Chapter 2
Development of the Atomic-Resolution Environmental Transmission Electron Microscope

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Abstract The development of the novel atomic-resolution environmental transmission electron microscope (atomic-resolution ETEM) for directly probing dynamic gas–solid reactions in situ at the atomic level under controlled reaction conditions consisting of gas environment and elevated temperatures is described. Applications of the ETEM include investigations of catalytic reactions such as biofuel synthesis from biomass, hydrogenation reactions of interest in synthetic fuel cell technologies, and hydrocarbon oxidation along with various other mainly supported metal catalysts. In other fields, the ETEM is used to study steels, graphene, nanowires, etc. In this chapter, the experimental setup of the microscope column and its peripherals *are* described.

2.1 Introduction

The transmission electron microscope has generated substantial results and various fields. From heterogeneous catalysis (Boyes and Gai 1997; Gai and Kourtakis 1995; Haggin 1995; Gai 1998, 1999, 2002a; Hansen et al. 2001, 2002; Jacoby 2002; Gai and Boyes 2003; Lopez-Cartes et al. 2003; Liu et al. 2004; Helveg et al. 2004; Helveg and Hansen 2006; Gai et al. 2007) to studies of carbonaceous materials and devices (Helveg et al. 2004; Hofmann et al. 2007). However, traditionally, these

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investigations have been carried out in high vacuum conditions. Typically not the working environment of the samples in question. In a quest to expose samples to more realistic surroundings, various modifications and adaptations are made to the microscope setup. These include holders for interacting with the sample in the form of adding heat, contacting, indenting, magnetizing, etc. Modifications could also be allowing for the samples to be exposed to a gaseous atmosphere. These latter modifications will be the topic of this chapter.

Mainly two routes have been pursued in order to maintain a locally high pressure around the sample inside the microscope. One approach involves encapsulating the sample between electron-transparent windows. The other approach involves confining the gas around the sample using small apertures and evacuating the gas using pumps in sequential steps. Whereas the former approach, known as the windowed method, can be realized using a specially designed sample holder, the latter approach, known as the differentially pumped column, requires modifications to the microscope column itself. In either case, the sample region is often referred to as the Environmental Cell or ECELL. The technique of exposing samples to gases is frequently referred to as ETEM.

In differentially pumped column approach (Boyes and Gai 1997), the ECELL capabilities have been combined in a single instrument allowing atomic resolution (HRTEM), STEM, and PEELS/GIF functionalities. The combination is required to aid simultaneous determination of the dynamic structure and composition of the reactor contents. The ETEM system is used as a nanolaboratory with multi-probe measurements. Design of novel reactions and nanosynthesis are possible. The windowed approach will be discussed in a different chapter. The structure and chemistry of dynamic catalysts are revealed by atomic imaging, electron diffraction, and chemical analysis while the sample is immersed in controlled gas atmospheres and at the operating temperature. For chemical microanalyses, a commercial energy filter system (or an EDX detector) can be fitted, to provide elemental analysis during in situ experiments with low gas pressures and fast and minimally invasive high-resolution chemical mapping with filtered TEM images, in addition to an EDX detector. The analysis of the oxidation state in intermediate phases of a catalytic reaction is possible. In studies including the determination of the size and subsurface location of particles, the dynamic STEM system (integrated with ETEM) provides complementary methods for chemical and crystallographic analyses.

Many technological processes occur at the gas–solid or liquid–solid interface at the atomic scale. For example, in heterogeneous catalysis, chemical reactions catalyzed by solid surfaces take place at the atomic level and play a major role in the production of industrial chemicals, energy sources, and environmental emission controls. The dynamic atomic structure of catalysts under reaction conditions plays a crucial role on their performance in these reactions. It is often not possible to infer the dynamic state of the material from postmortem examinations of the static material, and these data often cannot be obtained directly by other means. Atomic-resolution environmental transmission electron microscopy (atomic-resolution ETEM) for direct in situ observation of the dynamic nanostructural evolution at

the solid surface under controlled reaction conditions of gas/vapor/liquid and temperature environments is therefore a powerful scientific tool in the materials and chemical sciences for the nanostructure-dependent information.

Of particular interest are the properties of solid-state heterogeneous catalysts of interest for gas reactions in technological processes; to better understand the fundamental reaction mechanisms and the atomic scale structure–property relationships is important in the development of new materials and processes. Atomic-resolution ETEM under controlled operating environments is of vital importance to probe catalyst structure–property relationships under working conditions in catalysis. Probing catalysts directly under reaction environments is key to gaining insights into catalytic reaction mechanisms, active reaction sites, defect structural evolution, and the nature of bonding in redox reactions. The unique contribution of atomic-resolution ETEM under operating conditions is the ability to characterize the dynamic catalyst local structures, which may be aperiodic (such as dislocations), and determine their nature, composition, and adjacency of particles of different types.

Since chemical reactions take place at the atomic level, this chapter focuses on the novel development of *atomic-resolution* environmental transmission EM (atomic-resolution ETEM) with a new design of an integrated environmental cell (gas reaction cell) reactor. For earlier in situ studies carried out with an old and different environmental cell (ECELL) technology using (ex situ) reactor aperture assembly (jig), inserted between polepieces of the objective lens (Butler and Hale 1981; Gai et al. 1990) in the microscope column (or window cells) to carry out reactions at modest resolutions, readers are referred to other chapters in this book. Such jigs were made interchangeable, necessitating the frequent opening of the microscope to air to insert the jig and rebuilding of the microscope to effect the changeover in functionality. Window cells that have been used to contain gases, solvent vapors, and hydrated samples may present difficulties in reliably sustaining a large pressure difference across a window that is thin enough to permit electron penetration; and in heating and tilting samples.

