Atomic scale structure-function relationship of heterogeneous catalysts: investigation of gas-solid interactions by ETEM

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INTRODUCTION

Catalysts play a pervasive and indispensible role in industrial processes used to produce many essential chemicals and fuels. Heterogeneous catalysts, solid catalysts that promote reactions among gaseous reactants, are particularly important in refining conventional fossil fuels and in efforts to develop new renewable fuel and feedstock resources. To succeed in these efforts, researchers need to understand relationships between structure and performance at the atomic scale as they seek to apply rational design strategies to create new catalysts.

Transmission electron microscopes (TEMs) allow scientists to visualize geometric and electronic structure as well as chemical composition at the atomic scale, but conventional TEMs require high vacuum (at $\leq 10^{-5}$ Pa) in the sample chamber, limiting their ability to observe catalysts in a functional environment. Differentially pumped environmental TEMs (ETEMs), as described in [1, 2], are uniquely designed to permit some gas in the sample chamber while balancing the detrimental effects of electron scattering by gas molecules, thus preserving the atomic scale resolution of conventional TEM [3]. ETEM has proven to be an extremely powerful tool for catalysis research (e.g. [4, 5]), where it permits dynamic, in-situ observations of heterogeneous catalysts in operational (or near operational) conditions.

Several aspects of the design of the latest generation of ETEMs (such as the Titan ETEM G2 from FEI) contribute directly to their ability to provide time resolved atomic scale observations of catalysts during exposure to reactive gas environments and elevated temperatures. For example, the Titan TEM platform provides the inherent mechanical and electronic stability as well as optical performance required to achieve sub-Ångström resolution. The use of spherical aberration correctors, among other things, relaxes the constraints on optical design that would otherwise limit the space available in the sample vicinity for the environmental cell and related experimental apparatus. The system accepts standard TEM sample holders and provides sufficient space for full double tilt 3D tomography. Gas inlets allow controlled introduction of inert and reactive gases, while the differentially pumped objective lens confines the gases to the sample vicinity without introducing windows in the beam path. Extensive safety

engineering, including a fully automated and interlocked vacuum system, ensures safe handling, even of certain flammable and toxic gases.

Pressures in gas experiments can be accurately preset from 10^{-3} Pa up to 2000 Pa (in the case of N_2). Software controls offer a range of settings to provide easy operation by novice users while preserving the flexibility demanded by more advanced users. The ETEM is equipped with a mass spectrometer (RGA) for determining gas composition in either the gas inlet system or the specimen area. A built-in plasma cleaner allows for cleaning of the specimen area after using a gas.

CATALYST NANOPARTICLES

Size, shape and structure in operational conditions

Catalytic activity, selectivity and stability seem to depend strongly on the size, shape and structure of the catalyst particles. While ex-situ characterization offers important insight into the catalyst's structure and composition, these observations may not provide information about changes in the catalyst's structure and properties while in its operating state. Such observations are fundamental to describing the catalyst's structure-property relationships because in operando the catalyst may undergo significant
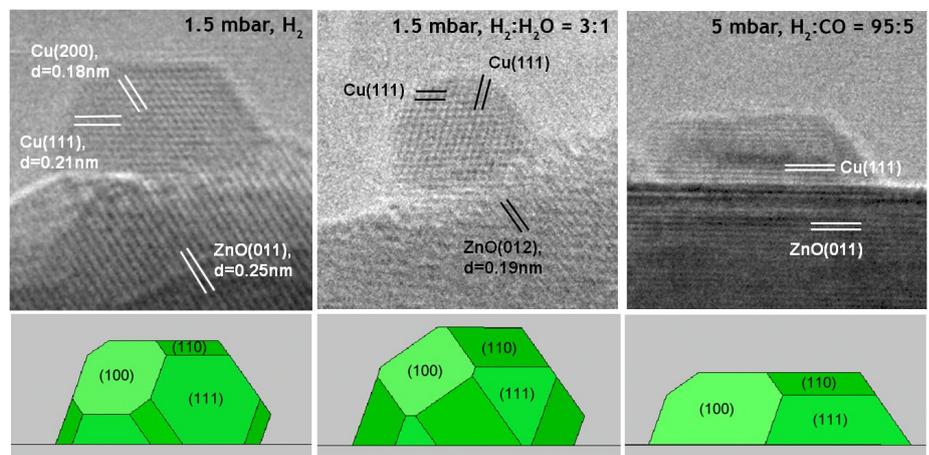

Figure 1
Cu nanoparticles on ZnO, used to synthesize methanol, change their structure in response to changes in the gas environment. (Details in [4]. Reprinted with permission from Science. Copyright 1997 AAAS.)
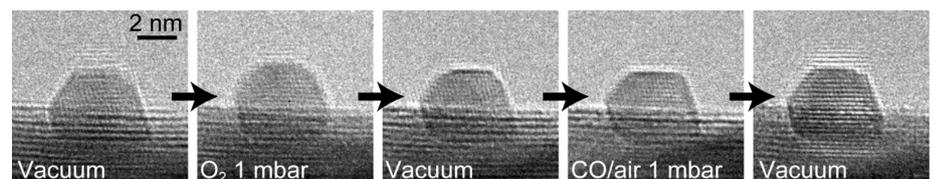

Figure 2
Gold nanoparticles on CeO$_2$, used to oxidize carbon monoxide, exhibit reversible structural changes, reverting to faceted 'vacuum' structure after changes induced by exposure to oxygen and a CO/air mixture. (Details in supplementary info in [8]. Reprinted with permission from Angew. Chem. Copyright 2011 John Wiley and Sons.)

