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***In Situ/Operando* Techniques for Characterization of Single-Atom Catalysts**

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Abstract

In situ/Operando characterization techniques are powerful to provide fundamental information about molecular structure-activity/selectivity relationships for various catalytic systems under controlled condition. However, the lack of model catalyst, as the major obstacle for deeper understanding on the nature of active sites and reaction mechanisms, hinders the further advancements in catalysis. Fortunately, the rapid development of single-atom catalysts (SACs) offers us new opportunities for capturing the reaction intermediates, identifying the active sites, and even monitoring the dynamic behaviors of both the geometric structure and electronic environment of the catalytic sites at atomic scale. In this review, the recent advances on the *in situ/operando* characterization techniques including X-ray absorption spectroscopy, scanning tunneling microscopy, Fourier-transform infrared spectroscopy, and etc. for the characterization of SACs are thoroughly summarized. The results from these *in situ/operando* measurements reveal the crucial role of SACs as model systems for sharpening our understanding on the nature of catalytic sites. Furthermore, the challenges and outlooks in developing *in situ/operando* techniques for single atom catalysis are discussed.

Keywords: single-atom catalyst, *operando* techniques, *in situ*, intermediate, active site

1. Introduction

Over the past few years, single-atom catalysts (SACs) have attracted increasing attention in heterogeneous catalysis owing to their unique electronic properties and maximal atom utilization efficiency.¹⁻⁵ More specifically, the undercoordinated single atom sites have been both experimentally and theoretically identified as the active sites for many catalytic reactions including water-gas shift reaction, CO oxidation, Suzuki coupling, chemoselective hydrogenation, electrochemical reduction/oxidation, and *etc.*⁶⁻¹² Therefore, the real-time observation on these reacting single atom sites via *in situ* experiments is highly beneficial for revealing the reaction mechanism and the electronic environment of the smallest catalytic blocks during catalytic processes.

In situ/Operando characterization techniques for studying the catalyst under reaction conditions can provide in-depth insights into the complex reaction kinetics, thereby strongly contributing to obtaining hints about the nature of active sites and reaction mechanisms.¹³⁻¹⁷ By definition, “*in situ*” describes the collection of spectra of the catalyst in the same phenomenon as it has been treated, or under conditions relevant to catalytic operation.¹⁸ While “*operando*” combines *in situ* characterization of a working catalyst during genuine reaction condition with simultaneous measurement of catalytic activity and selectivity.¹⁸⁻¹⁹ For a long time, the heterogeneity of active sites on support has been considered as the major obstacle for *in situ/operando* monitoring the real catalytic sites of the catalysts, which also leads to the complexity of the catalytic mechanism studies. Fortunately, the rapid development of SACs with uniform atomically dispersed active sites provides us with great opportunities for identifying the nature of catalytic sites and even monitoring the dynamic behaviors of the active sites at atomic scale in reaction. The knowledge thus obtained is

significant for investigating the molecular structure-activity/selectivity relationships as well as the underlying catalytic mechanisms, which are in turn critical for the rational design of catalysts with desirable activity, stability, and selectivity.

Recently, a number of *in situ/operando* techniques including transmission electron microscopy (TEM), scanning tunneling microscopy (STM), Fourier-transform infrared spectroscopy (FTIR), X-ray absorption spectroscopy (XAS), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), time-of-flight mass spectrometry (TOF-MS), and etc. have been applied on SACs as model systems for capturing the reaction intermediates, identifying the active sites, and even monitoring the dynamic behaviors of both the geometric structure and electronic environment of catalytic sites at atomic scale. The results from these *in situ/operando* measurements disclose the crucial role of *in situ/operando* techniques for sharpening our understanding on the nature of catalytic sites with SACs as model systems.

In this review, recent advances in the application of *in situ/operando* techniques for characterization of SACs are thoroughly summarized. Remarkable cases of study are highlighted including: (i) *in situ* TEM and STM for direct observation of the dynamic process of single atoms anchoring on the defects of supports; (ii) *in situ* FTIR CO chemisorption as an effective tool to assess the existence of atomically dispersed metal atoms; (iii) *operando* XAS for probing the geometric and electronic structures of single atom sites during CO oxidation and electrochemical (CO₂, O₂) reduction reactions; (iv) *in situ* AP-XPS to study the surface chemistry of single-atom alloy catalysts; and (v) *in situ* MS for tracking the evolution of liquid products over SACs. Additionally, the challenges and future directions for developing *in situ/operando* techniques in single atom catalysis are discussed.