Several approaches have been taken in order to maintain a controlled atmosphere over a sample in a transmission electron microscope while imaging. The main aim is to limit the high-pressure region to as small as possible a region around the sample in the z direction so that the electrons only have to traverse a thin slab of gas at relatively high pressure. This ensures that the sample is exposed to as high a pressure as possible while maintaining the performance of the microscope with only limited effect of the gas. For gas–solid reactions, the complications and potential for failure of windows can be avoided by substituting small apertures above and below the sample to restrict the diffusion of gas molecules, but to allow the penetration of the electron beam. Typically, pairs of apertures are added above and below the sample with differential pumping lines attached between them.

In most cases, the gas atmosphere is provided by a gas injection system in conjunction with a differential pumping system for evacuating the injected gas from the sample region. The differential pumping system is typically separate from

the conventional pumping system often consisting of ion getter pumps. Such system can sustain pressures approaching 2000 Pa.

In order to inject gases in a controlled way into the sample region of the microscope, certain modifications have to be made. A port for letting in the gas has to be made, and a differential pumping system has to be constructed. These are described below.

Atomic-resolution ETEM under controlled reaction conditions provides dynamic information on processes which take place at the atomic level, performance-critical defect structures, and subsurface diffusion of catalytic species. However, the development of ETEM for directly visualizing reactions under extreme conditions of gas pressures and temperatures at the atomic level is highly challenging.

2.2 Design and Development of the Differentially Pumped ETEM

The quest to probe gas molecule–solid catalyst reactions directly at the atomic level resulted in the pioneering development of in situ atomic-resolution ETEM at DuPont, USA, by Gai and Boyes (Boyes and Gai 1997; Gai and Kourtakis 1995). This development demonstrated for the first time that catalyst studies of gas–solid reactions at the atomic resolution was possible under controlled dynamic reaction conditions of gas pressure of a few millibars and at elevated temperatures. The development was featured by the American Chemical Society's Chemical and Engineering News (Haggin 1995). In this development, a new approach was taken to design an integrated atomic-resolution ETEM instrument that is dedicated to environmental cell (ECELL, or gas reaction cell) operations, and the ECELL is permanently mounted and integrated with HRTEM. Firstly, it was based on a modern computer-controlled Philips CM30T TEM/STEM system with proven high-resolution crystal lattice imaging performance. Secondly, the whole microscope column, and not just the region around the sample, has been redesigned for the ECELL functionality using the microscope sample chamber itself as the ECELL reactor. Thirdly, a custom set of polepieces incorporating radial holes for the first stage of differential pumping, with no deleterious effect on imaging, was designed for the instrument (Fig. 2.1).

The basic configuration of the ETEM is a short ($<$10 mm) path length of controlled environment with gas/vapor introduced, or in some cases with liquid injected onto the sample, and containing the microscope specimen in an otherwise high vacuum TEM column. The limited sample area is the only part of the system shared by both the chemical reactor stream and the microscope.

The basic geometry of the atomic-resolution ETEM system design (Boyes and Gai 1997) is a four-aperture system, in pairs above and below the sample (Fig. 2.1), but with the apertures now mounted in the bores of the objective lens polepieces