Figure 3
Co/CoOx catalysts, used in the Fischer-Tropsch synthesis to convert syngas (a mixture of hydrogen and carbon monoxide) into liquid fuels, exhibit changes in morphology in response to elevated temperatures and exposure to hydrogen. Reduction of CoO_X to metallic cobalt results in an increase in effective particle size. (Details in [15]. Reprinted with permission from ACS Nano. Copyright 2012 American Chemical Society.)
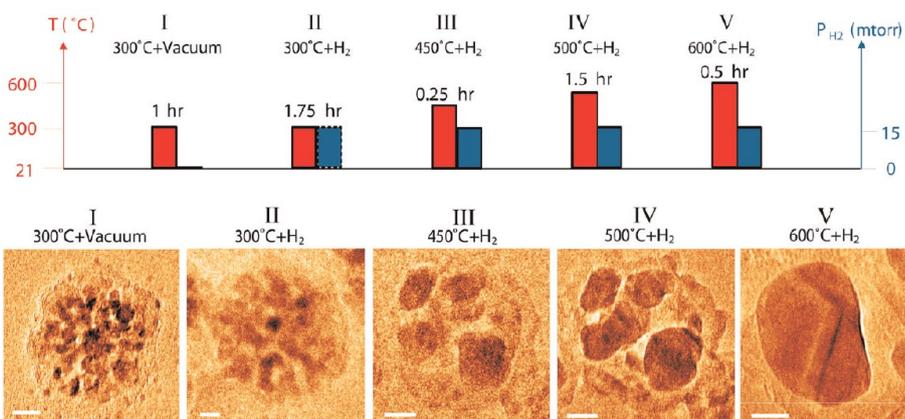
changes to become active. It is therefore essential to obtain structural information about catalysts under reactive conditions, such as at elevated temperatures and gas pressures, in order to understand and improve the activity, functionality, and stability of new catalysts (see examples in Figures 1-3).

AUTOMOTIVE CATALYTIC CONVERTERS FOR POLLUTION CONTROL
Ceria zirconia
Nanoscale ceria zirconia particles are a critical component in automotive catalytic converters, and have potential applications in other areas, such as fuel cells, where redox functionality is important. In situ studies by Wang et al. [6] have followed the dynamic redox process taking place in individual ceria zirconia nanoparticles. Observations have correlated catalytic activity with changes in the particle's oxidation state (Figure 4). The more active particle structure has predominantly disordered cations and shows no evidence of oxygen vacancy ordering during reduction.
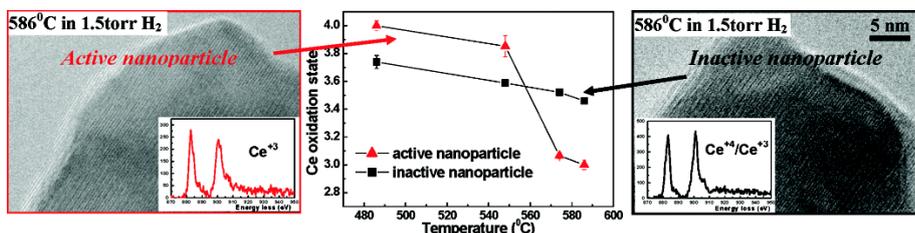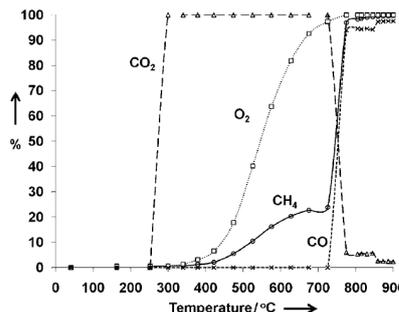
CATALYST ACTIVATION
Production of Syngas by partial oxidation of methane over Ni/SiO₂
Partial oxidation of methane (POM) is an important reaction for the production of syngas, a feedstock for the production of a variety of liquid hydrocarbons. POM may also be useful for other energy related processes, such as reforming fuel for high temperature fuel cell applications.