2. *In situ/operando* techniques

2.1. *In situ* TEM and STM

Visualizing single atom dynamics is essential for obtaining deeper insights into mechanisms of chemical reactions, and a critical guide to the development of novel SACs. The aberration corrected TEM provides a powerful and indispensable tool for nanomaterial characterization with sensitivity to detect single atoms. The recent technology developments of environmental TEM (ETEM) enable *in situ* characterization of structural evolution of SACs under gaseous and operational conditions, which becomes the common powerful approach for visualizing the dynamic state of atoms in real space and time.²⁰

In situ TEM with atomic resolution for direct probing of gas-solid reactions at high temperature (2000 °C) was first reported by Gai and Boyes, which opened up opportunities for *in situ* studies of single atom dynamics in an aberration corrected environment.²¹ Subsequently, *in situ* TEM studies were carried out on carbon supported platinum catalysts, which directly observed migration of single Pt atoms from particles under reduction and oxidation environments at operating temperatures (Figure 1A-C).²²⁻²³ The dynamic and reversible transformation between single Pt atoms, clusters and nanoparticles under redox conditions have been further confirmed by Liu et al.²⁴ As shown in Figure 1D, Pt clusters disintegrate and form highly dispersed Pt species at 200-400 °C, while agglomerate into Pt clusters or even small Pt nanoparticles at higher temperatures (600-800 °C). More recently, the transformation of noble metal nanoparticles (Pd, Pt, Au-NPs) to thermally stable single atoms (Pd, Pt, Au-SAs) above 900 °C under an inert atmosphere was also observed by Wei et al. with the application of ETTEM.²⁵ The results of these works provide new insights into the single atom dynamics that are of great importance for deeper understanding of the catalytic active sites.

Figure 1. Migration of single atom arrowed in (A) and (B), leading to the formation of clusters and increased facets of particles (C); Reprinted with permission from Ref ²². Copyright 2013 IOP Publishing. (D) Structural evolution of Pt species under CO + NO and NO + H₂ conditions. Reprinted with permission from Ref ²⁴. Copyright 2018 Springer Nature.

In situ TEM/STM have also been applied to give insights into the growth mechanism of graphene catalyzed by single atoms. For instance, via *in situ* aberration corrected TEM, Zhao et al. directly captured the catalytic growth of sp² carbon by a single Fe atom under electron irradiation.²⁶ Figure 2A-D present a typical translocation of an individual Fe atom diffusing along the graphene edge. The Fe atom changes from a pentagon structure (Figure 2A), absorbs some nearby carbon atoms and moves toward the right (Figure 2B). The motion of single-Fe-atom creates the dark shadow line (Figure 2C) and finally results in the formation of a pentagon again (Figure 2D). The corresponding atomic structures as shown in Figure 2E and the combination of four frames as shown in Figure 2F further highlight the entire growth process (Figure 2G). With combination of theoretical studies, the results of this work provide key insights into the catalytic action of single Fe atoms for the formation

mechanisms of graphene and carbon nanotubes.

Figure 2. One cycle in catalytic growth of graphene edge. (A-D) High-resolution TEM images from 0 to 3 s. (E) The corresponding atomic structures for A-D. (F) The combination of A-D, which shows the trajectory of the Fe atom during one-unit cell translocation. (G) The atomic structure for the entire growth process. (Scale bar: 0.5 nm). Reprinted with permission from Ref ²⁶. Copyright 2014 National Academy of Sciences.

More recently, the catalytic action of single Ni atoms at the edges of a graphene flake during real growth process was directly observed by *in situ* high speed STM measurements.²⁷ With identification of the Klein (k) and Zigzag (z) edge terminations of epitaxial graphene (EG) layer on Ni (111) as shown in Figure 3A, the bright features as shown in Figure 3B-C were attributed to mobile Ni adatoms. Mobile Ni adatoms moved randomly over the bare metal surface diffused parallel to the graphene edge with considerably longer residence time in the kink sites. Moreover, the Ni adatoms at the kinks are observed in most cases accompanied by C dimer attachment nearby, indicating the catalytic role of the single Ni atom. Results of this work experimentally prove the catalytic role of

single metal atoms for the chemical vapor deposition (CVD) growth of graphene on transition metals.