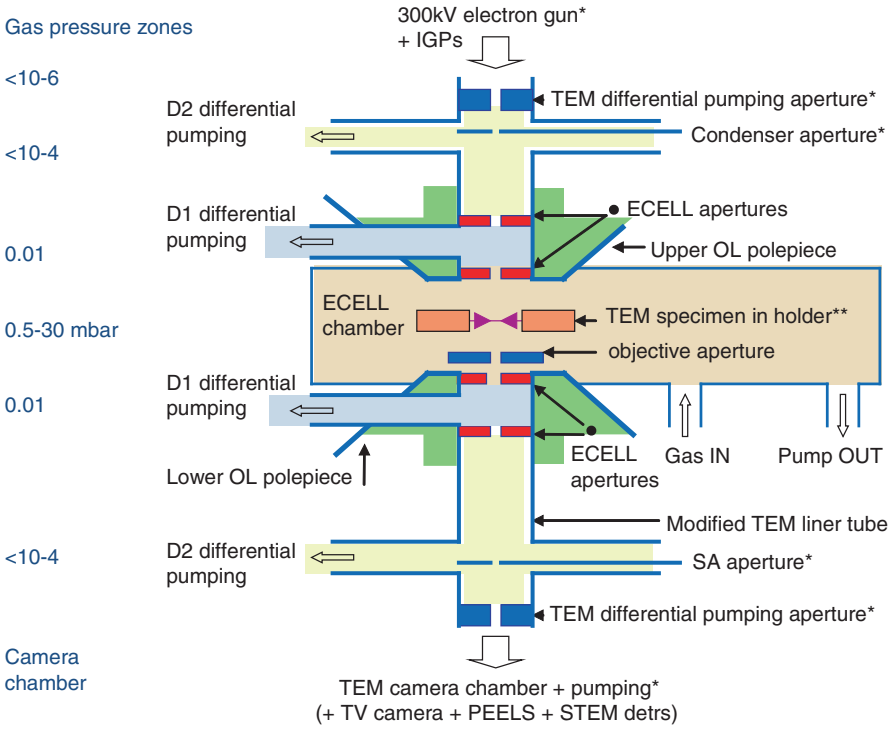

Fig. 2.1 Schematic (not to scale) of key elements of the pioneering development of the atomic-resolution ETEM design to probe gas–solid reactions at the atomic level (Boyes and Gai 1997; Gai and Kourtakis 1995). The basic geometry of the aperture system consists of radial holes through objective polepieces (OL) for gas lines at *D*. The OL polepieces are above and below the specimen holder, and the lower OL polepiece are indicated. Gas inlet, the first stage of differential pumping lines (*D1*) between the environmental cell (ECELL) apertures, condenser aperture, a second stage of pumping (*D2*) at the condenser lens, selected area (SA) diffraction aperture, parallel electron energy loss spectroscopy (PEELS), and TEM camera vacuum are indicated. The ECELL chamber is the gas reaction cell. The atomic-resolution ETEM design (Boyes and Gai 1997) is used for commercial production and now used by researchers worldwide

with regular microscope apertures in bushes in the polepieces. The controlled environment ECELL volume is the regular sample chamber of the microscope. Differential pumping systems connected between the apertures consist of molecular drag pumps (MDP) and turbomolecular pumps (TMP). This permits high gas pressures in the ECELL sample region. With regard to potential X-ray emissions, a combination of innovative internal Al-shielded Ta X-ray beam stops and extensive additional external lead shielding was used, with stringent auditing of both design and implementation. The manufacturing tolerances on the centering of selected regular microscope apertures and on machining tolerances for mounting them in a fixed alignment are fully adequate for the purpose. In this design (Boyes and Gai 1997), the regular adjustable objective aperture is retained inside the ETEM's ECELL section (Fig. 2.1) for its usual useful TEM functions.

Subsequent ETEMs have field emission guns (FEG) (Hansen et al. 2001, 2009, 2013; Yoshida et al. 2011, 2012, 2014a) and require additional stages of differential pumping added to the configuration described here. Fortunately, the vacuum conditions in the modern ETEM are significantly better than those in a regular TEM, greatly reducing the contamination issues critical for chemistry—and with which the ETEM apertures and gas flow can help even in older systems.

A conventional reactor-type gas manifold system enables the inlet of flowing gases into the ECELL of the ETEM apparatus, and a sample hot stage allows samples to be heated. A mass spectrometer is fitted to the ETEM for gas analysis. The atomic-resolution ETEM provides facilities for dynamic in situ experiments in an atomic resolution (<0.2 nm) TEM under controlled conditions of gas/vapor environment at regular operating pressures up to ~5000 Pa, and at selected and accurately known temperatures from 150 to 1100 °C, and in a few cases up to 2000 °C (Boyes and Gai 1997). Reviews of the important scientific impact of ETEM in solid-state chemistry and related fields, including catalysis research, are provided by references (Gai 1999, 2002a; Hansen et al. 2013; Hansen and Wagner 2014). For dynamic atomic resolution, a few millibars of gas pressure are used in the ECELL. Higher gas pressures are possible, but this compromises the resolution (due to multiple scattering effects of the electron beam through thicker gas layers). A video system connected to the ETEM apparatus or CCD camera facilitates digital image processing and real-time recording of dynamic events.

The atomic-resolution ETEM development of Gai and Boyes has been adopted for commercial production by EM manufacturers (Gai et al. 2007) and is being used by researchers worldwide (Hansen et al. 2001; Hofmann et al. 2007; Chenna et al. 2011; Booth et al. 2011).

In the ETEM the sample—but nothing much else—is shared between the chemical reactor on the horizontal axis and the vertical microscope column (Fig. 2.1). It is essential to ensure the effect of the electron beam is minimally invasive; or eliminated, in part by using low electron beam doses and sensitive recording methods, and by rigorous audit of results with and without the sample exposed to the electron beam continuously, under careful experimental conditions. In any scientific study, a hot stage at controlled and accurately known temperatures should be used; rather than uncontrolled beam heating of indeterminate intensity, wide variations in local effect and mostly completely alien to the real world. Of course, a rigorous approach is experimentally demanding; especially to obtain the most informative continuous dynamic data from a small selected area or feature at high resolution and magnification, as the environment, temperature, or other controlled conditions are varied systematically. After the basic data are recorded, they must always be confirmed in a rigorous comparison end-point experiment with the beam turned off during the reaction sequence, and used only for analysis at the end of the experiment. Data found to be influenced in any way by the electron beam are usually artifacts and should be discarded. This is obviously very dependent on materials and conditions, but it seems to be a much bigger problem using electron beam energies above 200 kV. Atomic-resolution ETEM can add valuable spatially resolved microstructure and defect data to wider studies, but must always be related to them.

Electronic image shift and drift compensation help to stabilize high-resolution images for data recording on film or with real-time digitally processed video. Minimally invasive electron beam techniques and calibration studies (described in the preceding paragraphs) are used throughout.

We want to point out that any modifications to an electron microscope, and especially a higher voltage TEM column, must be undertaken with a well-informed plan and rigorous procedures to ensure the outcome is as safe as the base instrument.

The emphasis in ETEM is on dynamic in situ studies of reaction and other change mechanisms under controlled, near real world, conditions of environment and temperature; with minimally invasive microscopy for analysis. Any compromises in TEM performance with the ETEM functionality added are now very limited.

