

Review

In Situ TEM Studies of Catalysts Using Windowed Gas Cells

Fan Ye ^{1,2}, Mingjie Xu ^{2,3,4}, Sheng Dai ^{5,*} , Peter Tieu ⁶, Xiaobing Ren ^{1,7} and Xiaoqing Pan ^{2,3,4,*}

¹ Frontier Institute of Science and Technology, and State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China; fye8@uci.edu (F.Y.); ren.xiaobing@mail.xjtu.edu.cn (X.R.)

² Materials Science and Engineering, University of California, Irvine, CA 92697, USA; mingjix1@uci.edu

³ Irvine Materials Research Institute, University of California, Irvine, CA 92697, USA

⁴ Department of Physics and Astronomy, University of California, Irvine, CA 92697, USA

⁵ Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

⁶ Department of Chemistry, University of California, Irvine, CA 92697, USA; ptieu1@uci.edu

⁷ Center for Functional Materials, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

* Correspondence: shengdai@ecust.edu.cn (S.D.); xiaoqinpan@uci.edu (X.P.); Tel.: +86-21-6245-3135 (S.D.); +1-949-824-2368 (X.P.)

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Abstract: For decades, differentially pumped environmental transmission electron microscopy has been a powerful tool to study dynamic structural evolution of catalysts under a gaseous environment. With the advancement of micro-electromechanical system-based technologies, windowed gas cell became increasingly popular due to its ability to achieve high pressure and its compatibility to a wide range of microscopes with minimal modification. This enables a series of imaging and analytical technologies such as atomic resolution imaging, spectroscopy, and *operando*, revealing details that were unprecedented before. By reviewing some of the recent work, we demonstrate that the windowed gas cell has the unique ability to solve complicated catalysis problems. We also discuss what technical difficulties need to be addressed and provide an outlook for the future of in situ environmental transmission electron microscopy (TEM) technologies and their application to the field of catalysis development.

Keywords: in situ TEM; catalysts; windowed gas cell; solid–gas interaction

1. Introduction

New generations of nano-sized and single-atom catalysts usually have much more complicated shapes and structures, such as faceted nanoparticles, nano frames, intermetallic phases, and core-shell structures. These structures have specific arrangements/configurations down to the atomic level, thus requiring precision control during the synthetic process. However, some traditional characterization techniques, such as X-ray diffraction (XRD) and X-ray adsorption spectroscopy (XAS), often lack the spatial resolution to study the correlation between the structure and the performance of nano-sized catalysts. Transmission electron microscopy (TEM) is a powerful tool for studying structures and analyzing chemical compositions at tiny scale [1–7]. Therefore, TEM technologies are widely used in the study of nano-catalysts, which can change the rate of chemical reactions without themselves undergoing changes [8]. Most of the catalysis reaction processes take place under a gas or liquid environment. Traditionally, high-resolution transmission electron microscopy (HRTEM) can only be performed under a vacuum and cannot achieve dynamic observations under environmental conditions. In this way,

the ex situ experimental process is operated outside the electron microscope. After the experiment is completed, the sample is placed in the electron microscope for post-reaction characterization. Images of the sample before and after the reaction are then compared to infer the changes in the catalyst structures during the intermediate stages, and thus lack the critical temporal resolution of the reaction process. On the other hand, in situ TEM provides the ability to visualize the atomic structure of nano-catalysts under real synthesis conditions and allows for the observation of structural evolution during gas–solid interactions, which provides valuable guidance of the structural evolution during the deactivation process and to the development of new generations of catalysts. In situ TEM refers to the process of observing and recording the microstructure evolution and characterization of a sample under stress, heat, electricity, magnetism, and/or chemical reaction directly at the atomic level in real time. With the adoption of the aberration corrector (AC) [9–12], which is now available in many TEMs, and the micro-electro-mechanical system (MEMS) [13–20] device, it is possible to monitor the actual reaction process, such as in atmospheric gaseous environment inside the electron microscopes at atomic scale. By utilizing some of the spectroscopic techniques, such as electron energy loss spectroscopy (EELS) [21], X-ray absorption spectroscopy (XAS) [22], Raman spectroscopy [23], and mass spectroscopy [24], reaction products and byproducts can also be quantified simultaneously during *operando* TEM, which gives direct evidence of intermediate states of catalytic materials during reactions.

This review is divided into three sections: Section 2 is a short introduction to the two major TEM techniques for solid–gas reaction study; Section 3 includes several application examples for catalysis study that use different techniques compatible with windowed cell TEM; and in Section 4, we discussed some of the common issues one might encounter when using such TEM techniques, as well as outlooked some new horizons for the future of windowed gas cell technologies that may benefit the field of catalyst study.

This review article emphasizes the technique perspective of windowed gas cells more, and hence some of the catalysis-related discussions are not fully covered. If the viewer is interested in a more detailed review of the catalysis application on gas cell, please check out this review written by Dai et al. in 2017 [25]. We hope that this review can provide the reader with a unique perspective on the field of catalysis development.

2. TEM Instrumentation for Solid–Gas Reaction Study of Catalysts

One of the signature features of traditional TEM is the high vacuum level. Maintaining good vacuum quality inside the TEM is especially important to protect the electron gun as well as minimizing electron scattering. However, such a feature contradicts the need to study materials in their natural environment, such as catalytic events under gaseous conditions. While high-resolution and nice contrast imaging can be easily obtained nowadays in high-vacuum environment, it seems quite challenging to achieve good imaging condition while simultaneously creating a gaseous environment in the specimen chamber and a high-vacuum level everywhere else inside the TEM. Fortunately, two approaches managed to achieve such conditions and allow for high-resolution in situ catalyst research inside the TEM. One technique is called the differentially pumped environmental TEM (DP-ETEM), and the other is called the windowed gas cell.

2.1. DP-ETEM

DP-ETEM relies on a modified TEM setup (Figure 1a). Three pairs of additional apertures are set above and below the sample, respectively, which are used to restrict the gas flow in the TEM column. The aperture must be large enough to allow incident, diffracted, and scattered electron beams to pass, but not too large to avoid excessive gas leakage. In order to maintain the pressure in the environmental cell (E-cell) and maintain very a high vacuum in the rest of the microscope, the effective pumping rate of the differential pumps should exceed the leak rate from the E-cell. Since DP-ETEM is an open system that exposes the sample directly to the electron beam without any obstruction, it maintains the original instrument resolution to the maximum extent, which is the main advantage of this technology [26].

In addition, most of the sample holders used in traditional high-vacuum TEM are also compatible with DP-ETEM. However, because the resolution decreases as the gas pressure increases, the pressure of DP-ETEM is limited to around 20 Torr [27–29]. The low gaseous pressure and the open architecture reduce the extrinsic scattering, making it suitable for electronic structure characterization by EELS. On the other hand, the lower series of differential apertures block the scattered electrons at high angles, which constrain the information collection with high angles, such as high-angle annular dark field (HAADF) imaging, and high-angle electron diffraction spots [30–32].