Figure 3. Graphene growth along the Klein (k) and Zigzag (z) edges. (A) k and z edges of a top-fcc epitaxial graphene layer on Ni (111) with kink structures highlighted by circles. High-speed STM sequence acquired at 710 K in quasi-constant height mode at the (B) z edge (C) k edge. Reprinted with permission from Ref²⁷. Copyright 2018 American Association for the Advancement of Science.

2.2. *In situ* FTIR

Despite that direct evidences for the presence of single atoms could be provided by aberration corrected TEM images, the existence of nanoparticles (NPs) could not be excluded. *In situ* FTIR, which is highly sensitive to the vibration mode of the adsorbed CO molecule on active site, provides a more decisive evidence to exclude the presence of NPs in SACs and is effective for tracking the reaction pathways of CO catalyzed on SACs.

Figure 4. *In situ* FTIR spectra of CO adsorption over (A) single-atom Pt₁/FeO_x, the band at 2080 cm⁻¹ represents linearly-bonded CO on Pt^{δ+}, (B) cluster Pt_x/FeO_x, the bands at 2030 cm⁻¹, 1860 cm⁻¹, 1950 cm⁻¹ are, respectively, ascribed to the linearly-bonded CO on Pt⁰ site, bridge-bonded CO on two Pt atoms and CO adsorbed on the interface between Pt clusters and the support. Reprinted with permission from Ref ¹, Copyright 2011, Springer Nature.

Over the past few years, *in situ* FTIR has been widely used and regarded as an effective tool to assess the existence of atomically dispersed metal atoms in supported SACs. In the work conducted by Qiao et al.,¹ which first introduced the terminology of SAC, *in situ* FTIR spectra of CO adsorption were acquired to prove the presence of only isolated and positively charged single Pt atoms in Pt₁/FeO_x SAC. As shown in Figure 4A, the independence of frequency for the linearly adsorbed CO

at 2080 cm^{-1} with CO pressure suggests good isolation of single Pt atoms. While the formation of bridge-bonded CO indicates the existence of dimer or Pt clusters in Pt_x/FeO_x (Figure 4B). The blue shift of the linearly bonded CO with CO pressure increasing due to the coupling of adsorbed CO molecules suggests the irreversible adsorption of CO on Pt^0 . Recently, *in situ* FTIR measurements were carried out by Yang et al. to confirm absence of Pt nanoparticles and presence of atomically dispersed Pt atoms on two different supports of titanium carbide ($\text{Pt1}/\text{TiC}$) and titanium nitride ($\text{Pt1}/\text{TiN}$).²⁸ Results of this work clearly indicate participation of support in SACs for electrochemical oxygen reduction reaction (ORR).

Figure 5. (A) $\text{AgPd}_{0.025}/\text{SiO}_2$ catalyst reduced at 250 or 500 $^\circ\text{C}$ at 10 Torr CO with subsequent evacuation. *In situ* FTIR spectra for $\text{AgPd}_{0.025}/\text{SiO}_2$ catalyst reduced at (B) 250 $^\circ\text{C}$ and (C) 500 $^\circ\text{C}$ as

a function of CO pressure (after subtraction of gas-phase CO spectra). Reprinted with permission from Ref²⁹. Copyright 2015, American Chemical Society.

In situ FTIR was also employed to assess the existence of atomically dispersed metal atoms in single-atom alloy (SAA) catalysts. For instance, Pei et al. carried out *in situ* FTIR measurements to shed insight on the nature of atomically dispersed Pd sites in the AgPd_{0.025}/SiO₂ catalyst.²⁹ As shown in Figure 5A-C, the bands at 2165 and 2041 cm⁻¹ observed on the AgPd_{0.025}/SiO₂ catalyst reduced at 250 or 500 °C were attributed to CO adsorbed on Ag^{x+} species and linearly adsorbed on isolated Pd sites, respectively. For the sample reduced at 250 °C, the relative intensity of the band at 2041 cm⁻¹ increased with increasing CO pressure as compared to the band at 2028 cm⁻¹, indicating the initial CO adsorption on the terrace Pd sites and subsequently on the edge/corner Pd sites. In addition, the band at 2028 cm⁻¹ disappeared after reducing the sample at higher temperatures, while the band at 2041 cm⁻¹ was observed independent to CO pressure, indicating loss of terrace Pd atoms at high reducing temperature. In another of their recent work,³⁰ a blue shift of 6 cm⁻¹ was observed in the CO adsorbed FTIR spectra of 0.06Pt–Cu/SiO₂ and 0.1Pt–Cu/SiO₂ when compared with that of monometallic Cu/SiO₂ catalyst, indicating modification on both electronic and geometric structure of Cu with atomically dispersed Pt with formation of Pt-Cu SAA structure. In the work performed by Giannakakis et al.,³¹ *in situ* FTIR was employed to study the dispersion of Ni on supported Au NPs. In the FTIR spectra, besides the Au-CO peak at 2117 cm⁻¹, a shoulder at around 2100 cm⁻¹ appears, indicating the atomic dispersion of Ni atoms in Ni_{0.005}Au/SiO₂.

