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**ATOMIC-RESOLUTION Z-CONTRAST IMAGING OF
ULTRADISPERSED CATALYSTS**

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Atomic resolution Z-contrast imaging of ultradispersed catalysts

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ABSTRACT: Using Z-contrast imaging in a 300 kV scanning transmission electron microscope, direct images of single metal atoms on a support material in industrial catalyst systems are formed. The simultaneously collected conventional bright-field images reveal orientational information about the support, which allows possible configurations of Pt atoms on a $\gamma\text{-Al}_2\text{O}_3$ support surface to be deduced. Image intensities also allow the three-dimensional configuration of a raft of Rh atoms on a $\gamma\text{-Al}_2\text{O}_3$ support to be determined.

1. INTRODUCTION

In the study of the atomic dispersion of a catalytic metal and its configuration relative to the support material, transmission electron microscopy (TEM) is an invaluable tool. Generally, the rough, insulating nature of the support precludes the use of any other direct imaging technique, such as scanning probe microscopy. Although single atom imaging has been demonstrated using conventional TEM (Iijima, 1977), a specially thin and smooth single crystal support was used. In the case of catalysts, the contrast that is observed from the support usually prevents the imaging of metal clusters smaller than about 1 nm in diameter (Datye and Smith, 1992). Using Z-contrast imaging in a high-resolution scanning transmission electron microscope (STEM), however, allows individual atoms to be observed on industrially relevant supports, such as SiO_2 and $\gamma\text{-Al}_2\text{O}_3$.

2. ATOMIC RESOLUTION Z-CONTRAST IMAGING

A Z-contrast image is formed in a scanning transmission electron microscope (STEM) by detecting the electrons that are scattered out to a large, high-angle annular dark-field (HAADF) detector as a focussed electron probe is scanned over the specimen. Because of the large size of the detector, it is an incoherent imaging mode (Jesson and Pennycook, 1995) that forms a direct map of atomic locations with intensities that are strongly dependent on the atomic number (Z) of the observed atom. This ability to distinguish between heavy and light atoms makes it a powerful method for the observation of supported metal atoms, and it is therefore extremely useful in the study of catalyst materials. Using a 100 kV STEM, clusters as small as three atoms have been detected (Treacy and Rice, 1989), but the individual atoms were not resolved.

The VG Microscopes HB603U 300 kV STEM ($C_s=1$ mm) at Oak Ridge National Laboratory is capable of forming a probe only 0.13 nm in diameter. Such a small probe enhances the signal-to-background ratio for supported metal atoms, so that single atom sensitivity is now possible for tiny clusters on real catalyst supports. Using a small axial detector in a STEM also allows the conventional bright-field (BF) image to be formed simultaneously with the Z-contrast image. Because it is formed coherently, the BF image is dominated by contrast due to scattering from the support material. When not too far from a

Fig.1. Simultaneously collected (a) Z-contrast and (b) BF images from a sample of 3 wt% Pt on γ - Al_2O_3 .

major zone axis, the BF contrast allows the orientation of the support material to be determined.

3. IMAGING OF PLATINUM ON γ -ALUMINA

Simultaneously collected Z-contrast and BF images from a sample of 3 wt% Pt on γ - Al_2O_3 are shown in Fig. 1. In Fig. 1a some of the clusters can be seen to be resolved into single atoms, whilst Fig. 1b is dominated by the support contrast. The strong $\{222\}$ γ - Al_2O_3 fringes visible in Fig. 1b allow the orientation of the support to be determined. The beam direction is close to $[110]$, and the orthogonal directions are indicated on Fig. 1b. Performing a bandpass filter on Fig. 1a results in Fig. 2. Trimers of Pt atoms were often observed in this sample, and Fig. 2 shows the possible surface sites that were deduced (Nellist and Pennycook, 1996). Near the bottom of Fig. 2, dimers can be seen that have configurations of one side of the trimer.

Fig. 2. A bandpass filtered version of Fig. 1a. From the orientational information in Fig. 1b possible γ - Al_2O_3 surface sites for a Pt trimer are indicated.

Fig. 3. Simultaneously collected (a) Z-contrast and (b) BF images from a sample of Rh on $\gamma\text{-Al}_2\text{O}_3$.

4. IMAGING OF RHODIUM ON γ -ALUMINA

Fig. 3 shows a simultaneous Z-contrast and BF pair of images from a sample of 1.2 wt% Rh on $\gamma\text{-Al}_2\text{O}_3$. The rows of Rh atoms in Fig. 3a are almost parallel to the facets of the $\gamma\text{-Al}_2\text{O}_3$, again suggesting an interaction with the support material. A bandpass filtered version of Fig. 3a is shown in Fig. 4. Most of the atom-like feature intensities in Fig. 4 have a similar intensity. Since part of the cluster has become obviously disordered, we may associate this intensity with the presence of one atom, and therefore the cluster is mainly a monolayer raft. Some of the features are more intense than the majority, with an intensity 2.5 times greater than the single atoms. Because of partial coherence along the beam direction, this intensity is consistent with these features being two atoms arranged in a column (Nellist and Pennycook, 1996). The position of some of these columns at the edge of the raft, or even isolated from it, suggests that something is providing the support for such a column. One possibility is that the Rh raft has become partially incorporated into the first few layers of the $\gamma\text{-Al}_2\text{O}_3$, which is providing the necessary support.

Fig. 4. A bandpass filtered image of a region of Fig. 3a.

5. IMAGING OF LARGER CLUSTERS

We have demonstrated how Z-contrast is able to image single metal atoms on a support. However, it is also useful in the study of larger metal clusters. In Fig. 5, the support is so thick that the conventional BF image barely shows any contrast arising from the Rh cluster. The Z-contrast image shows the cluster clearly, and it is possible to identify a twin near the centre of the particle.

Fig. 5. A simultaneously recorded (a) Z-contrast and (b) BF image of a Rh cluster supported on γ - Al_2O_3 .

6. CONCLUSIONS

The small illuminating electron probe now available in a 300 kV STEM allows direct imaging of the atomic configuration of supported metal atoms in industrial catalyst systems. The ability to simultaneously record the conventional BF image can allow the metal atom configurations to be related to the orientation of the support material, and possible surface sites deduced. Image intensities also reveal information on the three-dimensional configuration of such clusters.

With this information available, it should now be possible to relate the cluster configurations to the catalytic activity experimentally observed, and to study the changes in the cluster structures as the catalyst degrades.

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