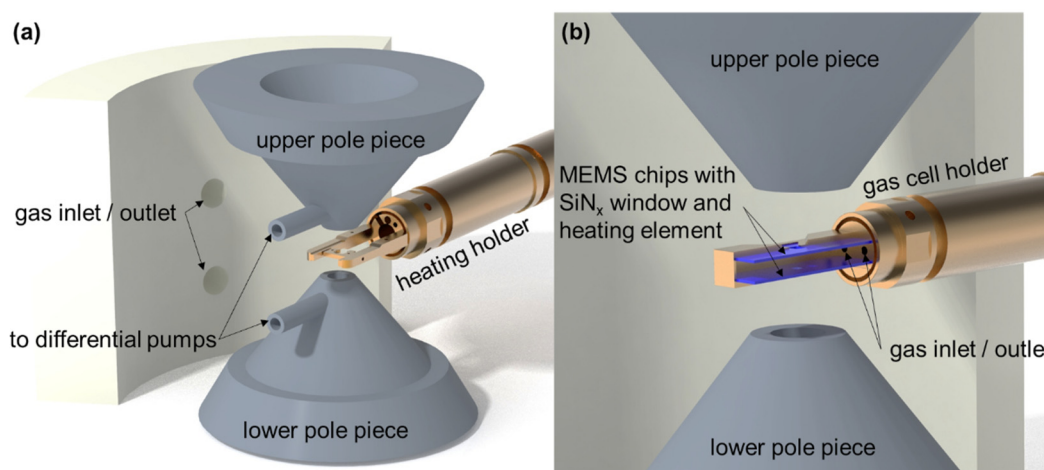


Figure 1. Comparison between environmental transmission electron microscopy (ETEM) and windowed gas cell systems. (a) is a schematic of an ETEM system. (b) is a schematic of a windowed gas cell inside a conventional TEM.

With proper modification, however, environmental scanning transmission electron microscopy (ESTEM) can also be achieved. At the University of York, a double aberration corrected JEOL 2200 FS TEM/STEM was innovatively modified to provide both ETEM and atomic resolution ESTEM [33]. Using this technology, many interesting works were done that utilize the advantages of atomic resolution HAADF-STEM including single-atom dynamics in chemical reactions [34], metal/oxide interface transition [35], shape-controlled nanoparticles [36], and bimetallic catalyst precursor transformation [37].

Due to the large-sized reaction chamber, ESTEM enables the vast possibility of atomic resolution STEM acquisition simultaneously with multiple stimuli such as light, force, and electric biasing. The only limitation, however, is still the relative low pressure that can be applied in the reactor, which inhibits some reactions that require higher partial pressure for saturation surface adsorption coverage.

2.2. Windowed Gas Cells

The other technique allowing for gaseous environment in TEM is the modification of the TEM holder with a gas cell. This type of special holder creates a close-to-ambient nano-reactor chamber inside TEM using a set of MEMS chips and gaskets which seals the sample and gas from the column, as shown in Figure 1b. Each MEMS chip is made of a silicon backing with a thin layer of an electron transparent “window” (usually made of SiN_x) to sandwich the specimen. The pressure difference is maintained by the MEMS chips, gasket, and clamping screws of the holder tip, and the holder is connected to a gas manifold where the environment, such as gas pressure, composition and temperature, can be precisely controlled (Figure 1b). Windowed gas cell and STEM imaging/spectroscopy have become increasingly popular because the holder is compatible with most TEMs and can achieve much higher pressure around the reaction region compared to ETEM. In addition, techniques such as aberration-corrected STEM and EDS/EELS can be easily achieved on gas cell systems, which makes it ideal to analyze the structural evolution of nanocatalysts.

3. Application Examples of Catalyst Study Using Windowed Gas Cell

3.1. HAADF-STEM Imaging: A Powerful Tool for Atomic Resolution Structural Analysis of Catalysts

For decades, high-resolution TEM (HRTEM) was used to study the atomic structure of nano catalysts. With the recent progress of aberration correctors, scanning transmission electron microscopy (STEM) can achieve atomic resolution with little efforts, which makes it increasingly popular compared with HRTEM. In STEM mode, there is a special imaging technique called high-angle annular dark field (HAADF) imaging, which is formed by a very high angle and incoherently scattered electrons. One of the advantages of HAADF-STEM imaging is that it is less sensitive to slight variations in sample thickness and small deviations in the sample orientation. Secondly, compared to HRTEM, which uses a phase contrast imaging method, the contrast of HAADF can reflect the real position of the atoms. Thirdly, the intensity contrast (C) of HAADF images is directly correlated to the atomic number (Z) as ($C \sim Z^{1.7}$) [38,39], and therefore, in some special cases, can be used as an alternative method to qualitatively map the chemical composition in the sample.

HAADF-STEM imaging technique is especially useful in catalysis research because new generations of catalysts usually have complex structures, such as intermetallic compounds, core-shell structures, or single-atom catalysts which are not easy to be determined using HRTEM. Although HAADF imaging does not have as high a temporal resolution as TEM imaging does, it still takes far less time to produce a chemical map compared to tradition spectroscopy techniques such as EDS and EELS. Such an advantage becomes even more pronounced for catalytic systems that may consist of mono-dispersed single atoms or heavy atom dopants, where EDS and EELS generally are incapable of producing high-quality maps.

More importantly, STEM provides better image quality in windowed gas cell because the SiN_x window membrane has far less contrast in STEM mode compared to TEM mode. Hence, it becomes increasingly popular to combine STEM with windowed gas cell to study the nano catalysts. In the following sections, we will discuss some of the newest work done using such a combination of techniques.

3.1.1. Spotting Precious-Metal Dopant in Intelligent Catalysts

Perovskite-based precious-metal catalysts are attractive because they can be used as three-way self-regeneration catalysts in automobile exhaust purification processes, which oxidize hydrocarbons and carbon monoxide while reducing nitrogen oxides into the harmless water, nitrogen, and carbon dioxide [40–43]. The precious-metal nanoparticles (NPs) in these “intelligent catalysts” are maintained in a high dispersion state due to the combined effect of two opposing processes, precipitation and dissolution of precious-metal NPs. Obtaining the real-time observation of the reduction and oxidation process is significant to study the mechanism of these continuously self-regenerating three-way catalysts for automotive exhaust-gas treatment. This requires the rapid separation of precious metal from the perovskite matrix under atmospheric conditions. In the study of intelligent catalysts, the observation of the dynamic structural behavior of precipitation and dissolution of precious NPs becomes challenging even for traditional ETEM, because the dissolved precious metal species are likely to become a monodispersed dopant, and such point defects are difficult to distinguish in HRTEM imaging conditions.