Figure 6. *In situ* FTIR studies of (A) the evolution of adsorbed CO molecules on 0.017% Rh/SiO₂ at room temperature (the catalyst was exposed to pure CO and purged with He for $t = 0$ min, thereafter, NO was introduced); (B) the evolution of surface species in a flowing mixture of 1.5% NO and 4.5% CO balanced with He during catalysis. Reprinted with permission from Ref ³². Copyright 2018, American Chemical Society. (C) FTIR spectra of the C-H stretching band of adsorbed ethoxy species. Reprinted with permission from Ref ³³. Copyright 2018, Elsevier B.V.

Recent studies have proven the important role of *in situ* FTIR for tracking the reaction pathways of the reaction catalyzed on SACs. In the work done by Zhang et al.,³² *in situ* FTIR was performed to study the mechanism for the reduction of NO with CO catalyzed on atomically dispersed Rh atoms anchored on SiO₂. As shown in Figure 6A, the stretching vibration of the linear adsorbed C-O upshifts from ~ 2058 cm⁻¹ to 2088 cm⁻¹ after NO is introduced, indicating co-adsorption of CO and

NO on single-Rh-atom sites. The evolution of adsorbates/intermediates for 0.017% Rh/SiO₂ in a flowing mixture of 1.5% NO and 4.5% CO during catalysis at different temperatures is shown in Figure 6B. From which, the characteristic vibrational double peaks of the product CO₂ (2280-2400 cm⁻¹) are detected at 150 °C, suggesting the reaction of co-adsorbed CO and NO on single-Rh-atom sites. Recently, via applying *in situ* FTIR, Shan et al. observed development of the C=O stretching peak of acetaldehyde at 1723 cm⁻¹ in Ni_{0.01}Cu SAA catalyzed non-oxidative ethanol dehydrogenation reaction (Figure 6C).³³ Results from this work demonstrate direct participation of Ni atoms in Ni_{0.01}Cu for C-H bond cleavage of ethoxy species at lower temperatures when compared to Cu NPs.

2.3. *Operando* XAS

XAS, including both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), offers a powerful technique to determine geometric and electronic structure of active sites in catalysts. For the XANES region, which results from the excitation of core electron to the valence and conduction bands, is typically used to determine the electronic state of the probed atom. While the EXAFS region, originating from the scattering interactions of photoelectron with the neighboring atoms, is commonly used for local geometric structure and coordination environment determination. With the combination of SACs as model platforms, *operando* XAS affords us a great opportunity for monitoring the dynamic behaviors of both the geometric structure and electronic environment of catalytic sites at atomic scale.

Figure 7. (A) Normalized *operando* XANES spectra, and (B) Fourier transformed EXAFS spectra for A-Ni-NG at various biases. Reprinted with permission from Ref ³⁴. Copyright 2018, Springer Nature.

Over the past few years, *operando* XAS studies have been widely carried out on SACs in electrochemical reactions. For instance, monitored with *operando* XAS measurements, the structural evolution of the NiN₄ site during electrochemical CO₂ reduction reaction (CRR) was studied by Yang et al.³⁴ As shown in Figure 7A, the Ni K-edge was observed shifted approximately 0.4 eV to higher energy in CO₂-saturated KHCO₃ solution when compared to the one in Ar-saturated KHCO₃ solution, indicating charge transfer from Ni(I) to the C_{2p} orbital in CO₂ with formation of CO₂^{δ-} species. In addition, the main peak of EXAFS spectrum for single-Ni-atom A-Ni-NG shifts approximately 0.04 $\text{\AA}$ to longer lengths during electrochemical CO₂ reduction (Figure 7B), suggesting the expansion of the Ni–N bond with the adsorption of CO₂ on single-Ni-atom sites. In the work conducted by Genovese et al., *operando* XAS measurements were carried out to study the connection between the high Faraday efficiency (97.4%) and selectivity to acetic acid in CRR and the N-coordinated single atom or polyatomic Fe species.³⁵ As shown in Figure 8A, the spectrum recorded at -0.5 V (vs. RHE) was fitted with the spectra of Fe(III) and Fe(0) components. The negative residual pre-edge intensity