Supported nickel (Ni) catalysts are less expensive than noble metal and have shown high conversion rates. Chenna et al. [7] have reported that during ramp up Ni catalysts proceed through an activation sequence in which they first transform to NiO shells at temperatures above 300°C, then back to Ni as further increases in temperature make the gas environment more reducing. Syngas formation only takes place during the later stages of NiO reduction, when Ni metal nanoparticles have broken through the NiO shell. When initially observed, the void-like structures were somewhat surprising as they had not been seen previously in used catalysts (see Figure 5).
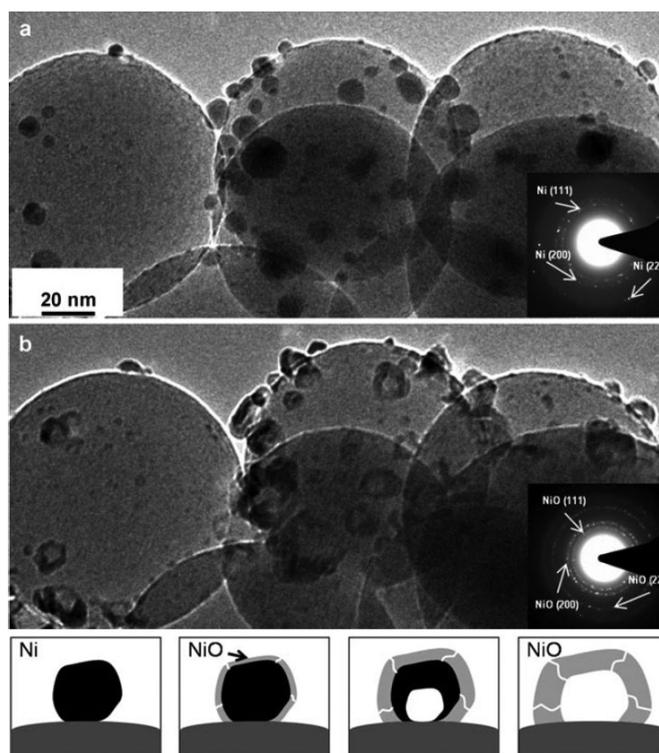
TEMPERATURE-DEPENDENT CATALYST ACTIVITY
CO oxidation over Pt/CeO₂
Low temperature carbon monoxide (CO) oxidation is needed in various applications, such as indoor air purification, safety devices (e.g. in laboratories using CO), submarine ventilation systems, and catalytic converters for cold-start
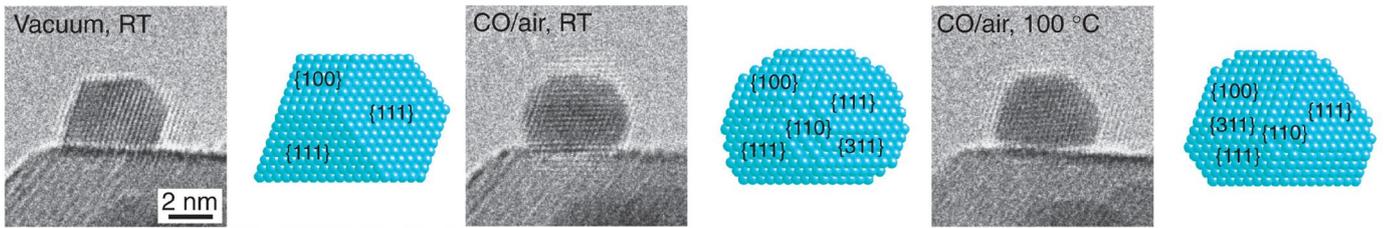

Figure 4 (above)
In-situ high resolution TEM (HRTEM) images (left and right) of nominally identical ceria zirconia nanoparticles recorded at 586°C in 1.5 Torr of H_2. The inserted electron energy loss spectra (EELS) indicate the electronic structure of the particle under observation. The derived graph in the center plots the oxidation state for the same two particles as a function of temperature to be able to identify the catalytically active nanoparticle. (Details in [6]. Reprinted with permission from NanoLetters. Copyright 2008 American Chemical Society.)

Figure 5
Above: Conversion and selectivity for partial oxidation of methane (POM) over a model 2.5 wt% Ni/SiO₂ catalyst. Left: The in-situ TEM images show the development of voided structures at 400°C as the gas environment is changed from 1 mbar H_2 (top) to 1 mbar 2:1 mixture of CH_4 and O_2 (middle). The lower image diagrams NiO void formation by the Kirkendall effect. (Details in [7]. Reprinted with permission from ChemCatChem. Copyright 2011 John Wiley and Sons.)

Vacuum, RT — CO/air, RT — CO/air, 100 °C

emissions control in automotive exhaust.

Another important application is the purification of hydrogen for use in fuel cells or as a feedstock for energy and chemical producing processes. The hydrogen rich gas mixture produced by steam reformation of hydrocarbon fuel typically contains ~1% CO. This relatively small amount of CO is still enough to poison active sites on a catalyst, such as the electrodes of a fuel cell. Selective catalytic oxidation is the most effective way to remove low levels of CO from hydrogen. An efficient CO oxidation catalyst must be highly selective, to avoid oxidizing the hydrogen, and resistant to CO_2 and H_2O deactivation. Noble metal catalysts on transition metal oxides have shown interesting performance in this application.

