Environmental and In Situ SEM/TEM

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Atomic-scale Observation of Catalysts in their Functional State using aberration-corrected Environmental Transmission Electron Microscopy (ETEM)

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Today's strong focus on efficient energy conversion and environment protection technologies relies on the advancement of (new) functional nanomaterials, such as heterogeneous catalysts. Characterization of the state and properties of such a nanocatalyst as well as of its activity, selectivity and stability demands detailed dynamic atomic-scale insights. High-resolution transmission electron microscopy (HRTEM) has become an indispensable tool for characterizing nanomaterials and provides the unique ability to image size, shape, as well as surface and interface structures at the atomic scale. With more recent advances in electron optics, aberration-corrected HRTEM is now able to detect the atomic structure ultimately with a resolution below 0.1 nm and with single atom sensitivity.

Standard TEM experiments are performed with the sample kept under high vacuum conditions inside the microscope column. But, such conditions might be inadequate to investigate the active functional state of a catalyst whose properties depend on varying reaction conditions. In those cases, studies should preferably be performed *in situ* under the exposure to a gas environment, matching the conditions encountered during the technical use of the nanosystem. Dynamic, atomic-scale visualization of structural evolutions *in situ* under reactive gas environments directly addresses the environment-dependent structure and dynamics of functional states of a nanocatalyst. This is a crucial step in R&D, because generally there is no evidence that the dynamic state of the structure can be derived from postmortem (high vacuum) examinations of the materials alone. State-of-the-art HRTEM imaging and spectroscopy capabilities can now also be applied for *in situ* studies of structure and dynamics of nanocatalysts induced by reactive gas environments. Differentially pumped environmental TEMs (ETEMs) [1,2] are uniquely designed to permit gas in the microscopes specimen area while preserving the atomic-scale performance of an aberration-corrected microscope (Titan ETEM G2) [3,4]. Application of ETEM shows to be an essential complement to theoretical approaches as well as to the arsenal of established spectroscopic techniques (e.g. applied at synchrotron facilities) that average information over length scales considerably larger than the dimensions of the nanostructures. It has been assumed that the added gas environment may affect the ultimate HRTEM image resolution and sensitivity. However, the 0.10 nm (= 1Å) resolution threshold can be maintained up to at least 10 mbar gas pressure inside the specimen area [4]. The optimal imaging conditions for atomic-scale *in situ* studies are determined by a careful selection of electron beam energy and dose-rate as well as image signal-to-noise (S/N) ratio (see Fig. 1) [4]. As an example a catalyst composed of gold (Au) nanoparticles (NP) supported on cerium oxide (CeO_2) has been examined [5]. Au nanoparticles supported on metal oxides such as CeO_2 become active for the oxidation of carbon monoxide (CO), even below room temperature (RT). In situ HRTEM experiments, shown in Fig. 2, depict that adsorbed CO molecules cause the {100} crystal facets of Au NP to reconstruct to Au{100}-hex during CO oxidation at RT. The stable Au{111} surface is considered to be oblivious to the presence of CO gas. The CO molecules adsorbed at the on-top sites of Au atoms in the reconstructed Au{100}-hex surface, and the energetic favorability of this reconstructed structure has been confirmed by *ab initio* calculations and image simulations (Fig. 2) [5]. The experimental data indicates that the active sites of the Au nanocatalysts are located at the particle-support periphery where gas species such as O_2 or -OH probably react with CO. The methodology demonstrated in this study has opened an experimental route toward the elucidation of Au nanoparticles catalytic mechanisms by direct observation of metal atoms and gas species at the particle-support periphery using aberration-corrected ETEM [5].

1. The growing number of application examples proves that a differentially pumped ETEM is a powerful tool for applied research and development on functional nanostructures (such as catalysts, batteries, fuel cells, etc.) that requires exposure to an operational/reactive gas environment. State-of-the-art ETEM techniques provide exclusive data from these dynamic *in situ* processes at the atomic scale.
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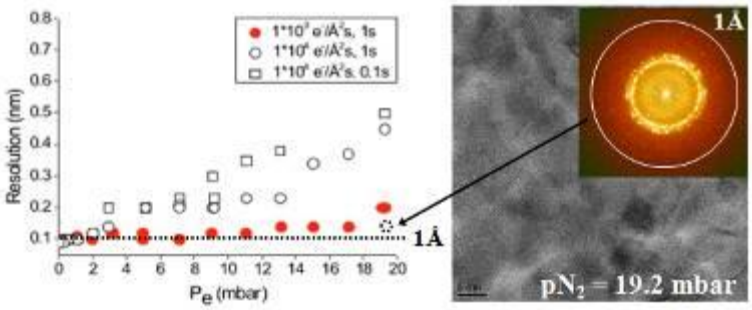

Figure 1. left side: HRTEM image resolution vs N_2 pressure in ETEM. **right side:** HRTEM micrograph taken under the lower dose-rate condition [4].

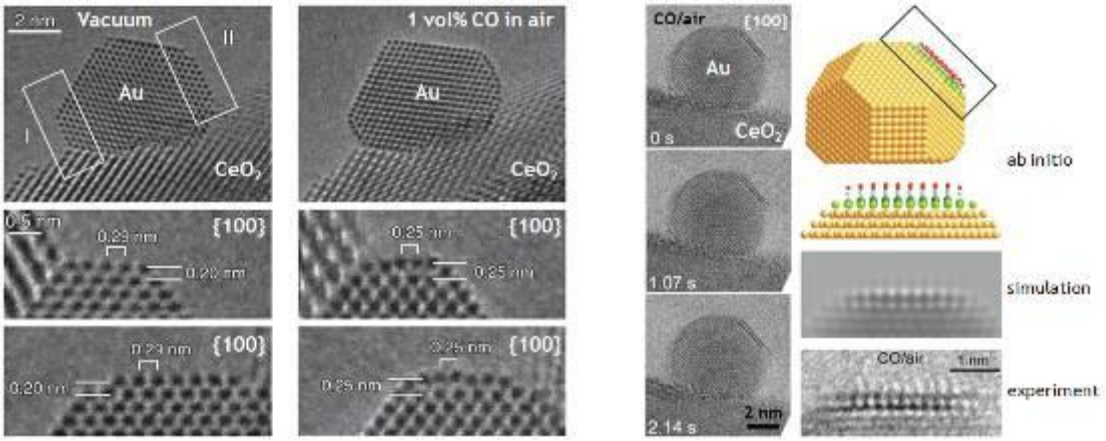

Figure 2. left side: Au/CeO_2 in vacuum and in reaction environment for CO oxidation. Under catalytic conditions Au NP exhibit Au{100}-hex reconstructed surface structures. (see {100} facets in the rectangular regions indicated by I and II). right side: Au/CeO_2 observed in reaction environment. An image feature appeared on the upper-right part of the Au NP & Au NP model with a Au{100}-hex reconstructed surface and adsorbed CO molecules. Comparison between corresponding calculated TEM image and the experimentally observed image confirms the presence of Au{100}-hex reconstructed surface with adsorbed CO [5].