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SINGLE ATOM SENSITIVITY FOR SOLVING CATALYSIS PROBLEMS

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Single-Atom Sensitivity for Solving Catalysis Problems

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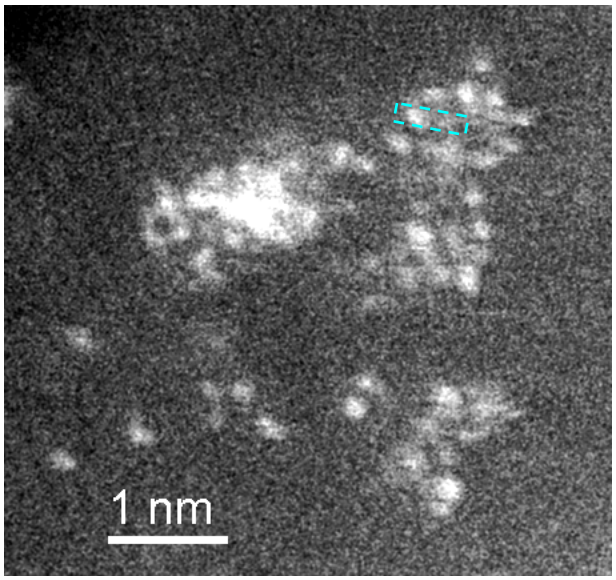
Aberration-corrected Z-contrast (HAADF) STEM offers significant advantages for catalysis research due to its superior resolution and sensitivity, which allows observation of atomic-scale phenomena with unprecedented detail. ORNL's 300 kV VG Microscopes' HB603U STEM with Nion aberration corrector has a probe size of ~0.7 Å and routinely allows us to image single atoms inside the materials and on their surfaces. This ability was found to be critical for determination of the mechanism of thermal stabilization of γ-Al_2O_3 with La dopant [1]. The combination of STEM studies and first principles calculations revealed that stabilization is achieved by single La atoms adsorbed on γ-Al_2O_3 surfaces. Better image quality also allows us to determine configurations of the catalytic metal clusters with higher precision, gaining new insights into their properties. For example, accurate measurement of the interatomic distances in Pt_3 clusters on a γ-Al_2O_3 surface and thorough theoretical analysis led us to discover that these units are capped with OH-groups [2], which affect electron density distribution within the clusters and, consequently, the catalytic activity of the system.

For the studies of bimetallic catalysts, Z-contrast STEM is invaluable as the distribution of different metal atoms within catalytic particles can be revealed. Figure 1 shows a STEM image of γ-Al_2O_3 supported Pt/Ru catalyst derived from $Pt_2Ru_4(CO)_{18}$ precursor. Metal atoms within particles have different brightness, and a line trace shows their intensity ratio is in agreement with that expected from the ratio of their atomic numbers ($Z^2_{Pt} : Z^2_{Ru} \approx 4:1$), clearly demonstrating that the bimetallic character of the precursor is retained in the resulting catalytic particle. A MgO-supported Pt/Fe catalyst derived from $Pt_3Fe_3(CO)_{15}$ shows quite different behavior, as illustrated by a sequence of STEM images in Fig.2. Here Pt is evidently segregated, forming particles and close-packed monolayers, loosely attached to the substrate (note changes in the configuration of the large particles from frame to frame). Remarkably, a single Pt_3 core of the original molecule can also be seen moving along the substrate, suggesting a multi-step transformation from the precursor to the final catalytic particle.

Additionally, the high convergence angle of the probe in aberration-corrected HAADF STEM results in depth sensitivity, enabling us to achieve vertical resolution in the nanometer range in addition to sub- Ångstrom lateral resolution [3]. This technique can be used to reconstruct the 3D-structure of mesoporous or polycrystalline substrates and characterize the vertical distribution of the catalytic particles. Prospects of in-situ HAADF STEM for catalysis will also be discussed.

References

[1] S. Wang, A. Y. Borisevich et.al., *Nature Materials*, in press (2004).
[2] K.Sohlberg et.al., *J. Am. Chem. Soc., submitted* (2003)
[3] S.J. Pennycook et al., these proceedings
[4] We are grateful to Prof. R.D. Adams and Prof. M. Amiridis for the provision of catalyst samples. This work was supported by USDOE under contract DE-AC05-00OR22725 managed by UT-Battelle, LLC.