CO conversion over platinum (Pt) nanoparticles supported on ceria (CeO_2) increases rapidly at around 40°C (Figure 6). As the temperature increases from room temperature in CO/air, the round Pt particles become partially faceted. Yoshida et al. [5] compared the shape of Pt particles under various conditions. Thereby it is possible to understand the mechanism for the shape change and the temperature dependence of
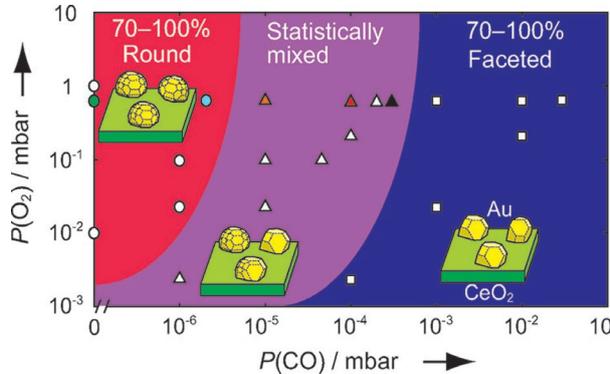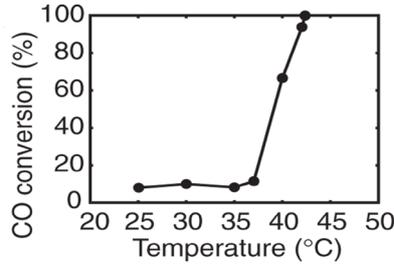

Figure 6
Left: CO oxidation over Pt/CeO_2 catalysts is a function of temperature.
Top: In-situ TEM images and corresponding Wulff constructions show changes in particle structure observed with changes in gas environment and temperature. Pt/CeO_2 particles exhibit low activity in vacuum at room temperature (top) and in CO/air at room temperature (middle). Conversion activity increases dramatically at elevated temperature (bottom). (Details in [5]. Reprinted with permission from Applied Physics Express. Copyright 2011 Japan Society of Applied Physics.)

Figure 7
The morphology of Au nanoparticles supported on CeO_2 changes as a function of the partial pressures of CO and O_2 in CO/air mixtures. (Details in [8] Reprinted with permission from Angew. Chem. Copyright 2011 John Wiley and Sons.)
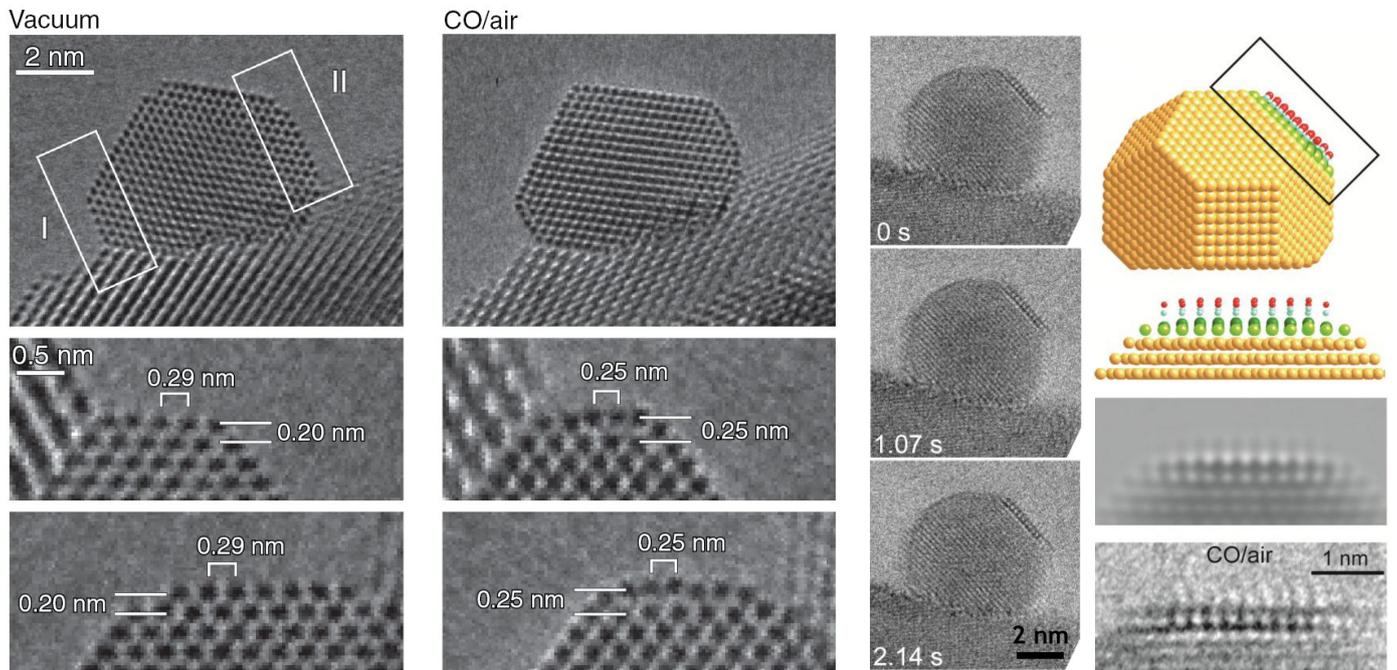

