

Revealing Structure-Activity Relationships in Supported WO₃/ZrO₂ Solid Acid Catalysts using Aberration Corrected High Angle Annular Dark Field Imaging

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Tungsten oxide catalysts supported on zirconia offer a promising alternative for many practical industrial applications involving acidic catalytic reactions, owing to their enhanced thermal and environmental stability. Previous studies suggest that the catalytic activity of tungstated zirconia catalysts depends on the nanostructure of the surface WO_x species present, which can include mono-tungstate, poly-tungstate, WO_x clusters, and 'bulk' WO₃ crystals [1, 2]. However, identification of the most catalytically active tungstate species in this catalyst system is still an issue of ongoing debate due to a lack of unambiguous imaging of these surface entities. Therefore, detailed experimental evidence at the atomic scale for the presence of the various tungsten oxide species on the ZrO₂ surface becomes a key criterion for identifying pertinent structure-activity relationships.

Here we report our recent progress in the study of WO₃/ZrO₂ catalysts in which the catalytically active species were directly imaged and identified using aberration corrected STEM high-angle annular dark-field (HAADF) imaging combined with other optical spectroscopy techniques. The structural information derived from our electron microscopy studies has subsequently been used for a catalyst design and optimization experiment. We also directly show that the deactivation of a WO₃/ZrO₂ catalyst is directly related to the progressive loss of the most active supported tungstate species.

Aberration corrected STEM-HAADF imaging was performed on two systematic sets of WO₃/ZrO₂ catalysts calcined at different temperatures and having different surface WO_x loadings. The catalytic activity of these materials was tested for the *n*-pentane isomerization reaction as shown in Figure 1 [3]. Representative STEM-HAADF images from a few select samples showing very different catalytic performances are shown in Figure 2. Individual W atoms and tungstate clusters are clearly resolved by HAADF as bright features against the ZrO₂ support by virtue of their higher atomic number. For the low activity sample, the WO_x was found to be highly dispersed on the ZrO₂ surface mainly as mono- and poly-tungstate species which have monolayer thickness (Fig. 2a). As shown in Fig. 2b, additional numerous disordered WO_x clusters around 1nm in size were found in the high activity samples. Although the exact composition of these nanoscopic WO_x clusters cannot be unambiguously determined, line profile intensity changes across individual clusters and image simulations suggest that there may be Zr cations intermixed within them. A rough estimate, based on the size and total intensity of the clusters, suggests that each should contain between 10 and 15 Zr/WO_x units. We have recently identified these ~1nm disordered Zr-WO_x mixed oxide clusters as the most active sites for the methanol dehydration reaction [2]. The inactive catalyst shown in Fig. 2c contains a predominantly amorphous ZrO₂ support structure due to the low calcination temperature employed. The WO_x species are highly dispersed on the amorphous ZrO₂ support surface as isolated WO_x units and probably some occasional poly-tungstate species. Systematic correlations of catalytic activity measurements with the HAADF images suggests that, for the *n*-pentane isomerization reaction, the disordered Zr-WO_x clusters are more active than the 2D poly-tungstate species, and the mono-tungstate species possess the lowest catalytic activity. The formation of a significant volume fraction of inactive bulk WO₃ crystals, as determined by SEM BSE imaging, was found to be the underlying cause for the decrease of average catalytic activity with very high WO₃ surface loading.

In an attempt to maximize the number density of the most active Zr-WO_x clusters and consequently optimize the catalytic activity, we developed a highly efficient non-aqueous solvothermal colloidal technique [4] for *ex-situ* synthesis of WO_x and Zr-doped WO_x nanoclusters. These colloids were subsequently deposited onto a ZrO₂ support followed by calcination at 500°C in order to remove the oleylamine surfactant (denoted WO_x-NP/ZrO₂). As shown in Fig. 3a, the uncalcined pristine WO_x clusters, when deposited onto a continuous carbon support films, were 1.0-1.6nm in size, and were estimated from HAADF images to contain 20-36 WO_x units. The new

WO_x-NP/ZrO₂ catalysts were expected to show high catalytic activity as compared with conventional WO₃/ZrO₂ catalysts discussed above; however, preliminary data showed that these new sol-immobilized materials were less active than those shown in Fig 2b. HAADF images (Figs 3b & c) revealed that the WO_x clusters tend to strongly wet the ZrO₂ surface, which effectively destroys the structural integrity of the clusters. Moreover, a significant fraction of ZrO₂ support was amorphous in nature, on which mono- and poly-tungstate species were found to be the predominant surface structures, which could explain the low catalytic activity of these materials. Further improvement and optimization of the sol-immobilization technique may allow retention of the cluster structure and thus significantly improve the catalytic performance.