(blue line) indicates the down-shift of the edge in the Fe(II) region, while the positive residual suggests the overestimated contribution of the metallic contribution. The EXAFS spectrum for Fe/N-C at -0.5 V (vs. RHE) shows a characteristic bimodal distribution of Fe-(O, OH) bonding lengths, which is explained as the partial reduction of Fe(III) to Fe(II) species (Figure 8B). Results of this work suggest that the formation of N-coordinated Fe(II) sites in the form of single atoms or polyatomic Fe species is critical for the activity to acetic acid at -0.5 V (vs. RHE) in CRR.

Figure 8. (A) Normalized XANES spectra, and (B) Fourier transformed EXAFS spectra for Fe/N-C at various biases. Reprinted with permission from Ref ³⁵. Copyright 2018, Springer Nature.

Operando XAS measurements were also carried out by Jiang et al. for probing the coordination environment and electronic structure of single-Ni-atom sites during CRR.³⁶ Negligible changes were observed in the XAS spectra recorded at various biases, suggesting the high stability of the single-Ni atom catalysts, which ensures their practical use in long-term CRR electrolysis. Similar results were also reported in a recent work performed by Zhang et al.,³⁷ negligible changes were detected in the XAS spectra of CoPc catalysts with well-defined Co-N₄ sites during electrocatalytic CRR, indicating that the coordination structure and valence state of Co²⁺ remained unchanged at reduced potential.

Figure 9. Normalized *operando* XANES spectra for (A) Co-N-C (Co0.5) and (B) Fe-N-C (Fe0.5) catalysts measured in N₂-saturated electrolyte at various biases. Insets in (A) and (B) are differential $\Delta\mu$ XANES spectra obtained at every potential subtracted the normalized spectrum recorded at 0.2 V (vs. RHE). Reprinted with permission from Ref ³⁸. Copyright 2017, Springer Nature. Fourier transformed *operando* EXAFS spectra recorded at multiple temperatures during CO oxidation for atomically dispersed Pd (0.5 wt%) supported on (C) alumina and (D) La-alumina. Reprinted with permission from Ref ³⁹. Copyright 2014, Springer Nature.

In the work performed by Zitolo et al., *operando* XAS measurements were carried out to study the structure and electronic state evolution of Co-N-C (Co0.5) and Fe-N-C (Fe0.5) catalysts during ORR.³⁸ The normalized *operando* XANES spectra for Co0.5 recorded in N₂-saturated electrolyte at various biases are shown in Figure 9A. Negligible changes of the Co K-edge XANES spectra in N₂-saturated electrolyte could be observed, while a clear variation of the Co K-edge XANES spectra was observed between 7720 and 7735 eV in O₂-saturated electrolyte, suggesting that the active sites

in Co_{0.5} are less oxytropic. However, a large change of the Fe K-edge XANES spectra with electrochemical potential was observed on Fe_{0.5} in N₂-saturated electrolyte (Figure 9B), indicating that the change in XANES spectra for Fe_{0.5} is primarily controlled by electrochemical potential instead of O₂ adsorption. The potential-dependence of the XANES spectra for Fe_{0.5} was attributed to the possible structural changes with reorganization of N/C ligands and/or spin-crossover of Fe(II).