Figure 8
Left: Under catalytic conditions the gold nanoparticles exhibit Au{100}-hex reconstructed surface structures. In the reaction environment the distance between the topmost and second topmost {100} surface layers increases (from 0.20 nm to 0.25 nm) and distance between adjoining atomic columns in the topmost surface layer decreases (from 0.29 nm to 0.25 nm).
Right: A gold nanoparticle supported on CeO_2 observed in reaction conditions displays a persistent and unusual feature at the upper right edge of the particle(left 3 images). The two illustrations at upper right show a model of the particle with adsorbed CO molecules. Images at lower right show good agreement between a calculated image based on the model and the experimentally observed image, confirming the presence of the Au{100}-hex reconstructed surface with adsorbed CO molecules. (Details in [9]. Reprinted with permission from Science. Copyright 2012 AAAS.)

the CO conversion rate (Figure 6). The change in shape of the Pt particles may be induced by the adsorption of CO molecules and O atoms.

SURFACE STRUCTURE AND GAS COMPOSITION:
Room temperature CO oxidation over Au/CeO₂

Bulk gold (Au), a noble metal, is stubbornly unreactive, but Au nanoparticles are quite different (Figure 7). Au nanoparticles supported on crystalline metal oxides, such as CeO_2, are very active towards the conversion of CO to CO_2, even at or below room temperatures [8]. The conversion has two steps: the cleaving of the O-O bond and the transfer of an O atom to a CO molecule. Direct visualization of surface facets, surface reconstructions, atoms and adsorbed gas molecules is vital to understanding the catalytic mechanism (Figure 8) [9].

REDUCTION–OXIDATION CYCLE
Reliability studies of SOFC fuel cell

A fuel cell is an energy conversion device that converts chemical energy into electrical energy through an electrochemical reaction (Figure 9). The most commonly used fuel is hydrogen (H_2) gas, but hydrocarbons, such as natural gas and alcohols can also be used. Solid oxide fuel cells (SOFC) are a class of fuel cell characterized by the use of a solid oxide material as the electrolyte. Advantages of SOFCs include flexibility of the fuel used (e.g. CO, H_2, CH_4), delocalization of energy production, and reduction of pollutants such as mono-nitrogen oxides (NO_X) and sulfur oxides (SO_X). SOFCs also offer high efficiency, long term stability, low emissions and relatively low cost.

A standard SOFC design uses an anode of porous ceramic-metal composite yttria (Y_2O_3) stabilized zirconia (YSZ) and nickel (Ni). In-situ investigation, such as by Jeangros et al. [10], can help in understanding decreasing performance of fuel cells caused by structural changes in the anode during operation cycles (Figure 9).

DIESEL AUTOMOTIVE EXHAUST CLEAN–UP
Soot oxidation over CeO₂

Carbonaceous nanoclusters, such as soot particles in the exhaust of diesel engines, have a negative impact on our climate and constitute a health risk. Increased awareness of these effects has resulted in new environmental regulations that impose stricter limits on exhaust emissions. Soot particle emissions may be reduced either by optimizing the combustion inside the engine or by removing the carbonaceous particles from the gaseous exhaust stream. The particles may be removed with a filter but the filter will eventually fill up and need replacement or regeneration. One approach to onboard regeneration involves functionalizing the filter for catalytic oxidation of the deposited soot.

