an increase in metal dispersion using the scCeO_2 support.

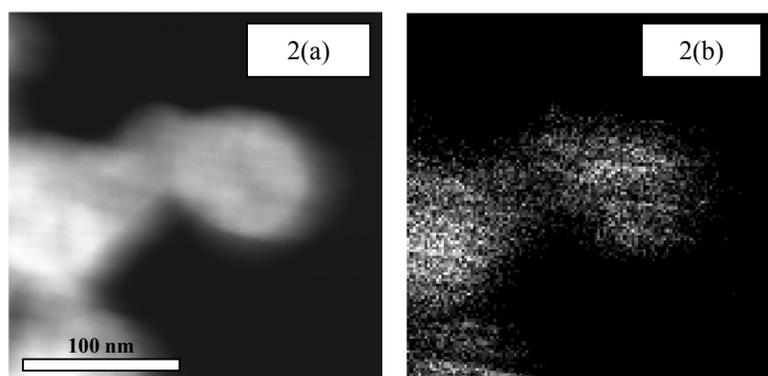
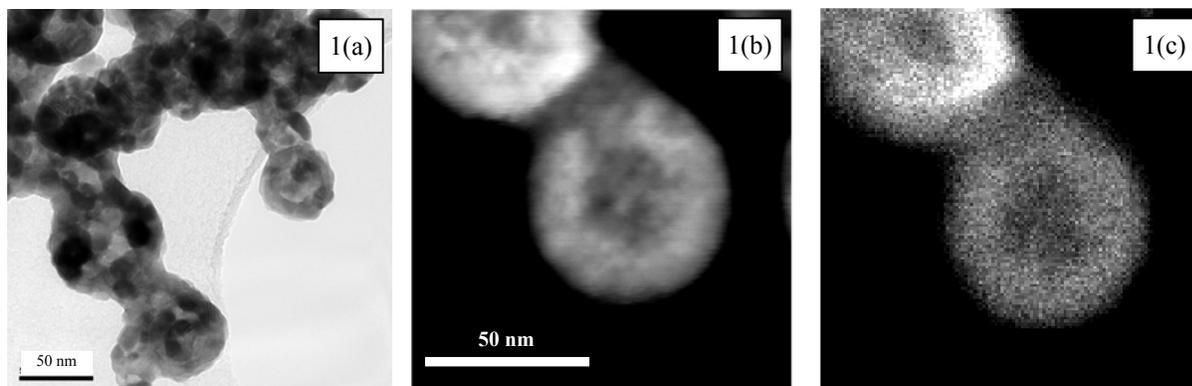


Figure 1 – Bright-field TEM image (a) and complimentary HAADF-STEM image (b) and Ce-L_α STEM-XEDS map showing hollow, spherical, and polycrystalline agglomerates in the scCeO_2 support.

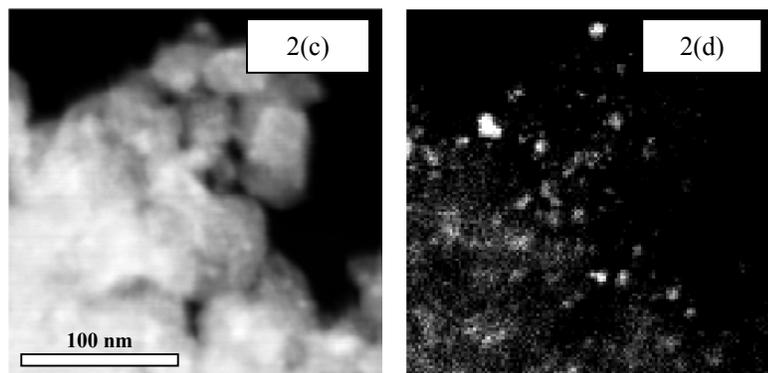


Figure 2 – HAADF-STEM images and the corresponding Au-L_α X-ray maps of the best 2(a and c) and worst 2(c and d) scCeO_2 catalysts. Note the superior dispersion of the Au in the higher activity catalyst.

References

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