In contrast, HAADF-STEM imaging has the ability to resolve the precious-metal species from the oxide supports because this technique is sensitive to the atomic number (Z) of the materials. Dai et al. used in situ HAADF-STEM imaging obtained with a gas cell to monitor the reduction and oxidation processes in Rh-doped CaTiO_3 (CTO) catalyst [44]. As a good candidate for intelligent catalyst, Rh NPs can repeatedly dissolve into the CTO matrix under reductive conditions and precipitate when the environment becomes oxidative, hence maintaining its highly dispersed morphology. Figure 2a–d shows the dissolution and precipitation of Rh NPs during the reductive and oxidative cycling of the in situ STEM experiment. In order to locate the exact doping site of Rh inside the CTO matrix, the sample

was heated to 500 °C under 760 Torr forming gas (5% H₂ in Ar) for 12 min until many bright regions (denote Rh NPs) disappeared. The atomic sites of Ca, Ti and Rh can be distinguished in the HAADF image taken along the [001] pseudocubic direction of CTO particles, as shown in Figure 2e. The bright spots (marked by yellow arrows) correspond to the Rh atoms, which are distributed randomly on the CTO substrate. Compared with the different contrast in the HAADF image, the Ca (blue) and Ti (magenta) columns can be identified, and the Rh arises from arrays of single atoms located on Ti sites [45], as shown in Figure 2f,g. The HAADF-STEM imaging technique provided direct evidence that the Rh NPs truly dissolve into the CTO matrix and occupy the Ti sites under a reductive environment, which proves to be an effective and powerful tool in the study of the dynamic structural behavior of catalyst nanomaterials at the atomic scale.

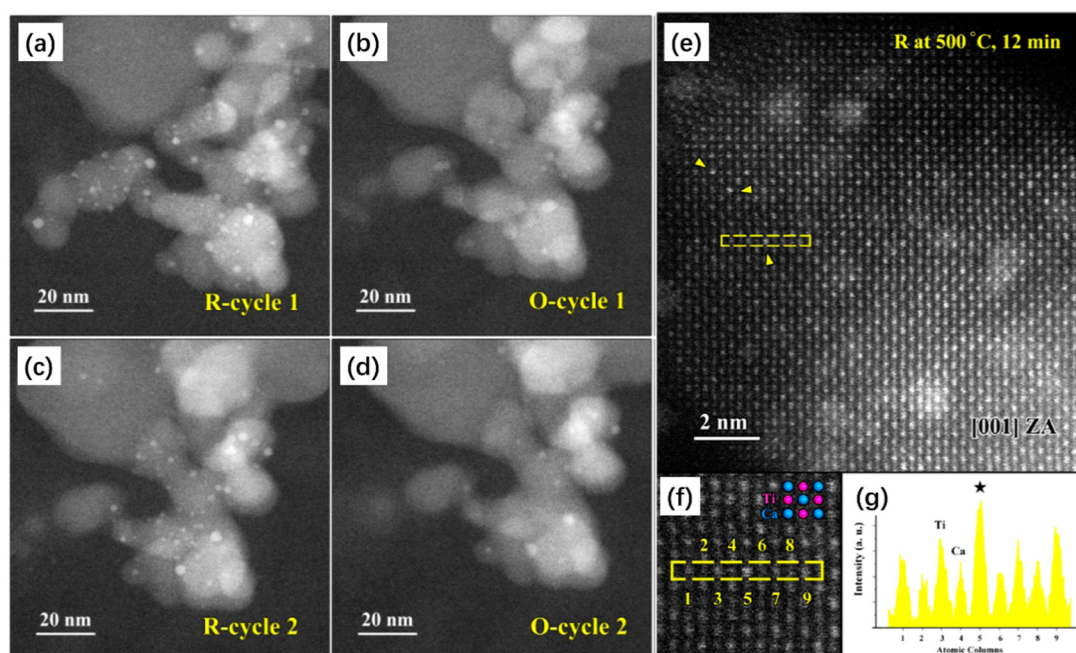


Figure 2. In situ gas-phase TEM of Rh/CaTiO₃ (Rh-CTO) in windowed gas cell. (a–d) HAADF images of Rh-CTO catalyst during reduction-oxidation cycles in 760 Torr of 5% H₂/Ar (labeled by R) or pure O₂ (labeled by O) at 600 °C: (a,b) the first reduction-oxidation cycles (labeled “1”) and (c,d) the second reduction-oxidation cycles (labeled “2”). (e,f) Atomic resolution in situ HAADF image of Rh-CTO catalyst in reduction atmosphere (labeled R) after 12 min at 500 °C: (e) HAADF image taken along the [001] pseudocubic direction of one of CTO particles. The large field view shows the diffuse subnanometer bright regions without discernible structure and occasional bright spots (marked by yellow arrows) (f) enlarged image, containing the dashed yellow rectangular box in (e). The atomic site of Ca (blue) and Ti (magenta) can be distinguished by different intensity of Z contrast. (g) Intensity along a line scanned from left to right with the rectangular box in panel (f). Reproduced with the permission from [43], ACS Publishing Group, 2017.

3.1.2. Revealing Core-Shell Formation of Pt-M Nanoparticles

Performance and cost are the two most concerned factors for the commercialization of oxygen reduction reaction catalysts. Core-shell structures consisting of a precious-metal shell and a non-noble metal core can reduce the amount of precious metal used during synthesis without losing the desired performance. Disordered alloys or transition metal cores are usually chemically unstable and can be leached out, resulting in a hollow Pt shell or forming a new shell on Pt. On the other hand, if the core is made of ordered intermetallic compound, the stability of the core-shell will be greatly enhanced.

The heat treatment of the catalysts with different gases can endow the catalyst with different catalytic activities [46,47]. Ex situ TEM or ETEM studies were carried out to investigate modifications

of catalyst morphology during heat treatment [48–52]. However, the characterization of such a complex structure becomes increasingly challenging because these structures have very well-defined atomic arrangement and cannot be spatially resolved by traditional techniques. In addition, ex situ TEM cannot observe the evolution of the catalyst during the environment changes, and the atmosphere pressure of ETEM is too low, which is a big difference from the actual application of the catalysts. With the maturity of gas cell technology and AC-STEM imaging techniques, the characterization of nanocatalysts under atmospheric pressure can be easily realized.

Dai et al. explored the formation of an oxygen-driven core-shell in Pt_3Co nanoparticles by in situ HAADF-STEM imaging [53]. The reaction happened in a Protochips Atmosphere gas cell system, which can provide elevated gas pressure and temperature. A phase transition of Pt_3Co , which went from disordered face-centered cubic (FCC) to ordered primitive cubic (L12), took place in pure oxygen at pressures as high as one atmosphere (760 Torr) at 720 °C [54–58]. In order to monitor the behaviors of Pt and Co atoms, distinguishing these atoms at atomic scale is necessary. No element information can be obtained from the contrast of HRTEM image. However, these atoms can be distinguished easily by the Z contrast in HAADF-STEM imaging. The Pt atoms are brighter than the Co atoms, as shown in the results from a Pt_3Co NP after oxygen annealing at 720 °C for 30 min. According to the Fast Fourier Transform (FFT) pattern of a NP in HAADF-STEM image, both the (100) and (110) superlattice spots, which are hardly observed in disordered structures, can be observed at this time. Therefore, it can be inferred that NP undergoes an orderly structural phase transition from disordered FCC to ordered L12 [59,60]. In addition, Z-contrast HAADF-STEM imaging shows the distribution of different atoms directly, because Pt columns have a higher intensity than Co columns. At the surface of (100), an initial two-layer Pt-rich shell formed through surface segregation, which effectively blocks Co oxidation. According to the in situ STEM observation, Pt atoms from other clusters migrated and attached onto the (100) Pt surface of the ordered Pt_3Co NPs gradually, when the temperature was down to 300 °C. The in situ STEM observation was taken at the moment when the temperature reached 300 °C. The HAADF-STEM images of Figure 3a–f show the evolution of the Pt_3Co NP surface in the oxygen atmosphere at 300 °C. The (100) Pt shell grew layer by layer during annealing.