CeO_2-based materials are widely used for this purpose. In situ TEM observations of the oxidation of soot particles on CeO_2 by Simonsen et al. [11] show the particles growing shorter but not decreasing in diameter, which suggests that the oxidation occurs near the CeO_2 surface (Figure 10).
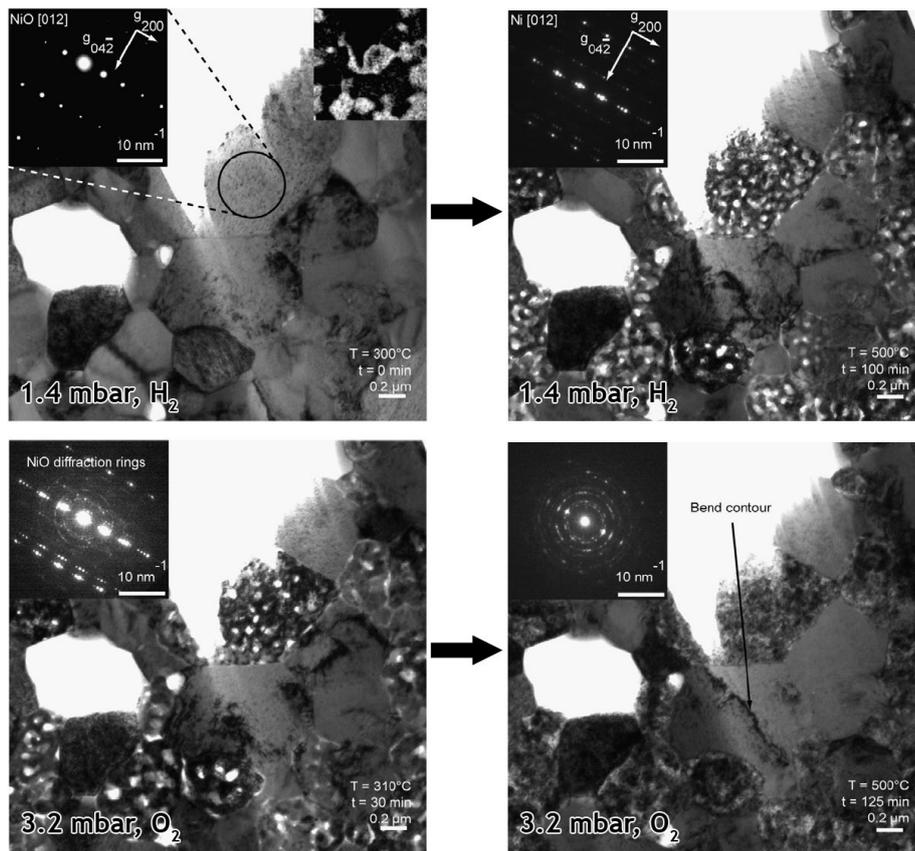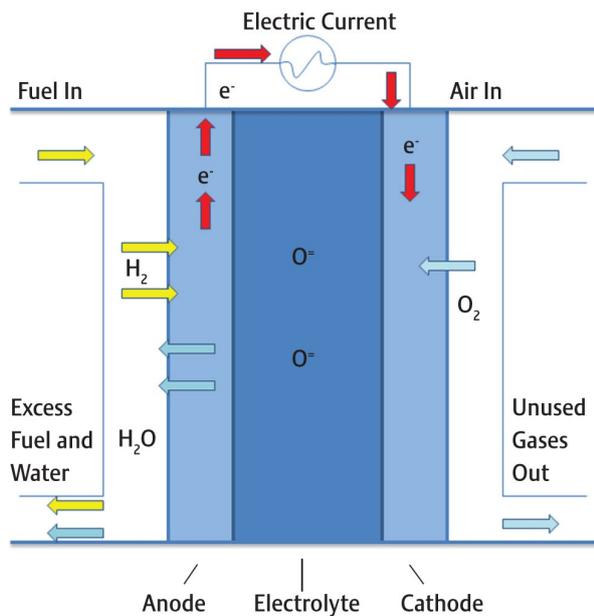

Figure 9
Left: Reduction oxidation cycle in a SOFC fuel cell. Right: The upper in situ TEM images show in situ reduction of NiO-YSZ anode precursor in 1.4 mbar of H_2. Nanoporosity is observed forming in the NiO grains as they accommodate the volume shrinkage that results from the reduction of NiO to Ni. Lower images show reoxidation in 3.2 mbar O_2. With increasing temperature, the nanoporosity that was created during in situ reduction is filled by polycrystalline NiO. This occupies a larger volume than that of the as-sintered grains. Stress is observed in the YSZ phase, accumulating over successive redox cycles. (Details in [10]. Reproduced with permission from Acta Materialia. Copyright 2010 Elsevier.)

Figure 10
Top: In situ TEM image sequence of soot particles attached to CeO_2 are oxidized by exposure to 2 mbar of O_2 at 475°C. The reduction in the length of the particles while the diameter remains constant suggests that the oxidation is occurring near the CeO_2 surface.
Below: Oxidation of soot particles on CeO_2. The left figure plots particle diameter (open points) and distance to CeO_2 (closed points) over time. The middle figure plots the mean change in distance (velocity) as a function of temperature for CeO_2 (boxes) and Al_3O_3 (Xs). The right figure is an Arrhenius plot of the mean velocity. (Details in [11]. Reproduced with permission from SAE Int. J. Mater. Manuf. Copyright 2009 SAE International.)
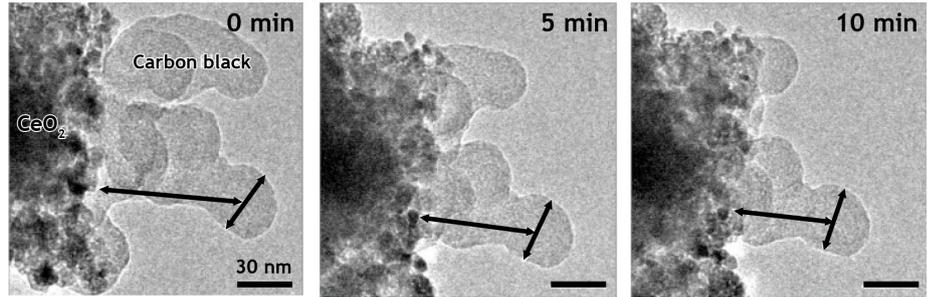
CATALYST DEACTIVATION BY CARBONACEOUS LAYER GROWTH

In a vast number of commercially relevant catalytic chemical processes, the deposition of coke (carbon) is a by-product of the underlying reactions. This can cause catalyst deactivation and reduce process efficiency. There is ongoing interest in stabilizing the activity of supported catalytic nanoparticles and understanding the processes by which carbon layers form and accumulate on their surfaces.