2.3 Gas Injection and Cleaning

Being able to evacuate gases from the column microscope column is only half the challenge of environmental transmission electron microscopy. The other part is controlled injection of gases around the sample. In order to maintain the stability needed to acquire images with atomic resolution, the flow around the sample need to be stable. Furthermore, for many experiments a mixture of gases is desired. Whereas gas mixtures can easily be purchased, it is undesirable to compromise the vacuum by opening it in order to mount new gas supplies.

A versatile system can be constructed by using mass flow controllers and a battery of different gases permanently mounted to the ETEM system. By using digitally controlled mass flow controllers, high stability can be achieved and the flows of the individual gases can easily be controlled and changes can be made on the fly. However, as the gas flows involved in ETEM experimentation are typically low, on the order of 10 mL/min, the residence time of the gases in the system can be quite long, and the time it takes for gases to reach the sample can be longer than expected. The time it takes for a certain gas to reach the sample can be monitored using residual gas analysis by mass spectrometry around the sample.

When working at low flows and pressures, cross-contamination can be a serious issue. Hence, experiments are often grouped in reduction and oxidizing experiments and experiments involving gases that can be challenging to desorb from the interior of the microscope column and separated in time. While extensive pumping can minimize the risk of cross-contamination considerably, a more thorough cleaning is sometimes necessary. This can be done by mounting a plasma cleaner on the ECELL itself (Hansen et al. 2010). Regular use of a plasma cleaner can lower the base pressure within the microscope column and limit undesired contamination of samples. Further measures that can be taken in order to limit the risk of sample contamination include plasma cleaning of the sample prior to inspection in the microscope and keeping holders under vacuum when not used along with frequent baking of the inlet and pumping lines.

2.4 Aberration Correction

Correction of aberrations is very important in ETEM (Gai and Boyes 2009), in helping to simplify image interpretation, particularly between 0.1 and 0.25 nm, improving imaging of small particle structures against a support background, allowing the use of wider gap polepieces with space for more stage manipulations and other in situ facilities such as straining. Therefore, aberration correction (AC) for atomic-resolution E(S)TEM under controlled environments was proposed (Gai et al. 2005). Aberration correction plays a key role in in situ ETEM studies as a single image close to zero defocus with full range of spatial frequencies without the contrast transfer function oscillations is possible as shown in Fig. 2.2 for a JEOL 2200FS double AC (S)TEM (Gai and Boyes 2009). Figure 2.3 shows an example of a multiply twinned particle (MTP) of gold in an AC atomic-resolution ETEM with gas modifications with the corresponding FFT (Walsh et al. 2012). The image illustrates displaced MTP axis (indicated by the yellow circle) and asymmetric strain fields, important in the surface structure and reactivity of gold nanoparticles (Walsh et al. 2012).

Because of the small amounts of solid reactant in the microscope sample, measurement of reaction products is generally performed on larger samples in a microreactor operating under similar conditions and used for the correlation between the catalyst structure and performance. The correlation is crucial for a better understanding of gas–solid reactions to aid the development of improved materials and processes. However, some attempts at monitoring reactions have been taken. These are described in a later chapter. Under carefully controlled conditions, data from in situ ETEM can be directly related to structure–activity relationships in technological processes (Gai and Boyes 2003; Miller and Crozier 2014; Chenna and Crozier 2012; Crozier and Chenna 2011; Hansen and Wagner 2012).

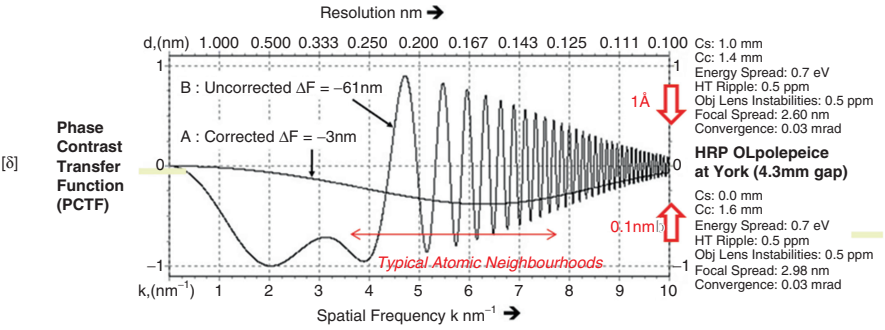

Fig. 2.2 Calculated contrast transfer functions (CTFs) for an aberration corrected (**a**) imaging conditions of the HRP version of the double aberration corrected JEOL 2200FS FEG TEM/ STEM at the University of York (UK) (Gai and Boyes 2009) (CTF for the uncorrected conditions is shown in (**b**) for comparison

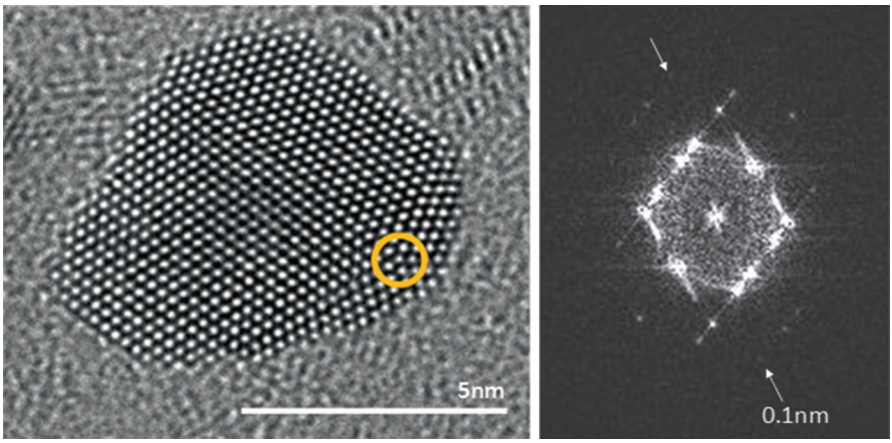

Fig. 2.3 Multiple twinned particle decahedral particle with fivefold axis shifted close to the surface (Walsh et al. 2012)

