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Structural Characterization of WO_3/ZrO_2 Catalysts using HAADF Imaging

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Tungsten oxide supported on ZrO_2 is receiving increased attention as a solid acid catalyst due to its important industrial applications, such as the isomerization of C4-C8 alkanes to upgrade gasoline octane number. It is known that the catalytic activity depends on the structure of WO_x species and their interaction with ZrO_2 support [1], so a thorough structural characterization is essential for establishing any structure-property relationships. Previous studies using a combination of XRD, optical spectroscopy and HRTEM revealed that WO_x at low loadings is highly dispersed on ZrO_2 as mono-tungstate or poly-tungstate species (Figure 1). Additional disordered WO_x clusters appear on samples having intermediate WO_3 loadings, which correlate with improved catalytic activity [2]. To date, however, no direct imaging studies of WO_x configuration or their interaction with the ZrO_2 support, which are important factors for catalytic activity, have been documented.

High angle annular dark field (HAADF) STEM imaging, (*i.e.* z-contrast imaging), is able to provide sub-Å spatial resolution as well as single atom sensitivity, and has been demonstrated to be a very powerful tool in the structural characterization of highly dispersed supported metal catalysts [3, 4]. However, no HAADF data has been reported on supported metal oxide catalysts partly because of the relatively low contrast of the overlayer on the relatively high mass support, since the metal atoms are diluted by interspersed oxygen atoms. Here HAADF imaging is used to directly observe WO_x distribution and configuration on the ZrO_2 support. The images were acquired on a 200 kV JEOL 2200FS FEG (S)TEM equipped with a CEOS aberration corrector and an Ω-energy filter [5]. The HAADF images presented have been low-pass filtered to remove high frequency background noise.

Figures 2A and B are representative HAADF and HRTEM images from a sample with low WO_3 loading. HRTEM does not show any evidence of isolated tungsten species. In contrast, individual W atoms are resolved by HAADF, and poly-tungstate species with as few as two connected W atoms are also observed. As a result of calcination treatment, these surface W species are actually oxidized and bonded to oxygen atoms (not visible by HAADF), a fact which has been experimentally verified by Raman spectroscopy [2]. The W atoms are found to be preferentially located above the Zr sites, suggesting strong bonding between the ultra-dispersed WO_x species and the underlying ZrO_2. Trimer species with projected W-W distances of 3.7-4.3Å (*c.f.* those in crystalline WO_3 (~3.8Å)) are also apparent, implying that similar W-O-W bonds exist in these highly dispersed species.

Three dimensional WO_x clusters ~0.8nm in size are found in both HRTEM and HAADF images (Fig. 3) for WO_3 loadings above the monolayer capacity. HRTEM (Fig. 3B) can just about resolve these clusters in profile view, but no detailed structural information can be obtained. HAADF, however, can be used to measure the cluster size and estimate the number of W atoms associated with each cluster. A typical cluster is estimated to have around 10 W atoms, but precise atom positions are not well defined due to the disordered nature of the cluster. Intensity variations within single clusters also suggest that Zr atoms may be intermixing with the WO_x. Features corresponding to mono-

tungstate and poly-tungstate species can also be distinguished in Fig 3A. A dramatic increase in catalytic activity was found in this heavier loaded sample as compared to that with the lower loading. Correlating the catalytic activity with WO_x species distribution for these two samples suggests that the disordered 3-D clusters are significantly more active than the highly dispersed species. The disordered 3D-WO_x domains may in fact act to stabilize additional electrons involved in the catalytic process. Information derived from such HAADF images can in theory be employed as input data for first-principle calculations of the electronic structure of these various supported WO_x species.

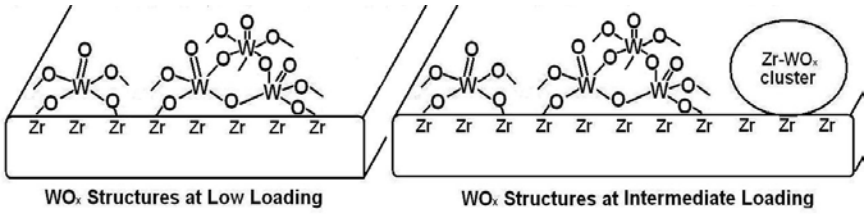

Figure 1: Evolution of mono-tungstate, poly-tungstate and '3D' species on ZrO_2 surfaces with increasing WO_3 loading.

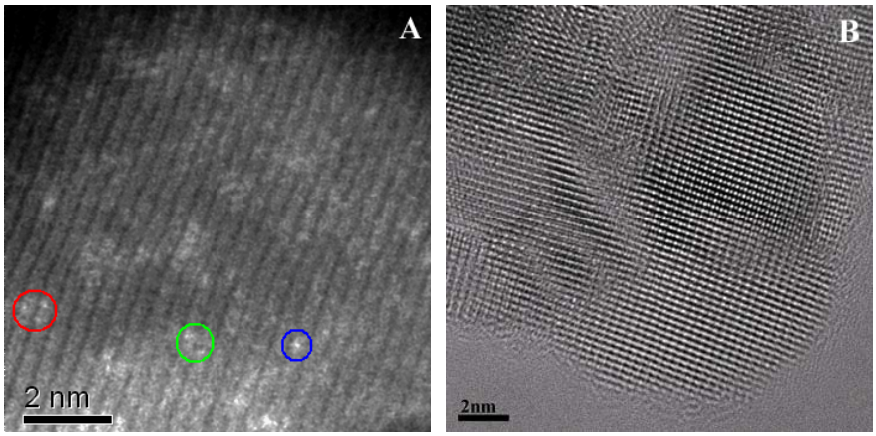

Figure 2: (A) HAADF image of WO_x species on ZrO_2 surface (low loading, low activity sample). Bright spots correspond to highly dispersed WO_x species. Red circle - WO_x trimer; Green circle - WO_x dimer; Blue circle- WO_x monomer. (B) HRTEM image from the same sample.

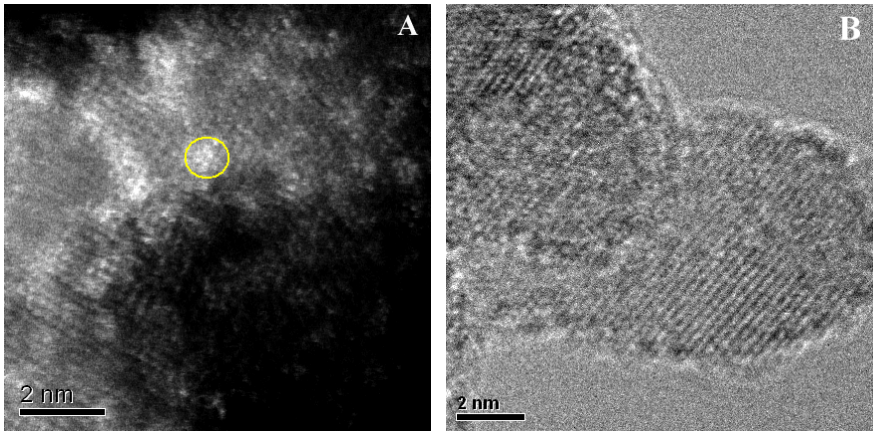

Figure 3: (A) HAADF image of WO_x species on ZrO_2 surface (intermediate loading, high activity sample). Besides highly dispersed species, 3-D WO_x clusters are also visible (in the yellow circle). (B) HRTEM image from the same sample.

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