Besides electrochemical reactions, *operando* XAS is also able to give deep insights into the nature of atomically dispersed active sites in CO oxidation reaction catalyzed on SACs. For instance, Peterson et al. carried out *operando* XAS measurements to examine the nature of atomically dispersed Pd sites in CO oxidation reaction as well as the structural relationship between La and Pd on alumina.³⁹ As shown in Figure 9C, the Pd-O peak intensity of Pd/alumina was observed decreased with increasing reaction temperature, accompanying with an increase in the Pd-metal peak intensity. However, for Pd/La-alumina, no Pd-metal peak could be noticed until 90 °C (Figure 9D). These results suggest that atomically dispersed La³⁺ might be critical for stabilizing atomically dispersed Pd on alumina surface. In addition, the decrease of Pd-O peak resulted in the average Pd-O coordination number significantly < 4, indicating presence of a third chemical state for Pd (Pd¹⁺) in Pd/La-alumina during reaction, which was considered as the active site for CO oxidation. Recently, *operando* EXAFS measurements at the Pd L₃ edge were carried out by Hermida et al. to probe the adsorption of CO at different temperatures.⁴⁰ A significant CO uptake on Pd surface was observed at room temperature, while no CO coverage at 250 °C, indicating fast CO desorption on the surface of Pd NPs. However, significant CO adsorption on Pd₁ catalysts could be still observed at 250 °C, suggesting the much stronger CO adsorption on single-Pd-atom sites.

Additionally, with application of *operando* XAS, Nakatsuka et al., monitored the structural

transformation of the active center from single-sites to nanoparticles during heat treatment in the synthesis of carbon-supported Co catalysts.⁴¹ Results of this work prove that single-site structure of Co–O–C and Co–N–C in Co(salen) complex can be retained at 450 °C and gradually transformed into metallic form at around 650 °C.

These recent works have clearly highlighted the advantages of *operando* XAS technique with SACs as model platforms for monitoring the evolution of both geometric structure and electronic environment of catalytic sites at atomic scale during reaction. However, the recent advances with the application of *operando* XAS technique appear to highlight the complexity of reaction mechanisms for various catalysis systems, which is probably the main reason for the large variations in the final results obtained from different research groups under similar reaction conditions. Even for a very clear change of the *operando* XAS spectra, which may result from the changes including valence state, coordination environment, electronic state, and etc., the analysis could be quite complex. To this end, the combined use of multiple *operando* techniques in single atom catalysis should offer the most effective way to give deeper insights into both the stepwise elementary reaction mechanism and the electronic environment of the smallest catalytic blocks.

2.4. *In situ* AP-XPS

X-ray photoelectron spectroscopy (XPS), as a highly surface-sensitive and element-specific technique, is powerful in studying surface elemental composition and oxidation state of heterogeneous catalyst.⁴² The recent fast development realized *in situ* AP-XPS experiments for probing the underlying mechanism of various heterogeneous catalytic processes under realistic conditions.⁴³ Recently, *in situ* AP-XPS technique has shown important role to study thermal stability and cationic states of atomically dispersed metal atoms in single-atom alloy (SAA) catalysts.⁴⁴⁻⁴⁵

Figure 10. *In situ* AP-XPS spectra of Pt 4d for (A) 0.1 at% Pt/Co₃O₄, (B) 0.5 at% Pt/Co₃O₄, and Pt 4f photoemission features for (C) 0.5 at% Pt/Co₃O₄, and (D) 0.5 at% Pt/SiO₂ during catalysis in reduction of NO with H₂ at different temperatures. Reprinted with permission from Ref⁴⁴. Copyright 2016, American Chemical Society.

In the work performed by Nguyen et al.,⁴⁴ *in situ* AP-XPS studies were carried out to probe the cationic state of Pt atom in singly dispersed bimetallic Pt₁Co_m sites during catalysis in reduction of NO with H₂ at various temperatures. As confirmed from the *in situ* EXAFS studies, the removal of lattice oxygen atoms in Pt-O-Co on the surface of Co₃O₄ through reduction step allows direct bonding between Pt and Co atoms to form bimetallic Pt₁Co_m sites. *In situ* AP-XPS spectra of Pt 4d for 0.1 at% and 0.5 at% Pt/Co₃O₄ are shown in Figure 10A-B. Negligible changes were observed for the peaks at 317.0 eV in the temperature range from 25 to 300 °C, which excludes the possibility of

formation of metallic Pt nanoparticles during catalysis. However, metallic state Pt was observed at 250 °C in the mixture of NO and H₂ with 0.5 at% Pt/SiO₂ as catalyst, indicating the distinctly different coordination environment of Pt in 0.5 at% Pt/SiO₂ as compared to 0.1 at% and 0.5 at% Pt/Co₃O₄ (Figure 10C-D). These *in situ* AP-XPS results clearly confirm that Pt atoms of singly dispersed bimetallic sites are in cationic state during reduction of NO with H₂ up to 300 °C.

