

Atomic Scale Characterization of the Metal-Oxide Interface in Catalysts.

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The phenomena known as the Strong Metal Support Interaction (SMSI) is of critical importance for a wide number of catalyst processes [1]. Understanding the nature of this interaction between the nanoscale metal clusters and the reducible supports is essential for the optimization of activity and selectivity in many applications. Previous work on one of the systems that exhibits this interaction, Pt/TiO₂, has focused on either structural properties [2,3], electronic properties [4] or electronic properties of specific TiO₂ surfaces [5,6]. Due to the complex nanoscale nature of the systems involved, little work has been performed on systems of direct relevance to industrial applications.

The aim of this study is to investigate the SMSI phenomenon at the fundamental atomic level on a more realistic system, through the combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM). In particular, the focus is on developing an understanding of the drastic changes in the activity and selectivity that the SMSI manifests in Titania-promoted catalysts. The combination of the experimental STEM techniques can be used to provide direct information on both the morphology and the electronic structure of the interface between the metal particles and the Titania support under different thermodynamic conditions (through in-situ heating capabilities). Here we present some preliminary results from our atomic scale characterization of the metal-oxide interface, with images of platinum particles of nanometer and sub-nanometer size on Titania support shown below.

The experiment was performed on the 200 kV JEOL 2010F STEM at the University of Illinois at Chicago. The spectra were acquired with an energy resolution of 1.2 eV and energy dispersion of 0.3 eV. The preliminary results from the Z-contrast images of two Pt/TiO₂ samples reduced in flowing H₂ at 250°C and 450°C, show that the average Platinum particles size is about 1nm. The Pt particle size ranges from a few atom clusters to 2nm particles size (figure 1). Figure 1b shows the the atomic columns of Titanium in the support are clearly visible with some brighter areas containing Platinum particles. The brightness is localized on the atomic columns with no diffuse intensity in between (circled area), suggesting a few atom clusters of Pt either on the surface in the positions of Ti atoms or substituting for Ti in the support. In this case, no noticeable structural difference between the two samples is observed despite a significant difference in the catalytic properties. Such results indicate that the particle size distribution is not sufficient to understand the changes in catalytic activity and selectivity that arise from different thermodynamic treatments.

To investigate the origin of the metal-support interaction, figure 2a shows an image of an edge-on Pt particle on anatase [010]. We can clearly see a distortion of Titania around the Pt particle, showing evidence for encapsulation of the particle. This is also supported by EELS measurements, which suggest that there is Titanium on the free edge of the Pt particles (figure 2b). Such analyses show that it is possible to obtain atomic scale information from individual nanoclusters and investigate the origins of SMSI. The presentation will include in-situ measurements that illustrate the development of this interaction as a function of environmental conditions [7]

References:

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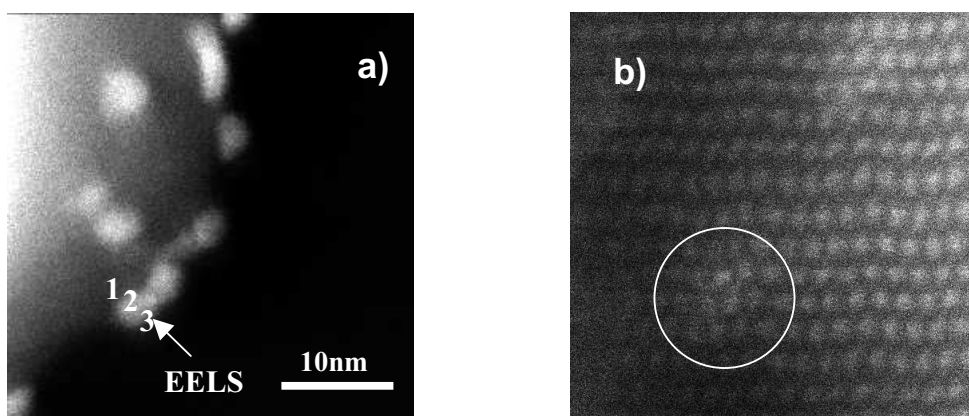


Figure 1: (a) Z-contrast image of Platinum on TiO_2 . This image shows a large size distribution of the Pt particles. (b) Atomic resolution Z-contrast image of Platinum on TiO_2 (250C). The circled area indicates a possible epitaxial or substitutional Pt on Ti atoms sites. Evidence of single Platinum particles on Titania and possible epithaxial growth.

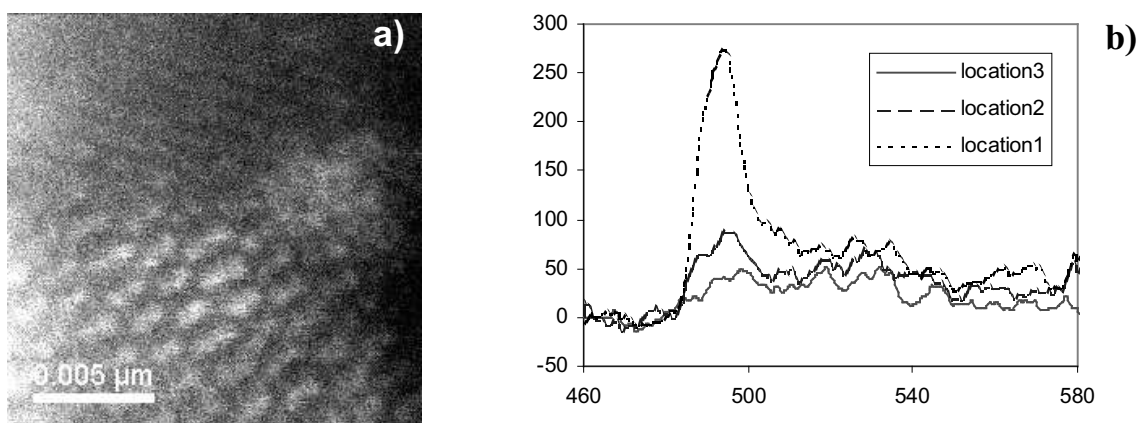


Figure 2: (a) Z-contrast image of Platinum on TiO_2 (450C) (Anatase [100] orientation). Evidence for distortion of Titania around the Pt particle. Encapsulation of the edge-on Pt particle. (b): EELS spectra after background subtraction and removal of the effect of multiple scattering, taken at the locations specified in figure (1a) above, showing the presence of traces of Titanium on Platinum particles. The acquisition time for each spectrum is 2s, dispersion 0.3 eV.