Scanning Transmission Electron Microscopy with Cs Corrector

Imaging of WOx Clusters on ZrO2 Nanocrystals in WOx ZrO2 Catalysts

Currently scanning transmission electron microscopy is a powerful tool for characterizing catalytic materials. The detection of electrons scattered by atomic nuclei with a high angle annular dark field detector generates images of contrasts which strongly depend on the atomic number. The probe size (0.1 nm) allows one to obtain images of W clusters smaller than 1 nm on the ZrO₂ surface.

Introduction

High-resolution transmission electron microscopy (HRTEM) provides invaluable information about the crystallography of a specimen in a chosen crystallographic orientation despite the limitations in chemical information [1]. However, when the particle size dispersed on catalytic support is smaller than 1.5 nm, it is difficult to locate them using HRTEM. For the characterization of heterogeneous catalysts, scanning transmission electron microscopy (STEM) is one of the most powerful techniques for obtaining atomic-resolution images using an electron beam [2]. Since, many catalytically significant elements have a high atomic number (Z) and are generally supported on a matrix with low Z elements (SiO₂, Al₂O₃, TiO₂, for example), the high angle annular dark field (HAADF) detector is of outmost importance. This detector collects electrons scattered by the atomic nuclei of the sample and provides HAADF contrast images which strongly depend on Z. The recent development of spherical aberration (Cs) correctors for electromagnetic lenses produces significantly smaller and brighter electron beams which allow single-atom imaging [3]. Therefore, the new instruments with Cs correctors could prove the presence of just one heavy atom on any catalytic support of light elements.

In this work, a transmission electron microscope with Cs corrector was used to reveal small WOₓ clusters on ZrO₂ crystals. W atoms dispersed on zirconia seems to be the more stable catalyst having strong acidic properties used to catalyze chemical reactions such as alcohol dehydrogenation, isomerization of alkanes, oxidative desulfurization, alkylation of hydrocarbon, etc. [4]. The catalyst is active
in the t-ZrO$_2$ phase annealing at 700°C.

At this temperature it is partially transformed into a monoclinic structure. A lot of effort has been put into finding better synthesis routes to stabilize and increase the concentration of t-ZrO$_2$ phase at activation temperatures. Incorporation of W atoms into the ZrO$_2$ lattice and their subsequent segregation on the surface has been widely studied [5]. The results show the presence of m-ZrO$_2$ and t-ZrO$_2$ structures coexisting with WO$_3$ crystals in different proportions. However, not all the W atoms are segregated as WO$_3$ crystals. Some of them still remain in the ZrO$_2$ lattice, stabilizing the tetragonal structure at a different concentration for each preparation method [6]. In fact, it is preferred that all W atoms remain dispersed on ZrO$_2$ crystals, since large WO$_3$ crystals are catalytically inactive. The HRTEM and STEM studies focused on, reveal small WO$_X$ clusters that were not detected by XRD.

**Experiment**

The samples were prepared mixing aqueous solutions of ZrO(NO$_3$)$_2$.6H$_2$O, (NH$_4$)$_6$W$_{12}$O$_{39}$.xH$_2$O and NH$_4$OH at pH between 9.5 and 10. The ammonium metatungstate solution was placed in a 4-L container and the other two solutions were added slowly under vigorous agitation conditions. Subsequently, the obtained white slurry was split into three parts. The first sample was aged for 24 h at room temperature, WZC. The second sample was refluxed at 100°C for 24 h, WZCR. The remaining sample was hydrothermally treated at 195°C at autogenous pressure, WZCH. A ZrO-OH sample was impregnated with (NH$_4$)$_6$W$_{12}$O$_{39}$.xH$_2$O by conventional impregnation. All samples were dried at 110°C for 18 h and annealed at 800°C for 4 h in an anhydrous air flow.

The TEM analysis was performed in a transmission electron microscope JEM-2200FS which operates at 200 kV. It has a Schottky field emission electron gun, an ultra-high resolution configuration (Cs = 0.5 mm; Cc = 1.1 mm; point to point resolution = 0.19 nm) and an omega energy filter in-column. In the STEM mode,
the microscope operates with an aberration-corrected CEOS device. It produces a smaller and brighter electron beam of 0.1 nm allowing single-atom imaging. Punctual chemical analysis at subnanometric size was performed by EDXS in a Noran spectroscope attached to the microscope.

**Results**

Polyhedral ZrO$_2$ crystals were observed in the bright field TEM images (fig. 1). In the sample WZC, the crystals were more agglomerated than in the samples ZWCR, ZWCH and ZWCI. In fact, single, small and large crystals can be clearly seen in figure 1d (WZCI). However, the size dispersion ($18 \pm 7$ nm) for this sample was larger than ZWC ($14 \pm 4$ nm), WZCR ($15 \pm 4$ nm) and WZCH ($14 \pm 3$ nm). These results are in good concordance with the DRX results [5]. The limitation was the identification and quantification of the ZrO$_2$ and WO$_3$ phases which were well analyzed by XRD [5]. Regarding the crystals' agglomeration, the surface energy was found to be different WZC > WZCH > WZCR > WZCI. Obviously, WZCI presents the lower surface energy because the W atoms remain on the surface while in WZC, WZCR and WZCH the W atoms would be in the crystalline lattice.

To reveal W atoms, single crystal images were taken at higher magnification (fig. 2). Atomic resolution was observed in the images. The strong phase contrast appreciated in the atomic lattice of figures 2a, 2b and 2d was generated by low-index crystallographic planes projected along the viewing direction. There was no direct evidence of W atoms. However, when the planes projected are high-index, the phase contrast of the atomic lattice is decreased and a small dark shadow is revealed on the crystal (fig. 2c), which could be related to the W clusters. In fact, this dark contrast could be increased with a de-focus of the image, but the atomic resolution of the crystal is strongly affected. On the other hand, due to the lack of chemical information, the interpretation could be wrong. Theoretical calculation from an atomic model could help to improve the interpretation.

For this system, the HRTEM images did not reveal W. But in the images obtained with HAADF detector, the W presence was very evident (fig. 3). Brighter dots of gray contrast on the ZrO$_2$ atomic lattice were clearly revealed from any viewing direction. The size of the bright dots was less than 1 nm (fig. 4a). The smallest were 0.2 nm and could be formed just by one or two W atoms (yellow circle fig. 3b and intensity profile fig. 4b). Tri-dimensional projection of a single crystal showed a rough surface, indicating that the W atoms remained on the surface as WO$_x$ clusters (fig. 4c). WO$_x$ clusters of a size larger than 1 nm were fully segregated from the ZrO$_2$ crystal surface as WO$_3$ crystals due to the incompatibilities between their crystalline lattices. These were the crystals detected by XRD. Finally, chemical
Analysis performed in both contrasts confirmed the results observed in the HAADF images. EDX spectra revealed more W atoms in the bright dots than in the gray contrast (fig. 4d and 4e).

**Conclusion**

The strong contrast produced between the W, Zr and O atoms in the HAADF images clearly revealed the W dispersion on ZrO$_2$ crystals at the subnanometric scale. Therefore, the W atoms that were not detected as WO$_3$ phase by XRD, remained as WOx cluster at sizes smaller than 1 nm on surface of the t-ZrO$_2$ and m-ZrO$_2$ crystals. They could, however, remain W atoms in the atomic lattice, stabilizing the t-ZrO$_2$ structure.

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**References**


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