Supported Pt nanoparticles are widely used to catalyze reactions such as dehydrogenation. Dehydrogenation is widely used to transform alkanes (hydrocarbons with C-C single bonds) to alkenes (hydrocarbons with C=C double bonds), as in the conversion of ethane to ethene. Catalytic conversion has the advantages of high selectivity for valuable alkenes and the formation of hydrogen as by-product. Alkenes are essential building blocks in the petrochemical industry. The C=C double bond gives them the ability to polymerize. Alkenes are an important starting material for the synthesis of alcohols, aldehydes, epoxides and amines, which in turn are the basis for products such as adhesives, fertilizers, carpets, paints and much more. Peng et al. [12] studied the formation of graphene layers on MgO-supported Pt nanoparticles using both in situ and ex situ high-resolution transmission electron microscopy (HRTEM) (Figure 11).

Helveg et al. [13] investigated the growth of carbon nanofibers by catalytic decomposition of methane over a catalyst consisting of Ni nanoclusters supported on $MgAl_2O_4$. In the in situ TEM image sequence and drawings in Figure 12 illustrate the positions and effects of mono-atomic Ni steps at the C-Ni interface. In some cases the formation of carbon layers is the primary objective of the research, as in the synthesis of carbon nanotubes.

CATALYST DEACTIVATION BY SINTERING
Pt/SiO₂

Metal nanoparticles dispersed on a porous support material are used as efficient heterogeneous catalysts for diverse applications in energy conversion, chemical supply and environmental protection. The high surface area of the nanoparticles is associated with an excess surface energy, so the particles represent a metastable state. Simonsen et al [14] found that, given sufficient thermal activation, some nanoparticles will sinter into larger particles while others will disappear. This coarsening causes unwanted reduction in metal surface area, which may affect
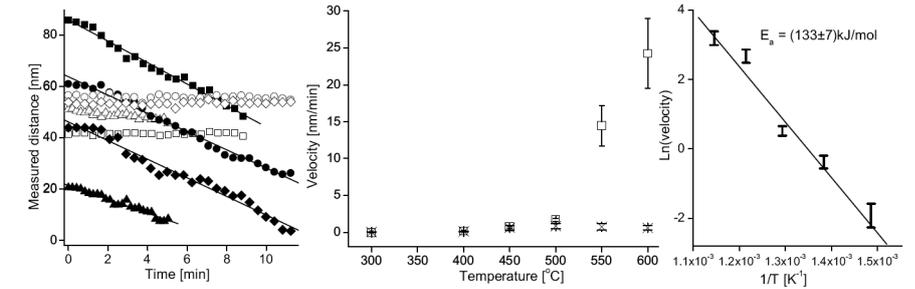

Figure 11
Catalyst deactivation process by carbonaceous layer growth on a catalyst nanoparticle (Pt on MgO) used to produce alkenes by the dehydrogenation of alkanes. (Details in [12]. Reproduced with permission from J. Catalysis. Copyright 2009 Elsevier.)
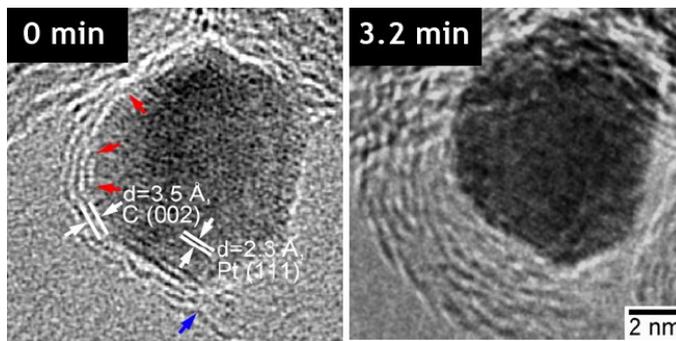