2.5 Instrument Performance

Naturally, the presence of gas around the sample will interfere with the imaging capabilities of the microscope. As the beam electrons impinge on the gas molecules above and below the sample, they can be scattered. Apertures and other parts of the microscope intercept most of these scattered electrons. Hence, the main result of this interaction is a loss of total intensity. With light molecules such as hydrogen and helium, this is usually not a big issue. But with heavier molecules such as oxygen, nitrogen, and carbon monoxide which are often used in experiments with catalysts, a substantial amount of the beam electrons can be lost when working in the higher end of the pressure range (above 500 Pa). Figure 2.4 shows the measured intensity on the fluorescent screen as a function of pressure for various gases often used in ETEM experiments. Whereas only a few percent of the total intensity is lost for hydrogen and helium at 300 kV, more than 80 % is lost for oxygen and nitrogen at 80 kV.

The presence of gas also has an effect on the resolution of the microscope. The resolution depends on several parameters: the gas pressure, the gas specie, and the beam current. Figure 2.5 shows the power spectra of an amorphous carbon films at increasing argon pressure. The loss of intensity variation is observed by the dampening of the intensity (Hansen and Wagner 2012). Figure 2.6 shows the resolution as a function of beam current in 400 Pa nitrogen. The resolution is measured by a Young's fringe experiment. As the beam current is increased, a significant loss of resolution is observed (Bright et al. 2013). The electron–gas molecule interaction is further described in a later chapter.

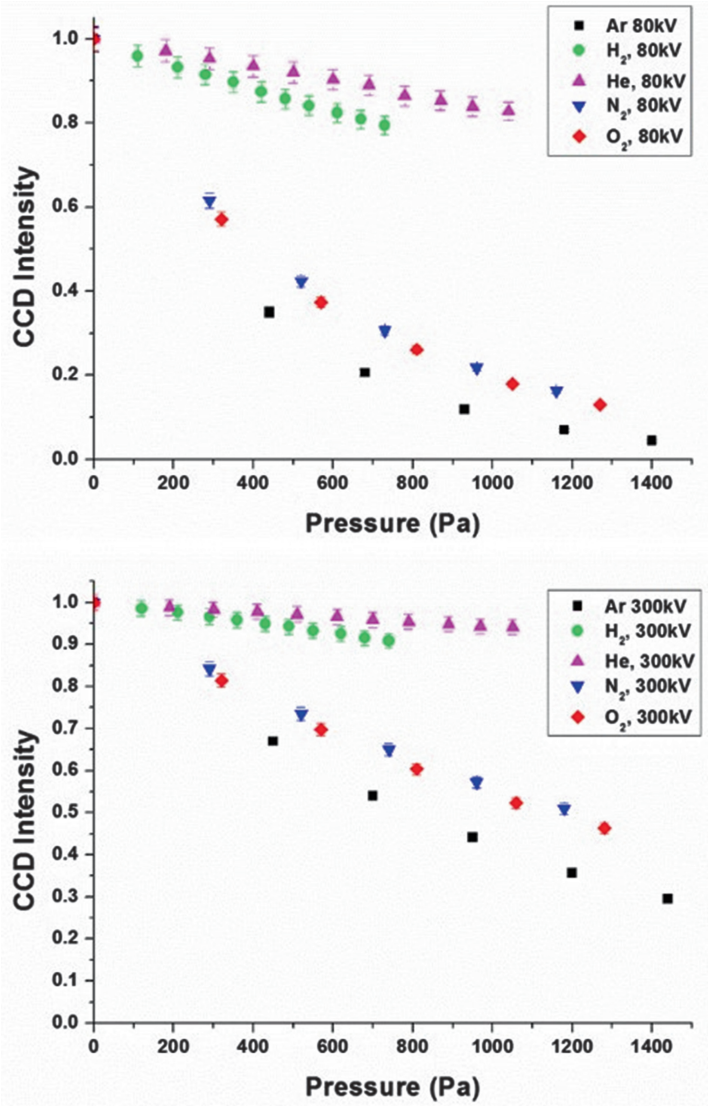

Fig. 2.4 Intensity recorded on the CCD camera as a function of gas pressure for 80 kV (*top*) and 300 kV (*bottom*) (Hansen and Wagner 2012)