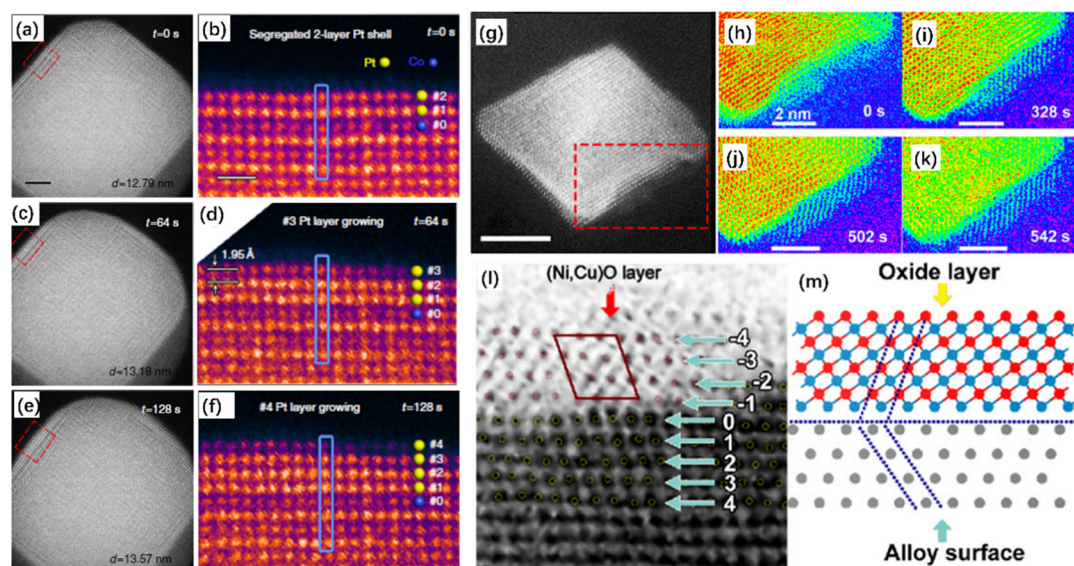


Figure 3. (a–f) Evolution of one (001) Pt shell during oxygen annealing [53]. Sequential high-angle annular dark field (HAADF) images taken at (a) 0 s, (c) 64 s, and (e) 128 s. (b,d,f) Corresponding enlarged false-color panels of (a,c,e), respectively. Reproduced with permission from [53], Nature Publishing Group, 2017. (g–m), oxidation evolution during in situ experiment [61]: (g) is the HAADF image of an octahedral Pt_2CuNi NP. (h–k) is the time series false-color BF-STEM images of a (111) facet marked in (g). (l,m) are enlarged BF-STEM and model schematic of the interface between the alloy and the oxide layer. Reproduced with permission from [61], ACS Publishing Group, 2019.

Furthermore, ternary Pt-M-N NPs which contain two transition metals are often found to be better performing than the binary systems. For example, the ternary Pt-Cu-Ni NPs show significant enhancement of the ORR activity at the cathode of polymer electrolyte membrane fuel cells (PEMFCs) compared with the binary Pt-Ni catalysts [61]. One reason for this improvement is the surface elemental distribution and atomic arrangements of Pt-Cu-Ni NPs during ORR, which makes in situ gas cell TEM the perfect tool for such a study. Shen et al. performed an in situ gas-phase AC-STEM study of octahedral Pt₂CuNi NPs under 160 Torr of O₂ and 610 Torr of Ar at 300 °C [62]. Figure 1g–m shows sequential in situ false-color BF-STEM images of one representative (111) facet, showing oxidative evolution during an in situ experiment. The cubic NiO_x/CuO_x oxide layer, confirmed by FFT analysis, was strongly compressed due to their lattice mismatch with the Pt₂CuNi, which suggests that the oxides may majorly be NiO_x due to their smaller d spacing, thus smaller strain at interface. As the reaction went, the d spacing of the inner bulk lattice slightly increased, indicating the outward diffusion of Ni/Cu which left the interface Pt rich, which, as a result, helps to tune the ORR activity of the Pt₂CuNi NPs. In these works, surface evolutions of nanoparticles were monitored by in situ AC-STEM at atomic-scale by gas cell, demonstrating its advantages in observing catalyst surface configurations during in situ gas-phase experiments.

3.1.3. Studying Single-Atom Catalyst in Real Working Conditions

In order to develop cost-effective catalysts, manipulating the size and surface facets is an effective method. When the particle dispersion reaches a single atom size, many new characteristics will arise, such as a sharp increase in surface free energy, quantum size effects, unsaturated coordination environments, and interactions of metals and supports. These characteristics give monoatomic catalysts a superior catalytic performance. The single-atom catalyst not only has a very low metal loading but also greatly improves the utilization efficiency of metal atoms; it can change the adsorption/desorption selectivity of the active components on the catalyst for different molecules, thereby affecting the reaction kinetics [63–74]. Among them, the oxide-supported isolated Pt-group metal atoms as catalysts show unique reactivity and efficient metal utilization [72,75,76]. However, it is sometimes challenging to establish the relationship between the structure of these active sites, dynamic response to environments and catalytic functionality using macroscopic or ex situ experiments. HAADF imaging with a windowed gas cell has several advantages: the gas cell can achieve pressure and temperature like the real reaction conditions; compared to ETEM, which is hard to distinguish the single atom catalysts from their supports in HRTEM images, Z-contrast imaging can accurately determine the single-atom site; compared to other analytical methods such as EDS and EELS maps, HAADF does not require a high beam dosage which risks mobilizing the single-atom catalysts. Therefore, HAADF-STEM imaging is highly suitable to observe the behaviors of a single-atom catalyst because of the different contrast between the support and single atoms.

The temperature and reactive conditions usually affect the catalytic activities of single-atom catalysts. Traditionally, Fourier transform infrared (FTIR) spectroscopy and X-ray absorption spectroscopy (XAS) are used to determine the averaged local coordination and oxidation state of single atoms. However, these techniques are usually indirect measurements and lack spatial resolution. By combining in situ TEM with the technologies mentioned above, DeRita et al. demonstrated that environmental conditions can affect single-atom Pt to adopt different local coordination environments and oxidation states on anatase TiO₂ nanoparticle supports, which alter the catalytic performance [77]. Figure 4b–d shows a series of atomic-resolution HAADF images of one Pt_{iso} atom on TiO₂ support taken under atmospheric pressure using Protochips Atmosphere holder. The Pt_{iso} was sequentially exposed to 760 Torr of O₂ at 300 °C, 5% H₂ at 250 °C, and 5% H₂ at 450 °C to examine the mobility of Pt atoms on the TiO₂ support. The results indicated that the Pt atom was relatively stable under the first two conditions during STEM observation. When exposed to H₂ at 450 °C for 30 min, the Pt atom moved 1.6 nm from the original site.

