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Double Aberration-corrected TEM/STEM of tungstated zirconia nanocatalysts for the synthesis of paracetamol

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Abstract. We report highly active tungstated zirconia nanocatalysts for the synthesis of paracetamol by Beckmann rearrangement of 4-hydroxyacetophenone oxime. Double aberration-corrected (2AC)-TEM/STEM studies were performed in a JEOL 2200FS FEG TEM/STEM at the 1 Angstrom (1 Å = 0.1 nanometer) level. Observations at close to zero defocus were carried out using the AC-TEM as well as AC-STEM including high angle annular dark field (HAADF) imaging, from the same areas of the catalyst crystallites. The studies from the same areas have revealed the location and the nanostructure of the polytungstate species (clusters) and the nanograins of zirconia. The AC (S)TEM was crucial to observe the nanostructure and location of polytungstate clusters on the zirconia grains. Polytungstate clusters as small as 0.5 nm have been identified using the HAADF-STEM. The nanostructures of the catalyst and the W surface density have been correlated with paracetamol reaction studies. The results demonstrate the nature of active sites and high activity of the tungstated zirconia nanocatalyst, which is an environmentally clean alternative to the current homogeneous process.

1. Introduction
Paracetamol (N-acetyl-p-aminophenol) is one of the most widely used analgesics. The rearrangement of ketoximes to amides or lactams in the presence of acid catalysts is commonly known as Beckmann rearrangement, relevant to the synthesis of paracetamol. The most prominent example for this reaction is the preparation of ε-caprolactam, the monomer used in the production of nylon 6, from cyclohexanone oxime [1-3]. Similar to the case of cyclohexanone oxime rearrangement, the use of solid acid catalysts offers significant advantages over homogeneous acid catalysts. However, much less work has been reported on solid catalysts which is compounded by the difficulty in identifying active surface sites in the reaction. When liquid sulphuric acid is used as a catalyst, including with promoters, N-acetyl-p-aminophenol is recovered from the reaction mixture by neutralization of oleum with aqueous ammonia, resulting in the formation of a large amount of ammonium sulfate. Rearrangement using an ion exchange resin as catalyst and acetic acid as a solvent under an inert atmosphere is reported as well as thionyl chloride in liquid sulphur dioxide [4]. However, sulphuric acid is toxic, corrosive and environmentally unsafe and the use of liquid phase requires special equipment. The use of an insoluble acid catalyst will allow easy separation workup (no neutralization step is required), catalyst recycling and will avoid equipment corrosion and contaminant wastes. Though this has been largely attempted for the Beckmann rearrangement of cyclohexanone oxime to
caprolactam, very few reports are published for the rearrangement of 4-hydroxyacetophenone oxime to paracetamol.

In this study, we have investigated tungstated zirconia catalysts for liquid-phase Beckmann rearrangement of 4-hydroxyacetophenone oxime to N-acetyl-p-aminophenol. Although zirconia-supported oxoanions have been examined as solid acid catalysts recently in industrial isomerization and alkylation processes instead of the highly corrosive and pollutant liquid acid, insights into the nanostructure and optimisation of the catalysts have remained a challenge. Tungstated zirconia possess some advantages such as higher stability under high-temperature treatments and reductive atmospheres, lower deactivation rates, and easier regeneration. Here we report nanostructures of novel tungstated zirconia (WZ) nanocatalysts for the liquid-phase Beckmann rearrangement for clean synthesis of paracetamol /acetaminophen.

2. Experimental Procedure
Tungstated zirconia nanocatalysts were synthesised with different W loadings from 5wt% to 35 wt% (hereafter referred to as 35%WZ). X ray-diffraction (XRD) data of the samples calcined at 973 K have shown that zirconia exists as a tetragonal phase. Double aberration-corrected (2AC)-JEOL 2200FS (S)TEM, configured to have a larger gap (HRP) objective lens polepiece [5] to enable tilting of the sample for alignment into a zone axis orientation as well as heating, was used for nanostructural studies.

3. Results and discussion
Figure 1a shows an AC-TEM image of 15%WZ, 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] zone axis orientation as indicated by the selected area FFT/ optical diffractogram in figure 1a, and a few in <110> orientation. Because the nanocrystallinity plays a key role in catalysis, we used dark-field STEM to determine the nanocrystal sizes. Figure 2(a) and Figure 2(b) are STEM images of 15%WZ and 35%WZ. These images revealed crystallites less than 5 nm in diameter constituting the larger zirconia nanocrystals. Average size of the ZrO2 crystallites was estimated as 2.6nm (with sample variance $\sigma^2 =0.334$ nm$^2$). Figure 1b shows the same crystal as in Figure 1a, slightly defocused, revealing the presence of nanometer scale polytungstate clusters (dark clusters indicated by arrows and identified by tungsten oxide clusters by lattice imaging and nanoanalysis), 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 Figure 1(c). Ultra high-resolution TEM (1.2M) clarified the 15%WZ nanocrystals are mosaic crystals with low angle grain boundary. A typical case of $\alpha = 182.14$ degree are presented in Figure 3. The correlation with catalytic activity has shown that the clusters form active Brønsted sites leading to high activity of the tungstated zirconia nanocatalyst. Z-contrast analysis [6,7] using aberration corrected- HAADF STEM further illustrates lattice images of tungstated zirconia particles, shown in figure 4(a-d). The areas shown by squares in (a) are enlarged in (b), (c) and (d). Small dots (indicating bright contrast) of less than 1 nm are observed on single crystalline zirconia particle and are identified as tungsten oxide clusters. Their concentration is found to be higher at the surface observed in the profile imaging in (c). In contrast, the 35% WZ catalyst sample showed much larger polytungstate domains and zirconia grain sizes.

4. Concluding remarks
The nanostructures of the tungstated zirconia catalysts for clean synthesis of paracetamol have shown clusters of active tungsten trioxide clusters located at the boundaries of zirconia nano-grains. This heterogeneous process is an environmentally clean alternative to the current homogeneous process.
Figure 1. (a) Cs corrected HRTEM and selected area FFT patterns of 15 wt% WZ catalyst. (b) a 30nm under focused transmission electron micrograph of 15 wt% WZ catalyst. (c) Schematic diagram of deposition mechanism.

Figure 2. STEM images of WZ catalysts. W concentrations were analysed as (a) 15wt% and (b) 35wt%. Average size of the ZrO₂ crystallites were estimated as (a) 2.6nm and (b) 15.5nm.
Figure 3. Spherical aberration corrected-TEM studies of 15 wt% WZ mosaic crystals

Figure 4. Spherical aberration corrected- HAADF STEM images of 15 wt% WZ catalyst. The areas shown by squares in (a) are enlarged in (b), (c) and (d).

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