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Double Aberration-Corrected TEM/STEM of Tungstated Zirconia Nanocatalysts for The Synthesis of Acetaminophen/Paracetamol

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Tungstated zirconia is very active for the synthesis of paracetamol by Beckmann rearrangement of 4-hydroxyacetophenone oxime and provides an environmentally benign alternative instead of the current homogeneous process [1]. The performance of the catalyst depends on the W surface density. Double aberration corrected-transmission electron microscopy and scanning transmission electron microscopy (2AC- TEM/STEM) at the 0.1 nanometer level from the same areas have been crucial in revealing the location and the nanostructure of the polytungstate species (clusters) and the nanograins of zirconia. Polytungstate clusters as small as 0.5 nm have been identified using the high angle annular dark field (HAADF) imaging in the AC-STEM.

Samples for electron microscopy studies were prepared by ultrasonically dispersing the tungstated zirconia catalyst powders containing 15% W/zirconia, and 35wt%W/zirconia, respectively, (hereafter referred to as 15% W-Zr and 35% W-Zr) in alcohol and placing a small amount of the solution on holey carbon coated copper grids. AC-TEM/STEM studies were performed in a JEOL 2200FS double aberration corrected FEG TEM/STEM at the 1 Angstrom (1Å = 0.1 nanometer) scale in the Nanocentre at the University of York. The instrument has been configured to have a larger gap (HRP) objective lens polepiece, to enable tilting of the sample for alignment into a zone axis orientation for electron microscopy studies of crystalline materials [2,3]. Image recording at close to zero defocus was carried out to observe the catalyst crystallites using aberration corrected high resolution (HR) TEM as well as HR STEM including high angle annular dark field (HAADF) imaging, from the same areas of the sample, with resolution of 1Å (0.1nm).

FIG.1(a) shows AC-TEM image of 15%W-Zr illustrating overlapping zirconia nanocrystals with random crystallographic orientations. The crystallite size of the larger nanocrystals in the image was more than 10 nm. The optical diffractogram obtained from the nanocrystals could be indexed based on the tetragonal zirconia structure with a = 0.3607 nm and c = 0.5175 nm. Many of the nanocrystals were observed to be in [001] orientation as indicated by the selected area FFT/optical diffractogram, and a few in <110> orientation as shown in FIG.1. To determine the nanocrystal sizes more accurately, we used the dark-field TEM using different Bragg reflections. (e.g. in FIG.2 in 200, 020,220, and -220 reflections). Significantly, the images reveal crystallites less than 5 nm in diameter constituting the larger zirconia nanocrystals. The average size of the ZrO_2 crystallites was estimated as 2.6nm (with sample variance σ^2 =0.334 nm^2). FIG.3(a) shows the same crystal as in FIG.1, slightly defocused, revealing the presence of nanometer scale polytungsate species (tungsten oxide) clusters (dark clusters indicated by arrows), uniformly distributed throughout the zirconia nanocrystals. Careful examination revealed that the majority clusters were segregated to the zirconia nanocrystal boundaries, as indicated in the schematic in FIG.3(b). The observation suggests that tungsten oxide clusters do not form solid solution with zirconia in this case. Z-contrast analysis using aberration corrected- HAADF STEM illustrates very small (0.5 nm to a few nm in size) polytungstate clusters as shown in FIG.4. In addition, the sub-nanometer W-oxide cluster (blue circle in the image) observed is about 0.5 nm and contains approximately 10 tungsten and oxygen atoms. The results are consistent with UV–visible absorption edge energies which suggest that the surface contains polytungstate species at these loadings [1].

References

[1] N.R. Shiju et al., 2009 (in preparation)
[2] P. L. Gai et al., proc. EMC 1 (2008) 479.
[3] P. L. Gai et al., Microsc. Res. Techniq. (2009) in press.
[4] We thank the University of York, regional development agency, Yorkshire Forward, the European Union through the European Regional Development Fund and JEOL (UK) Ltd for the Nanocentre facilities.

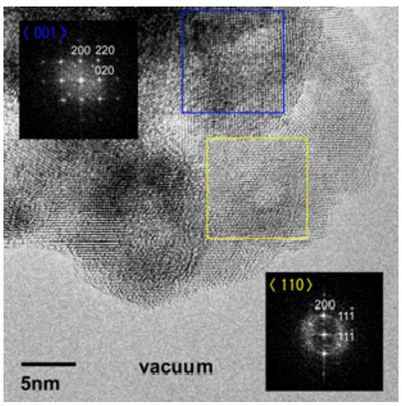

FIG. 1. Cs corrected HRTEM and selected area FFT patterns of 15 wt% W-Zr catalyst.

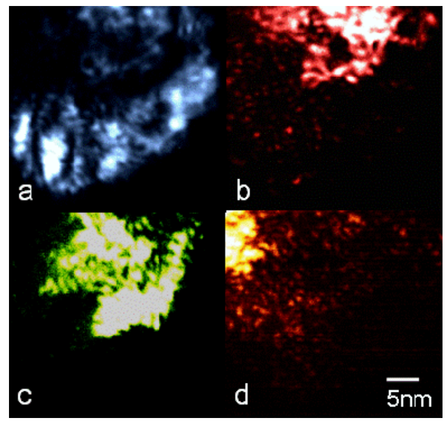

FIG. 2. Dark-field TEM of 15 wt% W-Zr. (a)-(b) ; ZrO_2 200, 020, 220 and -220 spots.

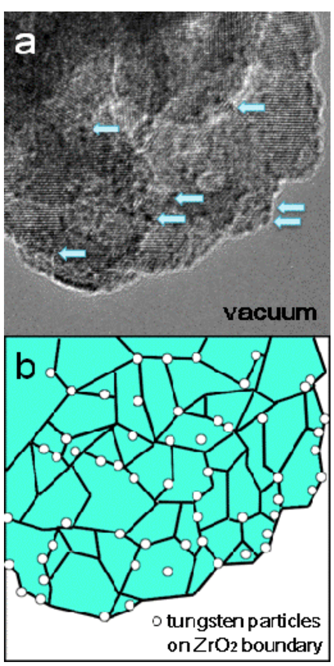

FIG. 3. (a) 30nm under focused TEM image of 15 wt% W-Zr (b) Schematic diagram.

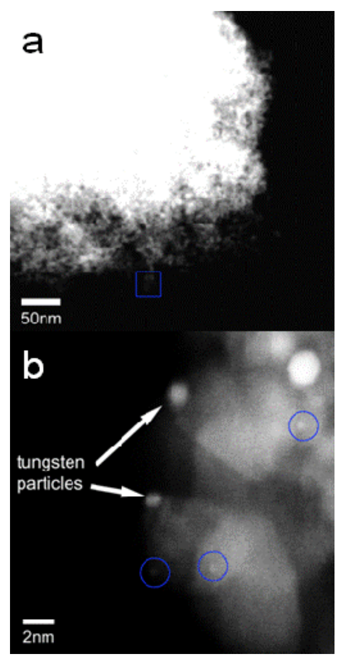

FIG. 4. Z contrast analysis of 15 wt% W-Zr by Cs corrected HAADF-STEM.

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