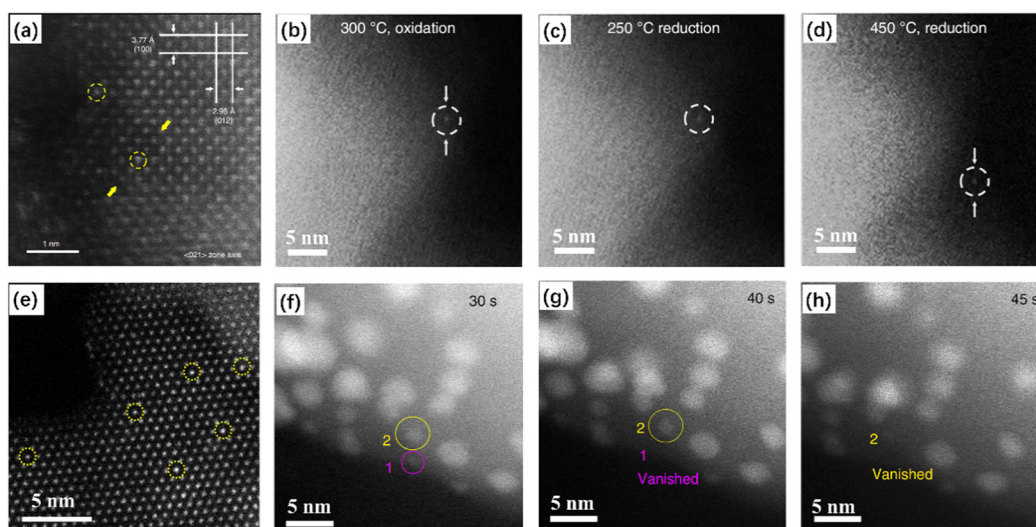


Figure 4. (a–d) In situ AC-STEM characterization of atomically dispersed Pt catalysts during sequential exposure conditions [77]. (a) HAADF image of Pt_{iso}/TiO₂ <021> zone axis. The HAADF images of Pt_{iso}/TiO₂ at (b) 300 °C, 760 Torr of O₂ for 30 min, (c) 250 °C, 760 torr of 5% H₂+Ar for 30 min, and (d) 450 °C, 760 torr of 5% H₂+Ar for 30 min. The yellow circles in (b), (c), and (d) identify the same Pt single atom. Reproduced with permission from [77], Nature Publishing Group, 2019. (e–h) In situ characterization of Pt/Fe₂O₃ NP oxidative dispersion [78]. (e) HAADF image of. (f) HAADF-STEM image of Pt/Fe₂O₃ NP being calcinated at 800 °C under 1 bar flowing O₂ for 30 s, (g) 40 s, and (h) 45 s. Reproduced with the permission from Ref. [78], Nature Publishing Group, 2019.

The same technology can be applied to most heterogeneous catalysts to easily distinguish the support and the loading materials. For example, Lang et al. studied the strong covalent metal-support interaction (CMSI) which acts as a non-defect-stabilization mechanism for Pt₁/FeO_x catalysts. This mechanism enables high concentrations of thermally stable single atoms even on low-surface-area materials [78]. Figure 4e shows a HAADF image of isolated Pt atoms dispersed on the <111> zone axis FeO_x support and according to the Z-contrast feature, many Pt atoms were aligned with the Fe atomic columns (highlighted by the dashed circles). Figure 4f–h revealed the disintegration process of Pt NPs during calcination under 800 °C and one bar of continuous O₂ flow using a DENSolutions gas flow and heating holder. The loss of Pt clusters within the first 45 s in the absence of coalescence or Ostwald ripening suggests the formation of atomically dispersed Pt entities.

3.2. EDS/EELS: Chemical Composition and Beyond

In situ diffraction and spectroscopy techniques such as X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) offer powerful approaches to study average changes in structure, composition, valence, etc., during reactions, and hence can be complementary with TEM study. However, the resolution of the most advanced XRD or XAS cannot reach atomic scale [79–82]. Therefore, the combination of atomic resolution imaging with spectroscopy, including X-ray dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS), becomes an important way to probe the chemical and electronic structure changes at nanoscale. For example, EDS can be used to determine chemical composition with atomic resolution, while the electron energy-loss spectroscopy (EELS) can determine the type and number of atoms, the chemical state of the atoms, and the collective interaction of the atoms with neighboring atoms. By combining EDS technique with the gas cell, it is possible to monitor the migration of copper in bimetallic phosphide (Ni, Cu)₂P nanoparticles [83]. Platinum-transition metal (Pt-Fe, Pt-Co, Pt-Ni, etc.) nanoparticles, used as cathode electrocatalysts in proton exchange membrane (PEM) type fuel cells, are of great interest. The composition at the surface is anisotropic in Pt₃Co nanoparticles exposed to an oxygen atmosphere at elevated temperature [84].

EDS was used to confirm the chemical composition [53,84–86], while EELS was applied to confirm the surface elemental composition in different faces [84].

One of the advantages of EELS over EDS for detecting chemical composition in gas cell is the high signal counts. Unlike EDS, where the signal gets easily reduced by the geometry of the holder and the size and position of the detector, most inelastically scattered beams can be collected and contribute to the EELS spectrum. In addition, EELS is more sensitive to light elements, which makes it a suitable tool to analyze many gas molecules containing C, H, N, and O [87]. However, EELS is strongly influenced by multiple scattering, which in the windowed cell mainly comes from the two SiN_x windows. Hence, a better detector with improved quantum efficiency such as direct detection device (DDD) can be used to improve the signal to noise ratio.

3.2.1. Improving EDS Signal for Gas Cell Experiments

One of the factors that hinders EDS in gas cell is the limited collection angle, resulting in the reduced signals. The X-ray signal can be blocked by the design of the window structures on the holder and eventually results in a decreased count per second (CPS) of EDS, as shown in Figure 5a,b,d,e. Moreover, the non-characteristic fluorescence created by secondary X-rays when scattered electrons or X-rays bounce off surfaces in the microscope will also reduce resolution. Even when the detector is shadowed, elements like Fe, Cu, Si and others are often detected (Figure 5c). It is important to distinguish the characteristic X-ray counts from secondary X-rays, as shown in Figure 5e,f. On the other hand, obstructions in the holder and chip, such as the sample geometry, pole piece gap, sample tilt and holder geometry can interrupt the line of sight, causing detector shadowing and lowered CPS. To address this problem, a newer design of in situ atmosphere holder was introduced by Protochips featuring a low-shadowing profiled front blade (Figure 5g,h). In the following study, this special EDS in situ holder was combined with the latest high-efficiency EDS detectors and AC-STEM to observe the behavior of bimetallic nanoparticles at elevated temperature and pressures [88]. The bimetallic catalysts have better performance than monometallic catalysts in activity, selectivity and stability for oxygenate coupling reactions [89–91]. However, observing the complex structural changes occurring during the reduction of a supported bimetallic catalyst at elevated temperature (up to 1000 °C) and pressure (up to 1 atm) is challenging in a TiO₂-supported PdCu bimetallic catalyst. Theoretically, the TiO₂ support, Pd and Cu all have different Z-contrasts and should be distinguishable using HAADF images. While in practice, the additional contrast caused by inhomogeneous thickness and the particle size make the task much harder. On the other hand, the EELS signal of Cu is too weak to distinguish from the noise. For example, in Figure 5i, the regions marked by red and blue boxes have similar contrasts. But according to the STEM-EDS elemental map for Cu (green) and Pd (red) by the EDS-optimized holder shown in Figure 5j, the blue boxed region contains a PdCu NP. In addition, the EDS mapping shows that the Cu distributed more homogeneously on the support in clusters than Pd. With such improved EDS signal design, interesting processes, such as the formation of Janus particles (the surface of the particle is divided into two distinct materials) and Cu-surface-rich PdCu NPs, can be monitored by this powerful tool, as shown in Figure 5k.