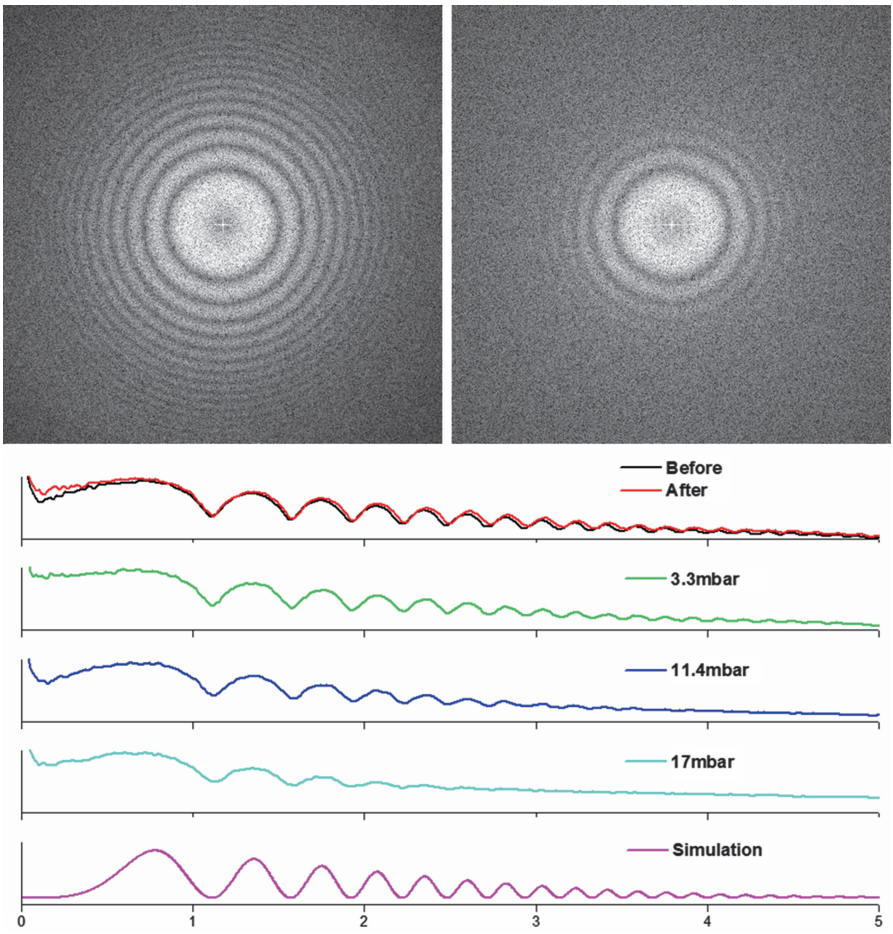

Fig. 2.5 Fourier transforms of images acquired from an amorphous carbon film in vacuum (*top left*) and at 1700 Pa argon gas (*top right*). From the FFTs, the radial intensity has been extracted (*bottom*). Values at intermediate pressures and a simulation made using CTFExplorer are also included in the plot (Hansen and Wagner 2012)

2.6 Atomic-Resolution Wet-ETEM: Reactions in the Liquid Phase

Many commercial hydrogenation and subsequent polymerization processes take place in liquid-gas environments or in liquids at operating temperatures and take place on the atomic or molecular scale. Probing reactions in solutions at the atomic level in the atomic-resolution ETEM, hereafter referred to as wet-ETEM, is therefore of great importance in the development of advanced catalytic technologies. In the past, to examine samples in hydrated environments for imaging at modest