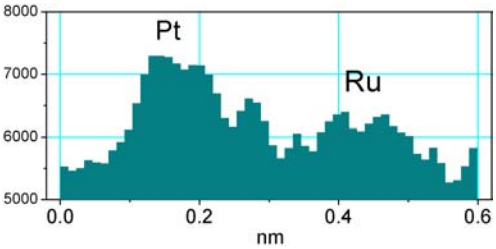
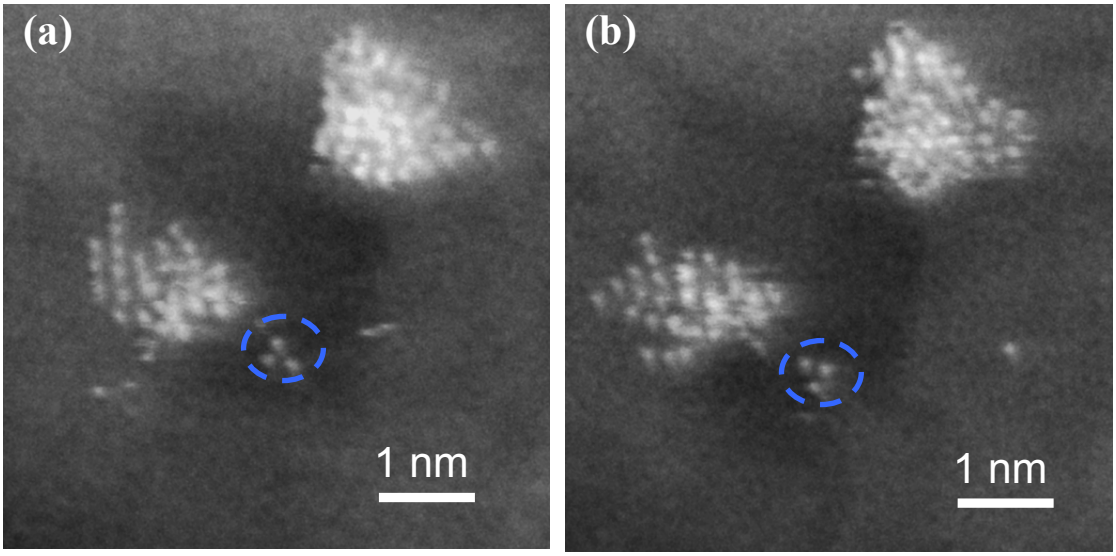


FIG.1. STEM image of γ-Al_2O_3 supported Pt/Ru catalyst derived from $Pt_2Ru_4(CO)_{18}$ precursor. Brighter spots correspond to Pt atoms, dimmer spots to Ru atoms. Line profile corresponds to the rectangle shown in the image.



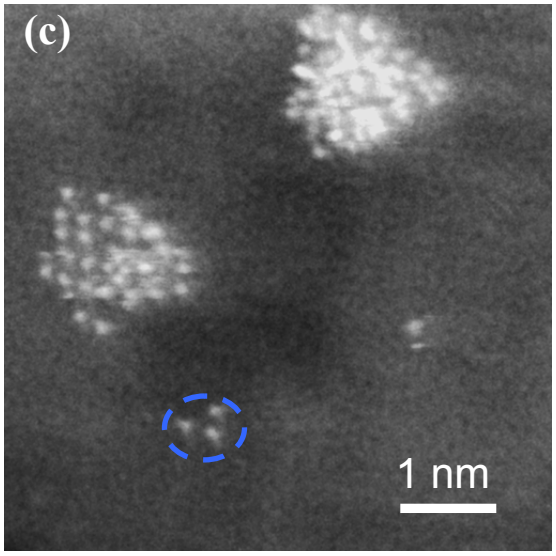


FIG.2. A series of STEM images of MgO-supported Pt/Fe catalyst derived from $Pt_3Fe_3(CO)_{15}$ precursor. Note changes in the configuration of the large particles suggesting weak interaction with the substrate and the Pt_3 core (highlighted by a dashed circle) of the initial molecule moving along the substrate. The images were taken sequentially within 5-10 seconds of each other.