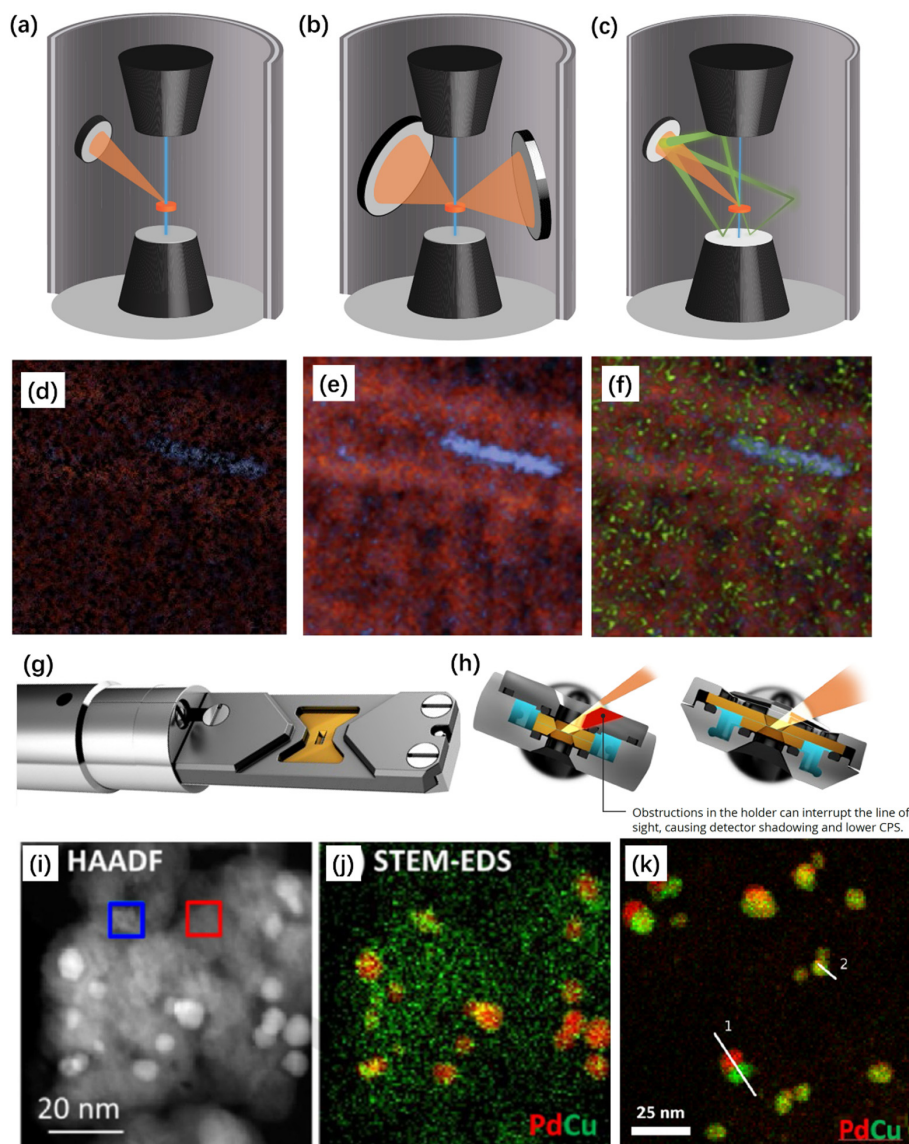


Figure 5. Techniques for improving x-ray dispersive spectroscopy (EDS) detection. (a–c) Schematic of EDS detector (a) EDS detector (b) EDS detectors with larger collection angles or multiple detectors. (c) EDS detectors that collecting both characteristic and non-characteristic fluorescence. (d–e) Comparison of (d) 50 counts per second (CPS) and (e) 500 CPS, which is the most important factors for EDS performance and accuracy. (e–g) Comparison of EDS maps without (e) and with (f) non-characteristic X-ray counts. (h) Schematic of a modified holder to decrease detector shadowing. Figures provided by Protochips, Inc. (i–k) Characterization of TiO_2 supported PdCu bimetallic catalyst [88]. (j–k) Comparison of (i) HAADF and (j) STEM-EDS, where the blue box shows a PdCu particle that has a similar contrast to the TiO_2 support marked in red box. (k) Composite STEM-EDS elemental map of Janus NPs for Cu (green) and Pd (red). (i–k) are Reproduced from [88] licensed under CC BY 4.0.

3.2.2. Using EELS for Chemical Composition and Valance Structure Analysis

EELS is a powerful tool to analyze the electronic structure and elemental information of materials inside the microscope. It utilizes the inelastically scattered transmitted electron beam to form a spectrum with respect to the loss of electron energy due to interactions with the materials. The EELS spectra usually consist of zero-loss, low-loss and core-loss regions. The low-loss region usually contains information on phonon modes, plasmon modes, and interband transitions, which are correlated to the optical properties, local bonding, and coordination of materials. The core-loss region contains

information due to electron excitation of the inner-shell of the material, and usually provides information on the chemical composition and valance state.

Unlike EDS, the EELS signal is not largely affected by the geometry of the gas cell. In addition, STEM-EELS allows for spatially resolved spectroscopy compared to ETEM-EELS, which makes it an ideal method to characterize the anisotropic surface segregation of some alloyed Pt-M NPs [57,58]. Since the high catalytic performance of Pt-M NPs is mainly determined by the chemical and structural configuration near or at the surface, it becomes crucial to understand the surface reconstruction and segregation in these NPs and correlate these with the dynamic structural evolution during in situ TEM studies. For example, an AC-STEM/EELS analysis on a truncated octahedron Pt₃Co NP along the {110} zone axis was carried out and confirmed that the {111} surface of Pt₃Co NPs has a higher content of Co than the {100} surface (Figure 6a,b) [84]. This explains why, during the in situ heating under oxidative environment later on, the CoO layers are found only on the {111} surfaces. These results provide direct evidence that the {100} surface plays an important role in maintaining the high activity of disordered Pt₃Co ORR catalysts.

The detection of valence is also of great significance in studying the catalysis such as the strong metal support interaction (SMSI) phenomenon. The X-ray photoelectron spectroscopy (XPS) is traditionally used to determine the composition, experimental formulas, and chemical and electronic states of the elements contained in materials. However, due to the limitation of spatial resolution, it is difficult for XPS to directly observe fine structures such as the formation of an overlayer with a thickness of several atomic layers on the surface of a nanoparticle. Since the low-loss or valence region of an EELS spectra provides valuable information about the band structure [92], STEM-EELS becomes a powerful tool to confirm the oxidation state of metals.

