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Synergy of Combined (S)TEM Imaging Techniques for the Characterization of Catalyst Behavior During In-Situ Heating

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Gold nanoparticles have generated considerable interest for catalytic applications for certain oxidation reactions [1]. Recently, a series of Au catalysts supported on Fe_2O_3 (hematite) were characterized with atomic resolution during elevated temperature treatments, using a novel in-situ heating technology (Protochips Aduro^{TM}) in an aberration-corrected STEM (JEOL 2200FS fitted with a CEOS GmbH hexapole corrector on the probe-forming lenses) [2]. In the present work, we extended the study to take advantage of the imaging capabilities in both STEM and TEM modes available in an Hitachi HF-3300 microscope, operated at 300kV. This instrument is fitted with a secondary electron (SE) detector, in addition to both bright-field (BF) and high-angle annular dark-field (HAADF) detectors for STEM imaging, and a Gatan 2k x 2k Ultrascan CCD camera for TEM imaging. The advantage of TEM recording during in-situ heating is the short exposure times (~1sec) relative to the slower scans required by STEM modes. This allows higher accuracy and more reliable analysis of the atomic structure via computed diffractograms (sample drift and scan artifacts can strongly affect STEM diffractograms). The capability of SE imaging in the Hitachi HF-3300 even at the high temperature afforded by the Protochips Aduro^{TM} heater system is an added benefit for complementary analysis of catalyst structure and behavior during elevated temperature treatments. SE imaging has been coupled with STEM and TEM imaging in the present study.

A World Gold Council Au/Fe_2O_3 (hematite) catalyst sample initially treated to leach away surface Au nanoparticles and other Au species was deposited onto an Aduro^{TM} chip by dry-dipping the chip into the catalyst powder. Earlier studies [2] showed the presence of voids in the hematite support particles, as well as some Au nanoparticles and highly dispersed Au species internal to the support and coating the void surfaces. At 250°C, no significant changes were observed for the voids or catalysts, but at 500°C the voids diminished in size and gradually disappeared, while internal Au species diffused to the surfaces to form new 1-2nm Au nanoparticles. In the present study, BF TEM images of a support particle are shown before heating (Fig. 1a) and after several minutes of heating at 500°C (Fig. 1b). A diffractogram from the particle in Fig. 1b shows periodicities consistent with *d*-spacings for the <112> zone axis orientation of magnetite (Fe_3O_4), indicating the reduction of the hematite particles during heating to 500°C in vacuum. Internal voids were observed to shrink during heating at 500°C, an observation consistent with earlier results [2].

Further heating at a higher temperature caused a gradual appearance of Au nanoparticles in the 1-2nm range on the surface of the leached catalyst support. The behavior of these nanoparticles is observed in Fig. 2, which shows a series of *unprocessed* SE images taken at 700°C. Figure 2a shows a relatively smooth surface at the beginning of the 700°C heating cycle and the presence of a number of 1nm Au particles. In Figs. 2b to 2f, acquired over a few minutes, the support surface developed terraces, and some Au particles migrated on the terraces to coalesce into larger particles (e.g. as arrowed). This study demonstrates that 1nm spatial resolution in SE imaging can be achieved even during in-situ heating at 700°C. Such a combined SE and TEM in-situ study is useful for nanomaterials research because information from the surface via SE imaging and bulk via TEM/STEM imaging can be simultaneously obtained [3].

References

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[3] We thank Niels de Jonge for insightful discussions. This work was supported by the High Temperature Materials Laboratory, sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program.

