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Dynamical Response of Catalytic Systems in a C_S Corrected Environmental Transmission Electron Microscope

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In industrialized countries, 85-90% of chemical production involves catalytic processes [1]. It has been estimated that 35% of global GDP depends critically on the use of catalysis [2]. Transmission electron microscopy (TEM) has been used extensively in catalysis research [3]. However, in contrast to chemical reactors, a conventional TEM is a high vacuum tool. Thus, observations do not always reflect the active state of materials. Environmental TEM (ETEM) provides the capability to expose samples to a gas atmosphere during imaging and analysis. Even though the gap between reactor and high-vacuum pressures has not been fully bridged, progress has been made towards observing materials in their working environment.

Many catalytically active materials consist of metals or metal alloys, which are deposited onto a support material as nanoparticles to optimize the exposed active surface area. In a catalytic reactor, the particles tend to sinter under reaction conditions resulting in the formation of larger particles and a loss of catalytic activity. Several models of sintering in different systems have been put forward [4,5]. However, most investigations have been post mortem studies, revealing only the final state of the catalyst.

For fundamental studies of sintering, we used a model system consisting of gold nanoparticles on a boron nitride support. Boron nitride powder was deposited onto a lacey carbon film on a copper grid and sputter coated with 0.7 nm of gold. The Au film readily formed nanoparticles up to 20nm in size. The particles were exposed to 1.3 mbar of H_2 gas at 410°C in an image C_S corrected FEI Titan 80-300 ETEM. Image sequences were acquired at 2 frames/s.

Under these conditions, mobility of the particles was clearly visible, while maintaining lattice resolution of both the BN support and the Au particles. Some particles remained immobile during observation while others moved on the support (Fig. 1) and sintered by migration and coalescence. Other particles were observed to shrink in size and finally disappear as neighboring particles gradually grew by Ostwald ripening. The observations also clearly indicated the affinity of particles to steps on the support material. Particles on steps were significantly smaller than those on terraces, indicating a stronger interaction of the metal and support at these sites. By quantifying these observations, fundamental insight into activation energies and energy barriers for sintering processes can be studied.

The surface structures of catalytic materials are highly dependent on the surrounding atmosphere. The combined capabilities of ETEM and image C_S correction provide unique possibilities to study this relationship. However, in order to fully quantify image contrast from such experiments, a deeper understanding of the scattering of fast electrons in the presence of gas molecules in the pole piece gap of the microscope is needed. In Fig. 2, the relative intensity measured on the CCD camera in the absence of a solid specimen is shown as function of Ar pressure in the pole piece gap.

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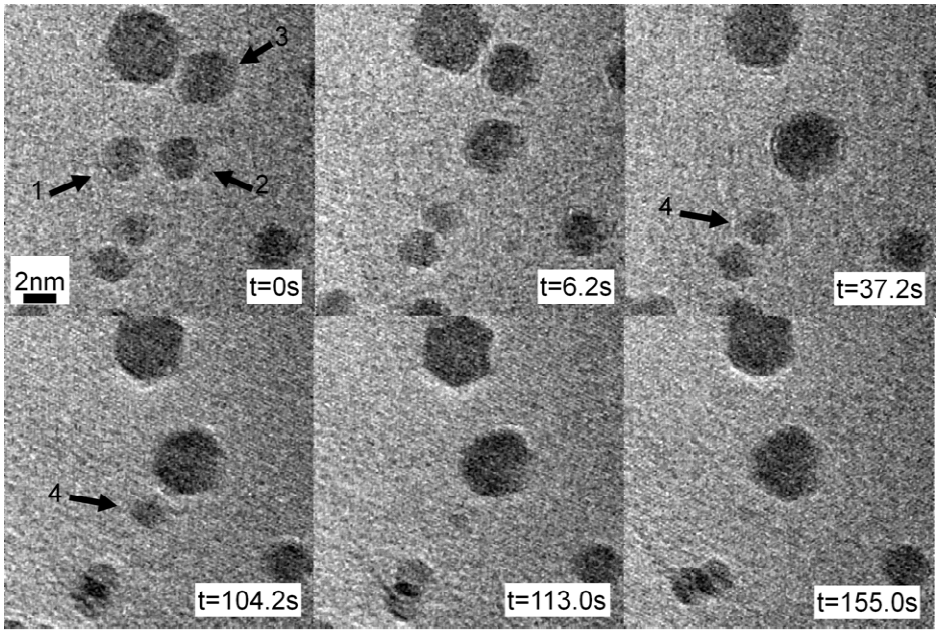

FIG. 1. Frames extracted from an image sequence acquired in an environmental TEM in 1.3 mbar of H_2 gas at 410°C. Arrows indicate the positions of coalescence events and Ostwald ripening. The time indications are relative to the first frame shown.

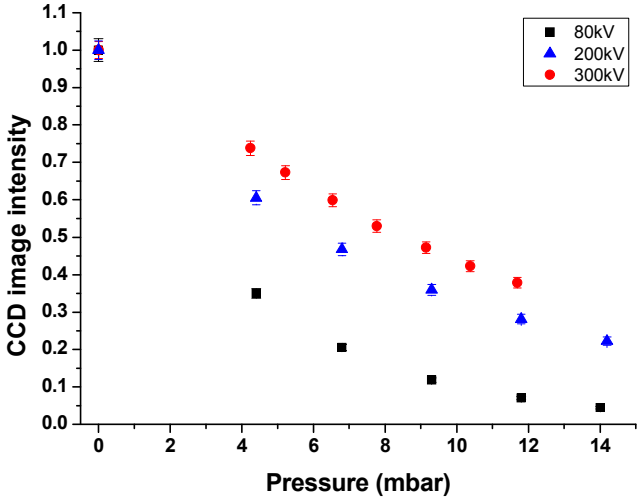

FIG. 2. Relative intensity measured on the CCD camera in image mode plotted as a function of Ar gas pressure for the microscope acceleration voltages indicated.

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