Zhang et al. observed the reversible formation of the TiO_x overlayer on Pd nanocrystal in palladium/titania (Pd/TiO₂) under SMSI by combining state-of-the-art in situ TEM and the Protochips Atmosphere system, which can provide elevated temperatures and pressures of different gaseous environments [93]. An amorphous layer forms on the Pt NPs by low-temperature reduction (H₂ (5 vol %)/Ar at 1 atm, and 250 °C), while a bilayer that is almost epitaxial with the (111) plane covers the surface of Pd NPs when the temperature increased to 500 °C, as shown in Figure 6c,e. In order to confirm the fine structure of Ti in the TiO_x surface layer, an EELS scan was taken in situ under this high-temperature reduction condition along the line ABCD, as shown in Figure 6d,f. The valence of Ti transforms from +4 (Point A, the TiO₂ support region) to +3 (Point B and C, the Pd NP regions). Point D is in the region without any sample as a background reference. According to the calculation, the double overlayer in Figure 6c,d are hexagonal k-phase Ti₂O₃ layers, which agrees well with the STEM-EELS data.

John C. Matsubu et al. used Rh/TiO₂ and Rh/Nb₂O₅ as the model catalyst to catalyze the CO₂ + H₂ reduction reaction. The main products of the CO₂ + H₂ reaction are CH₄ and CO. They found that if the catalyst is previously reduced by H₂ at high temperature, CH₄ is the main product (up to approximately 100%); however, if the catalyst is treated in a CO₂ + H₂ atmosphere for a period of time, it will significantly increase the selectivity to CO, and the selectivity of CH₄ will be greatly reduced. Interestingly, according to in situ STEM, the surface of the Ru / TiO₂ catalyst treated with a 20 CO₂:2 H₂ atmosphere at 250 °C formed a thin (1–3 nm) amorphous TiO_{2-x}. It can be seen from the STEM image that this amorphous TiO_{2-x} is still significantly different from the highly crystallized TiO_{2-x} formed by the conventional SMSI process (Figure 6g,h) [94]. They named this process as adsorbate-mediated strong metal-support (A-SMSI). Differences in oxidation states of TiO_x in SMSI and A-SMSI overlayers can be detected by in situ EELS. The crystalline bilayer formed by SMSI process contains exclusively Ti³⁺ on the surface of Rh nanoparticles [93,95–98]. In contrast, the Ti in the amorphous overlayer formed by the A-SMSI process exists in a combination of ~30% Ti³⁺ and ~70% Ti⁴⁺. At the same time, in situ infrared spectroscopy also found that this amorphous TiO_{2-x} layer also contains more carbonates and formate salts. These species are considered to have a greater impact on the catalytic performance of Rh. The authors speculate that this amorphous surface structure will significantly affect the adsorption

performance of CO molecules on the surface of Rh nanoparticles, thereby regulating the selectivity of the CO₂ hydrogenation reaction. Finally, the author also extended the phenomenon observed in the Rh/TiO₂ system to other supported Rh catalyst systems. They found that the Rh/Nb₂O₅ samples showed different SMSI phenomena. This difference should be caused by the nature of the different carriers. The combination of EELS and TEM techniques can determine the valence of the catalyst at the atomic level, which is of great benefit for studying the catalytic mechanism of the catalyst.

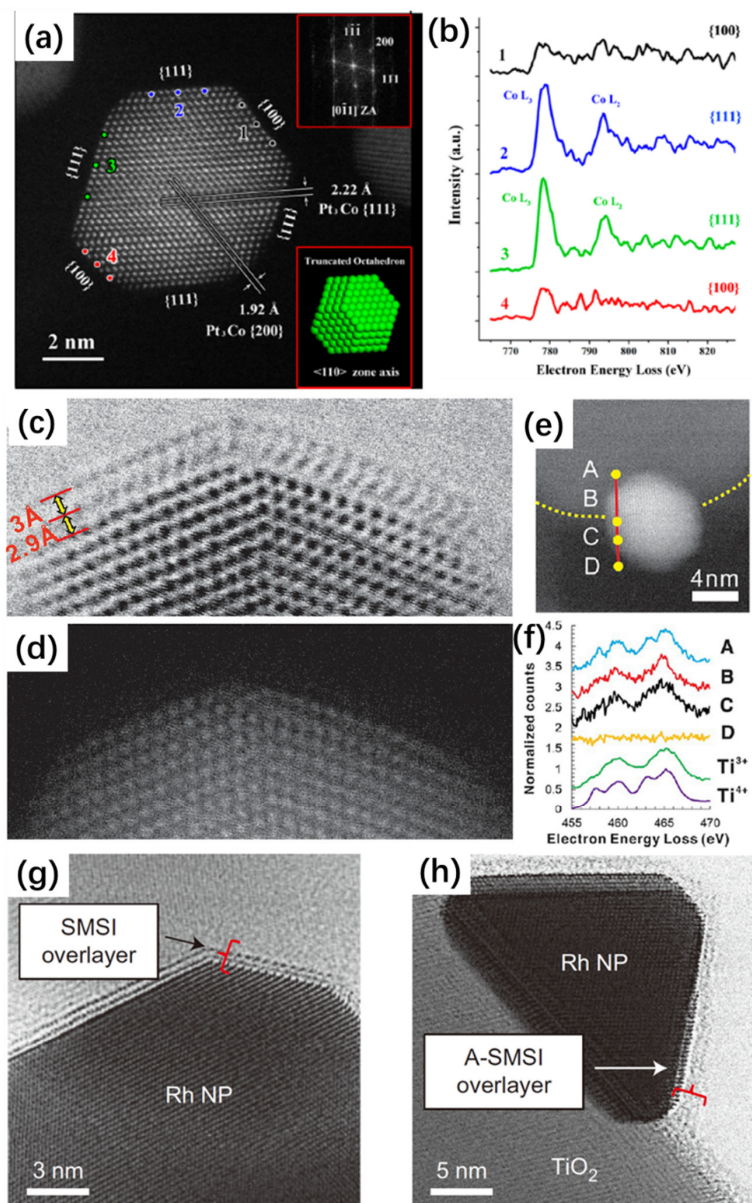


Figure 6. STEM-EELS technique. (a,b) [84] Characterization of the original Pt₃Co NPs (a) HAADF image of a Pt₃Co NP along the <100> zone axis. The inserts are the corresponding FFT pattern and the model of a Pt₃Co NP as a truncated octahedron. (b) Average electron energy loss spectroscopy (EELS) spectra of different facets of the NP at locations marked in (a). (c–f). Reproduced with the permission from Ref. [84], ACS Publishing Group, 2017 [93]. TiO_x overlayer on Pd nanocrystal in Pd/TiO₂. (c,d) A Pd NP surface showing unique double layer TiO_x overlayer. (e) Another Pd NP sitting on TiO₂ support. (f) EELS spectra taken at location marked in (e). Reproduced with permission from [93], ACS Publishing Group, 2016. (g–h) SMSI and A-SMSI states [94]: (g) Rh NP with crystalline SMSI overlayer. (h) Rh NP with amorphous SMSI overlayer. Reproduced with permission from [94], Nature Publishing Group, 2016.

