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High-Resolution Aberration-Corrected TEM of Oxidation Catalysis

R. Schlögl

Department of Inorganic Chemistry, Fritz-Haber-Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

Professor Schlögl's specific areas of interest include : in-situ analysis of polycrystalline catalysts, based on silver, copper, molybdenum and vanadium oxides, and used for selective oxidation and activation of small alkane molecules; carbon allotropes as catalysts and supports for nanoparticles; the function of solid acids in alkane activation and isomerisation on zirconia-based systems; synthesis protocols of catalytic nanomaterials for aqueous molecular precursors using in-situ analytical control techniques; and preparation and functional analysis of model catalysts based on epitaxial thin-oxide films and metal and oxide clusters.

In his work, Dr. Schlögl seeks to construct a bridge between surface science, chemical engineering and synthetic chemistry in the field of oxidation catalysis. His group's expertise in observing the structural dynamics of reacting catalysts also provides a unique way to study the synthetic steos necessary to create catalytic solids. These seemingly 'simple' processes of precipitation and calcination are in fact, as complex as the dynamic behaviour of the resulting catalyst, but have received little attention from the scientific community.

Transmission electron microscopy (TEM), with its ability to reveal structural and crystallographic characteristics on the atomic scale, plays a central role in Dr. Schlögl's research. However, until recently, TEM has been limited in its ability to examine structures that did not exhibit continuous translational symmetry. For heterogeneous catalysts, where the catalyst is typically a solid particle participating in a gas or liquid phase reaction, this is a critical limitation. The features of greatest interest on such a catalyst are the terminal atoms at the particle surface – by definition a discontinuity in the crystalline structure. FEI's recently introduced Titan TEM provides a solution to this problem, permitting atomic-scale resolution of the surface atoms where the catalytic processes actually occur.

A TEM is in many ways analogous to a light microscope, but uses electrons rather than visible light. A collimated beam of electrons illuminates the sample and magnetic lenses focus transmitted electrons into a magnified image. The primary limitation of TEM resolution is spherical aberration in the magnetic lenses. Unlike optical lenses, the round magnetic lenses used in a TEM exhibit only positive aberration, thus precluding correction by combining lenses with negative and positive values. Aberration correctors are available but their benefit has been limited when retrofitted to uncorrected optical systems. The Titan is the first TEM designed specifically to optimize performance with aberration-corrected optics.

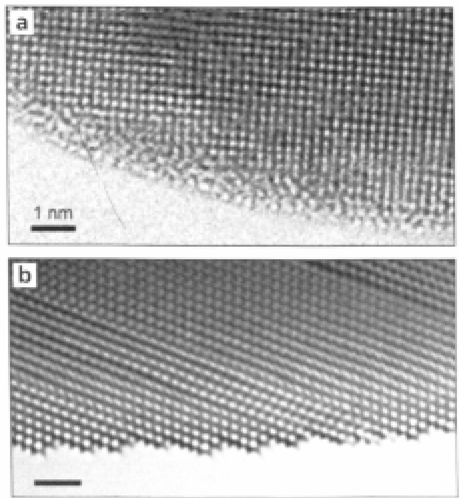

Figure 1: Transmission electron micrographs of silver particles. The terminal atoms can only be imaged with aberration –corrected transmission electron microscopy.
(a)The surface of a precipitated silver catalyst particle is highly disordered.
(b)Particles prepared by the incipient wetness technique maintain their internal crystalline structure out to the surface where terminal structure shows numerous kinks and discrete atomic dislocations.
Scale bars = 1 nanometer.

Spherical aberration results when the power of a lens varies with radical distance from the optical axis. For positive aberration, radially distant rays are brought to focus closer to the lens than paraxial rays. As a result, a point in the object becomes a disc in the image plane. Spherical aberration degrades TEM imaging performance in several ways. It causes a general blurring of the image as the discs from adjacent object points overlap in the image. It also causes a phenomenon known as delocalization whereby electron waves interfere with one another over an extended area in the image. Delocalization appears in TEM images as an extension of regular crystalline structure beyond the limits of the actual structure. For instance, the crystalline structure of a catalyst particle may appear to extend into empty space beyond the edge of the particle, obscuring detail precisely where it is most critical. Finally, spherical aberration introduces a radially dependent phase shift in the electron wavefront. High-resolution imaging in a TEM relies on phase contrast and the phse shifts induced by aberration result in contrast reversals that are dependent on the spatial frequency of the information. Though current generation TEMs offer sub-angström 'information limits', these phase effects limit directly interpretable image resolution to 2-3 A in uncorrected systems. Aberration correction provides a threefold improvement in usable image resolution by bringing the point resolution down to the information limit.

Schlögl's group, among the first to take delivery of a Titan, demonstrated the value of aberration correction in a recent study of silver particles used to catalyze the hydrogenation of acrolein to allyl alcohol. The catalytic activity of silver in this reaction is known to vary with the specific pretreatment protocol. Particles treated with the incipient wetness techniques show greater selectivity for hydrogenation than do particles created by precipitation.

Images of the surfaces of the two types of particles reveal a highly disordered surface layer on the precipitated particles (Figure 1). In contrast, the internal crystalline structure of the incipient wetness particles extends to the surface, where it terminates abruptly in numerous kinks and displacements among the surface atoms. The investigation attributes the increased catalytic activity of the incipient wetness particles to active sites associated with the kinks in the terminal structure. These structures are only visible with spherically corrected electron optics.