Figure 12
Left: In-situ TEM image sequence during synthesis of carbon nanofibers by the decomposition of methane over Ni nanoclusters supported on $MgAl_2O_4$. Right: The drawings illustrate the positions and effects of the mono-atomic steps at the C-Ni interface. (Details in [13]. Reproduced with permission from Nature. Copyright 2004 Nature Publishing Group.)
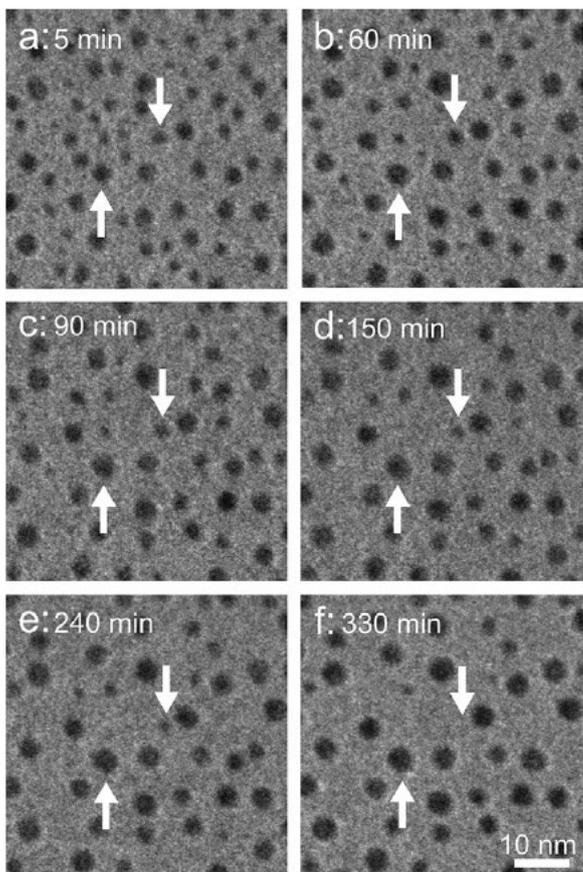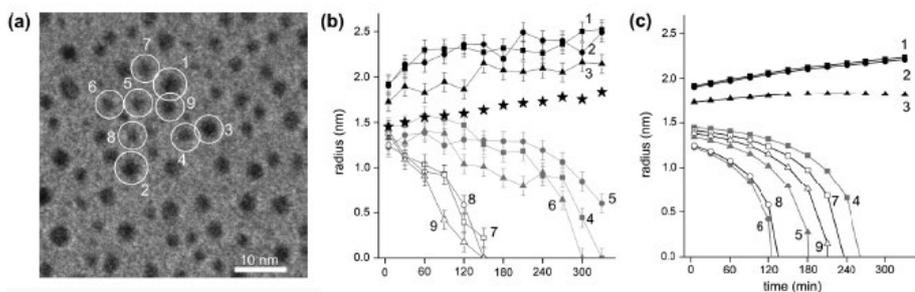
Figure 13
Left: Observations of Pt/SiO2 catalyst over several hours of exposure to 10 mbar air at 650°C reveal mechanical and kinetic information about Pt nanoparticle ripening. This information permits detailed comparisons of the temporal evolution of observed nanoparticle sizes with predictions made from different ripening models. The arrows indicate examples of a growing particle (up arrow) and a decaying particle (down arrow).

Below: (a) Nine particles were selected to follow changes in size.
(b) The graph in the middle plots particle radius over time for the nine selected particles and the average particle radius (stars) for the whole image.
(c) Calculated time-dependent particle radii for particles 1-9. The calculations used an interface-controlled ripening model based on a mean-field assumption. (Details in [14]. Reproduced with permission from J. Catalysis. Copyright 2011 Elsevier.)

BIOGRAPHY
Joerg R. Jinschek has a Dr. rer. nat degree in physics from the Friedrich Schiller University in Jena, Germany. In 2001 he was awarded a Feodor-Lynen-Fellowship of the Alexander-von-Humboldt Foundation. From from 2001 to 2005 he was a postdoc at the National Center for Electron Microscopy, Lawrence Berkeley National Lab, CA, USA., and next established a new TEM lab as a Research Assistant Professor at Virgina Tech in Blacksburg, VA. In 2008 he joined FEI in 2008 as a Senior Research Scientist and is now Product Marketing Manager and Application Scientist for Environmental TEM (Titan ETEM) in the Materials Science Business Unit at FEI.

ABSTRACT
Catalysts are indispensable to chemical industrial processes that lead to products used everyday. To improve process efficiency, researchers need to understand at the atomic scale the relationship between catalyst structure and its function. Recent developments in ETEM now allow researchers to directly visualize structure as well as the chemical composition with high spatial resolution in (near) operational gaseous environments. Recent publications demonstrate ETEM's increasing role in catalysis research in a growing number of applications..

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the catalyst's performance (stability). Sintering on supported metal catalysts involves complex physical and chemical phenomena that make understanding the mechanisms difficult (Figure 13).

CONCLUSIONS
FEI ETEM's ability to provide temporally and spatially resolved images of dynamic processes in situ at the atomic scale has been widely applied to investigate the mechanisms of heterogeneous catalysis. Recent developments in system design make the ETEM safer, more powerful and easier to use. ETEM observations of changes in particle morphology, composition, and atomic and electronic structure are likely to play an increasingly important role in understanding and optimizing the performance of existing processes and in the rational design of new catalysts.

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