References:

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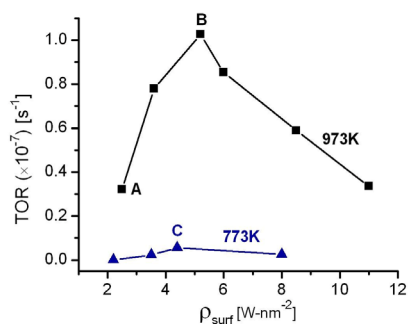


Figure 1. Steady state turnover rates (TOR) for the *n*-pentane isomerization reaction over WO₃/ZrO₂ catalysts as a function of tungsten surface density (ρ_{surf}) and calcination temperature [3].

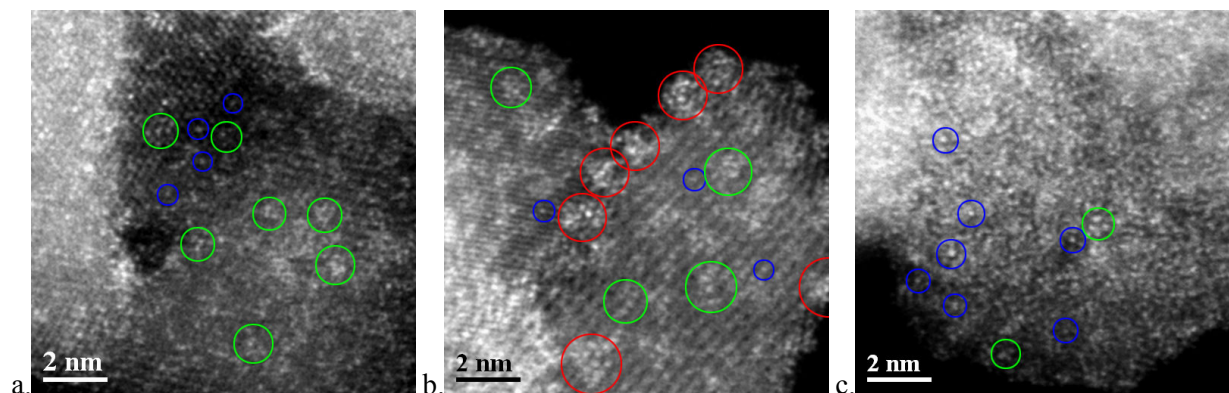


Figure 2. Representative STEM-HAADF images for (a) the low activity sample A, (b) the high activity sample B, and (c) the inactive sample C as indicated in Figure 1. *Blue circles*: surface mono-tungstate species; *Green circles*: surface poly-tungstate species; *Red circles*: sub-nm Zr-WO_x clusters.

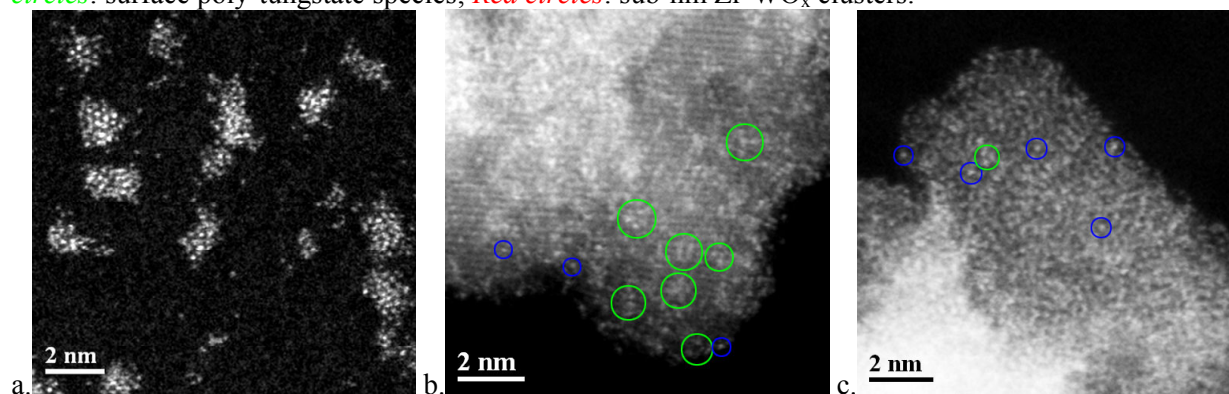


Figure 3. Representative STEM-HAADF images for (a) the pristine WO_x clusters deposited on a continuous carbon film, and (b&c) the crystalline and amorphous regions found in the calcined WO_x-NP/ZrO₂ catalysts.