3.3. Operando: Getting One Step Further Towards the Catalyst Fundamentals

Under *operando* conditions, the products and byproducts can be detected simultaneously during the catalytic reaction characterization. In addition to monitoring the structural change in the solid specimen, understanding the composition of the gas near the reaction region is also highly desired because the change in catalyst structure alone does not confirm whether the catalytic reaction is indeed taking place inside the microscope. In TEM, by using EELS, mass spectroscopy and other techniques, gas composition analysis can be performed during in situ TEM experiment. Such a combination enables an *operando* approach to TEM, which determines the structure and activity simultaneously.

In EELS, both core-loss and valence-loss EELS can be used to measure the gas composition inside TEM by using linear fitting between the experimental spectra and the reference spectra of each gas species [87,99–101]. In the study of CO oxidation reaction, core-loss EELS is particularly effective at measuring the composition change in CO and CO₂ because the carbon K-edges of CO (286.4 eV) and CO₂ (289.7 eV) are close together but not overlapped, which makes it straightforward to quantify [87,101]. However, there are limitations for *operando* using EELS: limited gas species (only can detect certain gas), loss of time resolution (EELS spectra needs a relatively long time, up to hundreds of seconds to collect, and video could not be captured at the same time), and reduced peak/background ratio in windowed gas cell system due to the SiN_x windows. Hence, alternative methods such as residual gas analysis (RGA, a mass spectrometer that can detect gas species in vacuum systems), FTIR, XAS, etc., are often used as alternatives in gas cell systems.

Unocic et al. studied a complex reaction sequence applied to the Ag/ZrO₂/SBA-16 catalyst using *operando* TEM with a closed gas cell system that was modified to include a water-vapor delivery system and a RGA [102]. During the *operando* experiment, the temperature was fixed at 325 °C, and the gas species was switched from an initial 760 Torr N₂, to 760 torr 10% H₂/N₂, and then finally 24% C₂H₆O/H₂. Using the RGA, the size, shape, and dispersion change of the Ag particles was correlated to the real gas environment, showing the results using *operando* TEM to perform a complex reaction sequence enabling real condition studies to understand the catalyst performance.

4. Discussion and Outlook

4.1. Beam–Gas–Sample Interaction

The use of windowed gas cell in TEM offers a way to study materials under chemically relevant environments. However, due to the interaction between electron beam and gas cell, many undesirable phenomena can occur such as degradation of resolution, electron beam induced contamination, ionization of gas molecules, as well as beam damage to gas molecules and samples.

The gas around the samples will decrease the intensity of the acquired images in the microscope, and the spatial resolution in general will decrease as the gas pressure increases. Due to the presence of two SiN_x windows, the chromatic blurring in windowed gas cell makes the resolution much worse than that under TEM mode of ETEM [31]. In STEM mode, however, this effect is largely suppressed because the ADF detector and BF detectors are solid state detectors and the resolution is more sensitive to the electron probe shape which can be corrected using aberration correctors. Hence, the spatial resolution for windowed gas cell is much better under STEM mode than TEM mode.

During in situ STEM using a gas cell system, carbon contamination becomes a more severe issue compared to ETEM because the beam is more focused and stronger in STEM mode which will break hydrocarbons more easily to form carbon, which then deposits on the sample and SiN_x membranes during scanning. Furthermore, the hydrocarbons cannot be easily pumped away once the cell is assembled due to the complicated reactor design, which allows for dead zones where gas is hard to remove. One of the simplest ways to avoid such contamination effect is through heating. Usually, once the nanoreactor is heated to above 300 °C, the subsequent carbon contamination will be suppressed. However, if this temperature is still too high for the experiments, a thorough cleaning and baking of

the chip and gas manifold system is recommended. One should also check the purity of the gas and make sure that no contamination is coming from the inlet gas.

A high-energy electron beam can easily ionize gas molecules and cause increased reactivity. In some cases, the ionized gas can expedite or completely change the reaction process during in situ environmental TEM experiments [103], while in other cases the ionized gas may actually protect the sample by providing extra ions in the sample vicinity to compensate the beam damage [52].

High current density will also damage or modify the sample. In general, two types of beam damage are considered in the TEM: knock-on damage and radiolysis. The former is caused by the displacement of atoms in the sample by momentum transfer from fast primary electrons to atoms in the sample. This can be minimized by lowering the energy of the electron beam [104,105]. Radiolysis is caused by fast electrons modifying the chemical bonds in the sample, leading to changes in the electronic structure, and thereby the stability of the sample. This type of damage is usually more sensitive to lower electron beam energies due to the larger interaction cross-section. Examples include beam-induced chemistry, which can be found in the electron-beam-induced reduction of molybdenum and vanadium oxides [106,107].

For beam-sensitive samples, a smaller probe current, a lower magnification, and a shorter acquisition time are used to reduce the electron dose, even though these methods will sacrifice the quality of image. It is necessary to find suitable parameters to balance the damage to the sample and ensure the quality of the picture. For example, in DeRita's in situ work [77], the electron beam was turned off except during image collection. In addition, comparative experiments are done to confirm that the beam condition will not introduce the movement of Pt single atoms on the TiO₂ surface.

4.2. Windowed Cell with Multiple Stimuli

On the other hand, realizing multiple stimuli inside a windowed gas reactor is much more complicated compared to ETEM because they all must be integrated onto a single holder. Fortunately, with the advancement of MEMS technology, many applied fields as well as sensors can nowadays be integrated to a MEMS chip set that fits in the in situ TEM holder. For example, quantitative mechanical testing can be realized by incorporating a capacitive load sensor and a thermal actuator [108]. In addition, windowed cells can also be illuminated by laser using a combination of fiberoptic and mirrors [109].

Recently, an Active Mechanical-Electrochemical-Thermal (AMET) Discovery PlatformTM was developed at the Center for Integrated Nanotechnologies (CINT) in Sandia National Laboratories which enables mechanical, electric, gas/liquid, and heating functions on a 4mm*6mm*1mm MEMS chip set [110,111]. This AMET system demonstrated the ability to combine chemical surroundings (such as gas or liquid environments) with two or more applied fields (strain, electric, thermal, etc.), and the involvement of such MEMS technology proves that the nanoscale probing of environmentally dependent mechanical, thermal, and electrical properties of materials can now be directly observed using TEM. Although there is not much follow up work on this system and it was not initially designed for catalysis but for mechanical testing under environmental conditions, the idea of integrating multiple stimuli on to a single set of MEMS chips provides a promising future to expand the capability of in situ TEM experiments.

5. Conclusions

As an alternative to ETEM, closed windowed gas cell allows for atomic resolution imaging of dynamic structural evolution of catalyst nanomaterials under a realistic environment. Compared to TEM imaging, HAADF-STEM imaging has the advantage of distinguishing complex and tiny structures such as intermetallic compounds, dopant, and single atom catalysts. The combination of AC-STEM with spectroscopy such as EDS and EELS forms a power tool to quantitatively correlate the structure and catalytic performance at unprecedented spatial resolution. The adaption of RGA, Raman and FTIR to the gas cell also provides the potential to perform *operando* TEM, which monitors the reaction condition in real time. However, when performing characterization using a gas cell system,

the potential artifact introduced by beam–gas–sample interaction must be considered and avoided to validate the result. We believe this technique, with future developments such as the integration of multiple stimuli and improved MEMS technology, will become a powerful tool for the field of catalyst research, and bring unique perspectives to the development of next-generation catalyst systems.

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