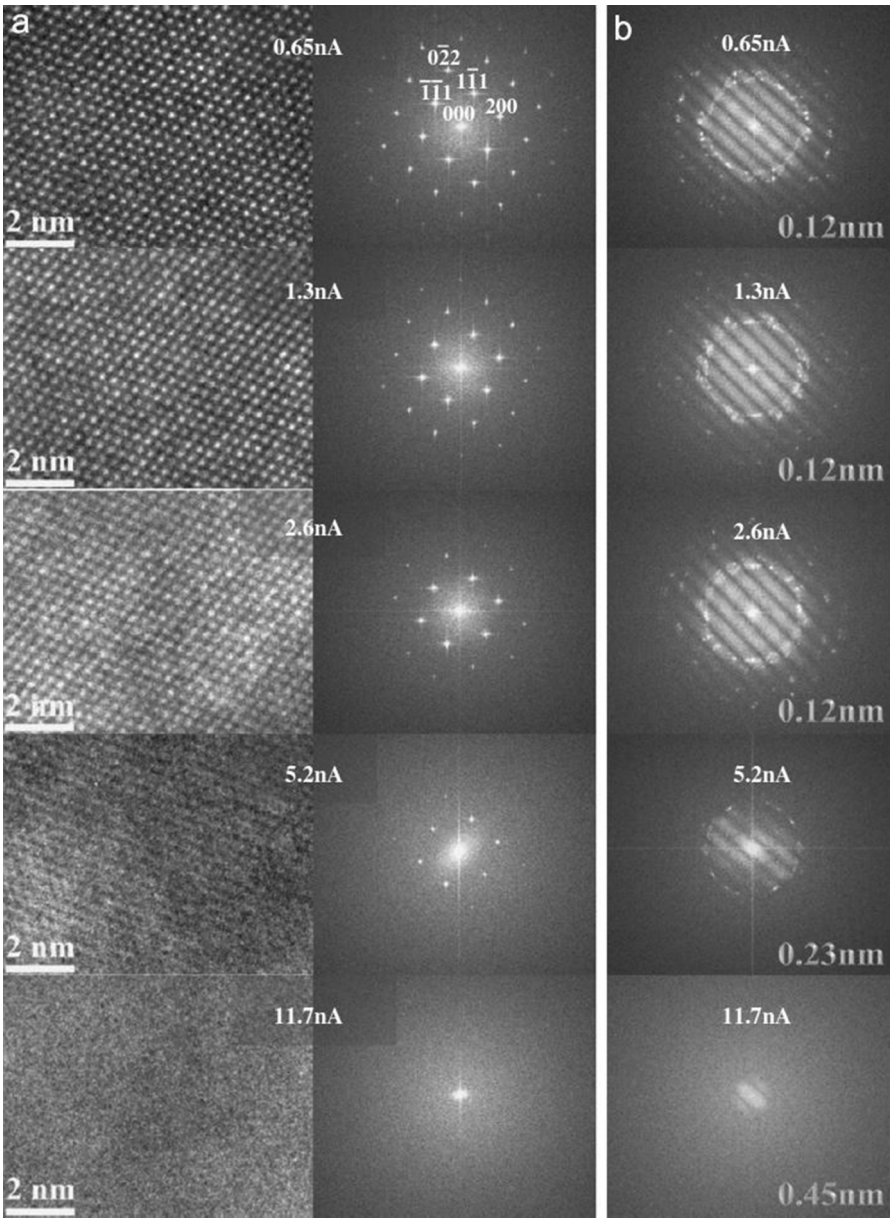

Fig. 2.6 HRTEM images taken with 4 mbar of nitrogen gas as a function of the total beam current (measured without gas). (**a**) Si <114> crystal lattice images with corresponding diffractograms, (**b**) Diffractograms of AuPd/carbon cross-grating HRTEM images used for measurement of information limit (displayed *bottom right*) (Bright et al. 2013)

resolution wet cells have been used, including windows to contain liquids, but without heating capabilities (Butler and Hale 1981). A wet holder for the atomic-resolution wet-ETEM has therefore been developed for atomic scale studies of polymerization reactions in liquids and liquid-gas environments over solid catalysts at operating temperature (Gai 2002b). Water vapor is also a major component in selective oxidation of hydrocarbons and in advanced fuel cell reactions. To visualize the influence of moisture on the performance of catalysts in real time at the atomic scale, an AC wet-ETEM system under moisturizing environments has been developed and water vapor is transported to the sample via a carrier gas (Yoshida et al. 2014a). This development involves the introduction of a thermostatic chamber and mass spectrometer enabling a stable moisturized N_2 environment in the ECELL and allows the direct detection of H_2O. The wet-ETEM system for the differential pumping ECELL with quadrupole mass spectrometer is shown in Fig. 2.7. This system plays a key role in investigating directly in situ reactions under water environments of importance in fuel cells and hydrocarbon catalysis (Yoshida et al. 2014a). An example in Fig. 2.8 shows the atomic scale modifications in copper supported ceria in carbon monoxide and water environments (Yoshida et al. 2014b).

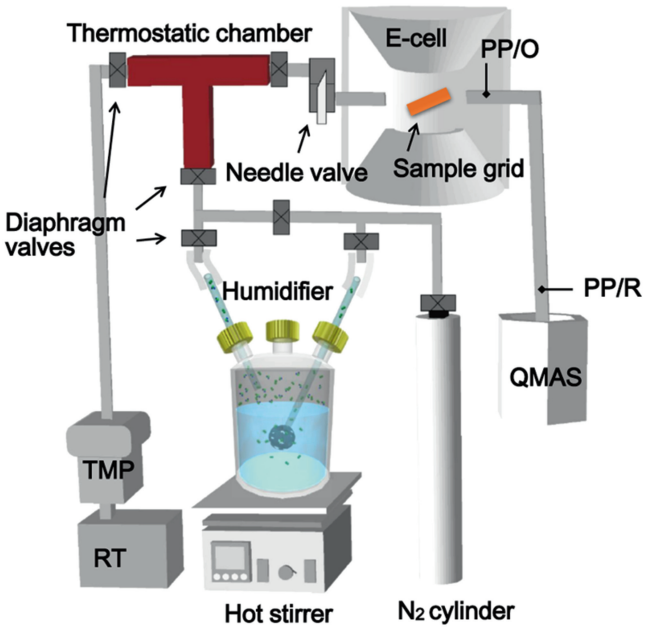

Fig. 2.7 Wet-ETEM system for the ECELL with humidifier and quadrupole mass spectrometer (QMAS) (Yoshida et al. 2014a). Wet-ETEM system for the ECELL with humidifier and quadrupole mass spectrometer (QMAS) (Yoshida et al. 2014a). *The figure reference is from the authors' (Yoshida, Boyes and Gai et al.) work in Nanotechnology 25, 425702 (2014) which is reproduced with permission by the Institute of Physics Publishers (IOPP)*

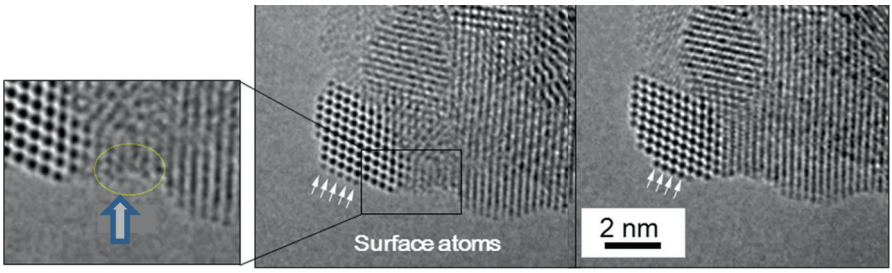

Fig. 2.8 Example of CO + water reaction on transition metals (Cu) supported on ceria. Surface atom movement on ceria (indicated by *small arrows*) is observed under hydrated conditions. The presence of Cu is shown by the *yellow circle* which also undergoes movement (Yoshida et al. 2014b)

In addition to calibration experiments, several conditions are required for successful studies using the ETEM. Electron-transparent samples and ultrahigh-purity heater materials and sample grids are required (such as stainless steel, Ti or Mo). For high-temperature studies in gas environments, samples are normally supported on finely meshed-grids of Ti or Mo with experiments carried out on crystals protruding from the edge of grid bars. Carbon support films are not suitable at high temperatures.