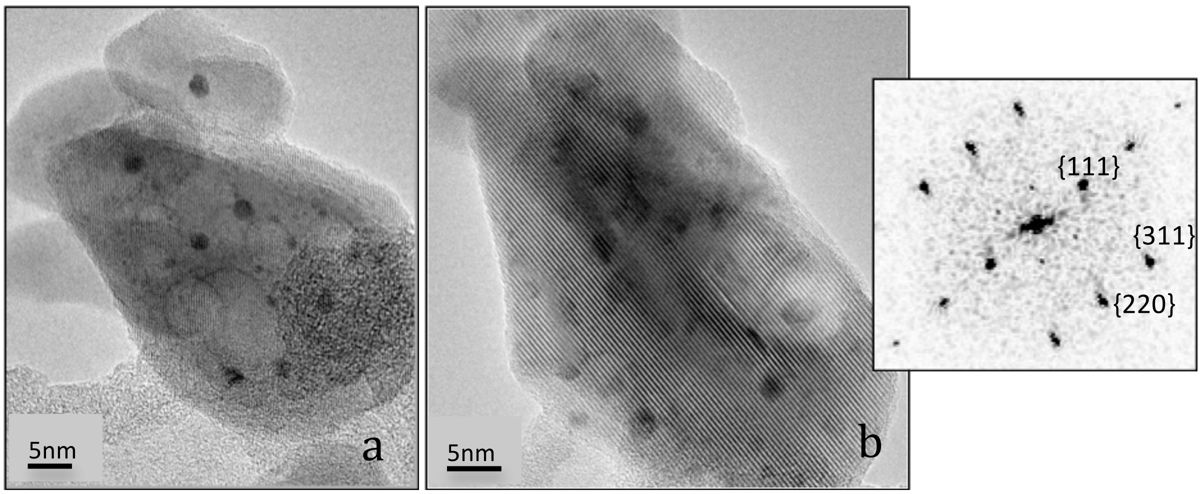

FIG. 1 a) Leached Au/FeOx (hematite, Fe_2O_3) catalyst at room temperature, showing voids and Au nano-particles in BF TEM; b) Same support particle imaged at 500°C, showing Au particle growth and void shrinkage; c) diffractogram from heated particle, consistent with a <112> zone axis of magnetite (Fe_3O_4).

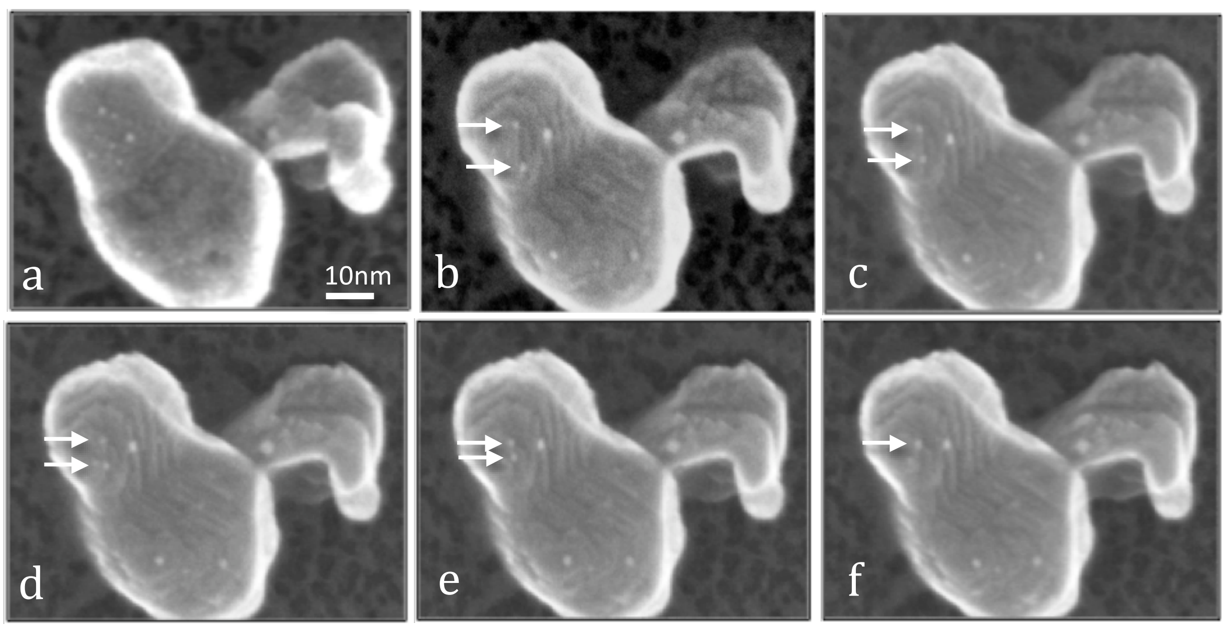

FIG. 2. Sequence of secondary electron images recorded at 300kV in the Hitachi HF-3000, with the same support particle held at 700°C; several Au nanoparticles are visible on the surface; a) initial image at the start of sequence; b)-f) SE images after several minutes at 700°C, showing the development of facets on the support surface and movement and coalescence of nanoparticles, as arrowed.

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