doi:10.1017/S1431927610060186
Microsc. Microanal. 16 (Suppl 2), 2010

Identifying Potential Active Species in Au/ZnO CO Oxidation Catalysts

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The low temperature oxidation of CO to CO_2 is a key reaction in the field of gold catalysis, not only because it represents Haruta's historic discovery of unexpected room temperature catalytic activity in nano-crystalline gold [1], but also because it is a commercially important reaction in fuel cell technology [2]. Gold supported on zinc oxide has been proven to exhibit good catalytic activity and stability for the CO oxidation reaction [3]. However numerous studies have as yet failed to conclusively reveal the identity of the catalytically active species in the Au/ZnO system [4].

The aim of this work is to understand the nanostructure-performance relationships that exist for the Au/ZnO catalyst system. State-of-the-art electron microscopy techniques have been used to characterize a systematic series of Au/ZnO catalysts made by a simple co-precipitation method [3]. The set of catalysts were calcined over a range of different temperatures (*i.e.* dried at 110 °C only, calcined at 200, 250, 300, 350, and 400°C) for a 4 hour-period. As shown in Fig. 1, the calcination temperature employed had a profound effect on the resultant catalytic performance, with those materials calcined at 250-300°C exhibiting the best CO conversion after 60 minutes on-line.

Conventional bright field and phase contrast lattice imaging was effective for following the changes in ZnO grain-size and morphology over this temperature range, as shown in Fig. 2. In addition, it was possible to characterize the Au particle size distribution by these methods, provided that the metal particles were greater than 1nm in size. However the use of aberration corrected high angle annular dark field (HAADF) imaging [5] has now clearly shown that the nature of the gold distribution on ZnO is far more complex than previously imagined. So far, five distinct gold morphologies have been identified by STEM-HAADF to *co-exist* on these ZnO supports; namely (i) isolated Au atoms, (ii) sub-nm Au clusters, (iii) ordered monolayer rafts of Au atoms, (iv) linear stripes of Au and (v) epitaxial Au nano-particles greater than 1nm in diameter, as shown in Fig. 3. Interestingly, the estimated number fraction of these five distinct Au species is observed to vary with calcination temperature of the Au/ZnO catalyst. In this presentation, we will describe our efforts to deduce the relative catalytic activities of these various forms of supported gold by correlating the measured catalytic activity with catalyst nanostructure.

References

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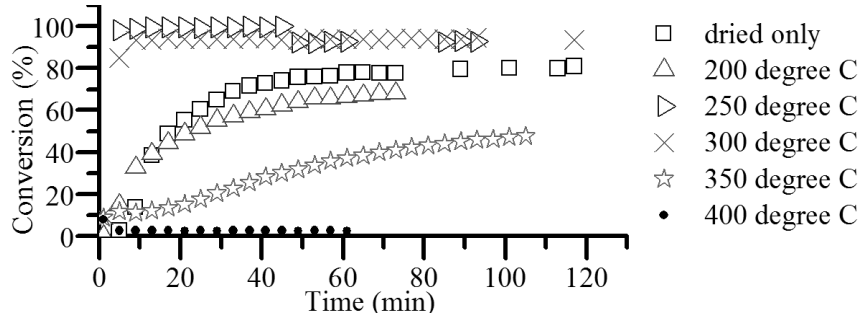

FIG. 1. Room temperature CO conversion as a function of time-on-line for a series of 5% Au/ZnO catalysts: reaction conditions, CO flow rate 21.4 ml/min, catalyst mass 50 mg.

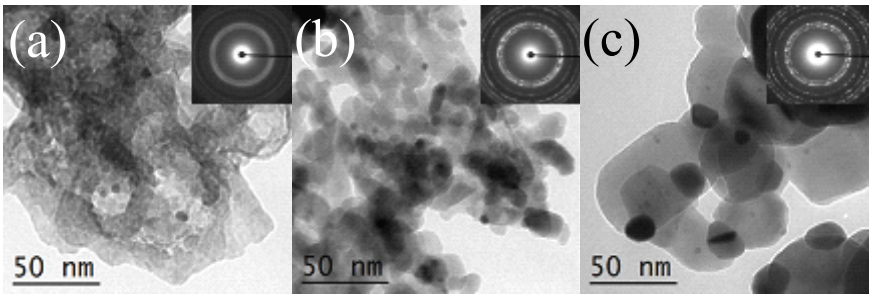

FIG. 2. BF images and SAD patterns showing the morphology of the ZnO support as a function of calcination treatment: (a) dried only, (b) calcined at 300°C, and (c) at 400°C

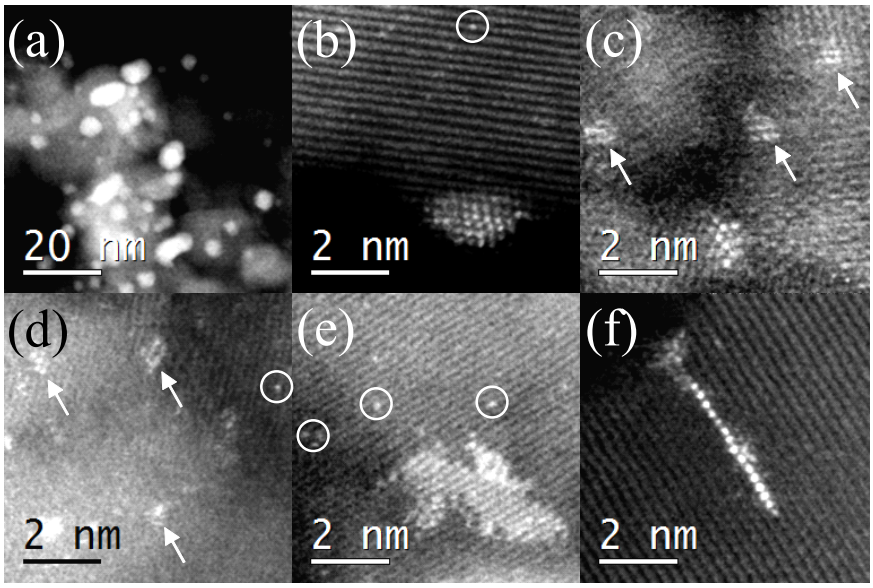

FIG. 3. Aberration-corrected STEM-HAADF images showing the various Au species co-existing on the ZnO support; (a), (b) 3-dimensional Au nano-particles; (c), (d) sub-nm Au clusters (white arrows) and isolated Au atoms (white circles); (e) ordered monolayer Au rafts and isolated Au atoms and (f) linear stripes of Au.

https://doi.org/10.1017/S1431927610060186 Published online by Cambridge University Press