2.7 Sample Heating

For many experiments, samples need to be heated in situ in the microscope. This poses a challenge as the geometry is already considerably confined within the sample region of the transmission electron microscope. Typically, samples are heated using a heating holder. These come in mainly two types. The most widely used is the furnace type holder. Here, the sample is placed in a cup containing an embedded heating filament, and the temperature can be measured using a thermocouple attached to the exterior of the cup. This design can accommodate samples of various geometries such as powders, focused ion beam (FIB) prepared samples, and wires. Different materials can be used for the sample cup providing compatibility with different gas environments and obtainable temperatures. For ETEM experiments, stainless steel (Inconel) is often used as this material is compatible with most gases and will resist corrosion at the high temperatures typically associated with catalysis. Whereas the versatility provided by this system offers a lot of advantages; there are also drawbacks. Thermal expansion of the cup during heating results in significant sample drift and makes imaging during temperature ramping challenging. Furthermore, residual magnetic fields caused by the heating filament may result in a loss of resolution.

The other approach for sample heating is using an MEMS (Micro-Electro-Mechanical Systems) fabricated heater chip. Two different approaches are used for MEMS heaters. Heating is either done by using an embedded heater filament (Creemer et al. 2008) or by passing a current through a thin film acting as a tiny hot plate (Allard et al. 2009). In both approaches, holes can be fabricated in the heater structure allowing for unhampered imaging. In both MEMS type heaters, only a very small amount of material is heated and hence the issue of thermal expansion is minimized. The drawback of this approach is the limited space for sample deposition and the lack of a direct temperature measurement.

2.8 Examples of the Atomic-Resolution ETEM

2.8.1 In Situ Catalyst Activation for Biofuel Synthesis

Atomic-resolution ETEM has been used to study the formation of biofuels from vegetable plant biomass. The biofuel reaction involves the esterification of triglycerides into fatty esters and glycerol. The activation of nanoscale magnesium hydroxide methoxide slurry precursors (containing a mixture of amorphous and crystalline regions) carried out in situ in the AC atomic-resolution ETEM revealed increased crystallinity and defects during the activation process. The defects form along <111> directions in (110) projection of nano-magnesium oxide (which adopts a cubic structure, with $a = 0.4212$ nm). Figure 2.9 illustrates the in situ reaction sequence at room temperature (RT), 500 °C and 700 °C, respectively. Defect analyses showed that they were formed by simple atomic movement (called Gai glide shear mechanism) (Gai et al. 2009). The study found excellent correlation between surface glide defects and the catalytic activity, with the glide defects creating active sites for the biofuel synthesis (Gai et al. 2009; Gai and Boyes 2012). During the activation, the glide

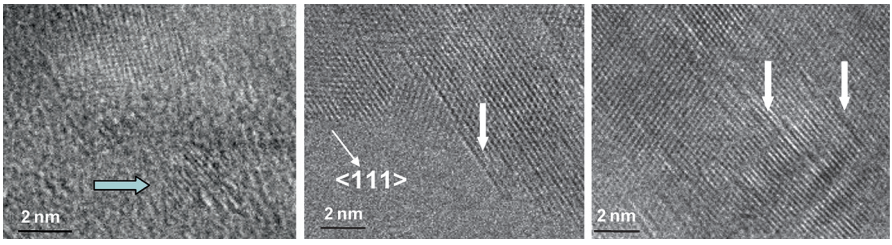

Fig. 2.9 In situ, real-time, dynamic studies of the activation of magnesium hydroxide methoxide precursors for biofuel synthesis at: (**a**) room temperature (RT); nanocrystals of only about 3–5 nms (*arrowed*) and amorphous areas are indicated. Crystallinity increases as the temperature is increased leading to nano-MgO. (**b**) Surface profile imaging of defects at 500 °C (indicated, e.g., by an *arrow*): The defects are along <111> direction and are at or near the surface. The defect analyses show that they are formed by simple atomic movement called glide shear; (**c**) profile image at 700 °C shows many defects (Gai et al. 2009)

defects are formed to accommodate the shape misfit between the reduced anion-deficient catalyst surface and the subsurface without collapsing the catalyst structure which is critical to the sustained operation of the catalyst. Other applications of atomic-resolution ETEM include carbon nanotube and filament growth and solid-state reaction mechanisms (Hofmann et al. 2007; Chenna et al. 2011).

Dynamic in situ experiments can be very efficient, and productive of data, in scanning a range of experimental conditions in a single session, and in mechanistic studies. Moreover, as is generally in the case of catalysis the active phase is metastable with respect to temperature and environment, the key data can only be obtained from dynamic in situ studies. The limits on the systems are a maximum gas pressure in the mbar range dictated by electron scattering and finally leakage into the gun. These in situ conditions are generally adequate to ensure the reacting surface is flooded with the desired species.

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