Figure 11. (A) *In situ* AP-XPS spectra of Pt 4f_{7/2} for Pt/Cu(111) SAA in sequence from top to bottom: the as-deposited surface in 20 mTorr CO at 300 K; after CO was pumped down and heated to 500 K in ultrahigh vacuum (UHV); after CO was introduced in 0.1, 2, and 20 mTorr at 500 K. (B) The corresponding fraction of each Pt component obtained at each indicated experimental condition. (C) Graphic mechanism for CO induced surface segregation of Pt atoms on Pt/Cu(111) SAA. Reprinted

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Recently, *in situ* AP-XPS experiments were performed by Simonovis et al. to study the behaviors of surface Pt atoms on Pt/Cu(111) SAA under reaction conditions.⁴⁵ As shown in Figure 11A, the Pt 4f_{7/2} spectra were fitted by three components with binding energy at 70.95, 71.40, and 72.25 eV, which could be assigned to free surface Pt, subsurface Pt, and CO bound surface Pt, respectively. The corresponding fraction of Pt components are shown in Figure 11B. As shown, after heating at 500 K in ultrahigh vacuum (UHV), the fraction of subsurface Pt was observed increased, suggesting occurrence of diffusion of surface and subsurface Pt atoms during heating. The fraction of CO-bound surface Pt was observed increased with increasing CO pressure, indicating adsorption of CO on surface Pt atoms. Moreover, the increase of the total detected amount of Pt from ~78% to ~95% indicates that the adsorption of CO could probably draw out Pt atoms in bulk (Figure 11C). Results of this work clearly demonstrate the significance of *in situ* AP-XPS technique for studying the changes of surface structure and composition of atomically dispersed atoms in SAAs under reaction conditions.

2.5. *In situ* MS

Identifying reaction intermediates is highly important for in-depth understanding of the underlying reaction mechanisms in catalytic processes. MS, by ionizing chemical species and sorting the ions based on their mass-to-charge ratio, has both qualitative and quantitative uses including identifying the structure of an unknown compound, quantifying the amount of a compound, and etc, which is powerful for the identification of reactive intermediates and reaction pathways.

Figure 12. (A) *Operando* DEMS signals collected during CV experiments in CO- or Ar-saturated electrolyte. Reprinted with permission from Ref⁴⁶. Copyright 2018, American Chemical Society. (B) The increased rate of the products at 0–600 min obtained from *operando* TOF-MS. The *operando* TOF-MS data collected from 1.0 (C), 1.5 (D), and 1.8 (E) MPa $^{13}CH_4$ in methane oxidation. Reprinted with permission from Ref⁴⁷. Copyright 2018, Elsevier Inc.

Kwon et al. applied *operando* electrochemical mass spectrometry (DEMS) to study the promoting effect of CO towards electrochemical hydrogen evolution reaction (HER) on carbon supported single Pt atom catalyst with high sulfur content (Pt/HSC).⁴⁶ As shown in Figure 12A, no detectable signals of methane, alcohol, and ethylene species could be observed during CV scans of Pt/HSC in CO-saturated electrolyte. In addition, no other non-volatile products were detected by *ex-situ* nuclear magnetic resonance. Results of this work indicate that the increased current density on Pt/HSC in the presence of CO is due to the enhanced HER kinetics instead of electrochemical CO reduction. In the

work performed by Cui et al.,⁴⁷ *operando* time-of-flight MS (TOF-MS) was carried out to track the evolution of liquid products in methane conversion reaction with graphene confined single Fe atom non-precious catalyst. By extracting and analyzing the products in real time throughout the reaction, CH₃OH and CH₃OOH were observed increased gradually over time, while HOCH₂OOH and HCOOH remained unchanged in the first 100 min and significantly increased in the last 300 min (Figure 12B-E), suggesting that CH₄ was first oxidized to CH₃OH and CH₃OOH, and then further oxidized to HOCH₂OOH and HCOOH.

Table 1. Selected techniques that are capable for characterization of single-atom catalysts.

Technique	Information probed	Limitations	<i>In situ/operando</i>
ETEM/STM	Directly imaging atom with real time atomic resolution	Local region of sample	<i>In situ</i>
FTIR	Vibration mode of probe molecules adsorbed on surface sites	Indirect information	<i>In situ/operando</i>
XAS	Bulk geometry included, Coordination environment, Electronic state	“Average” information, Limited beam time	<i>In situ/operando</i>
AP-XPS	Elemental composition, Oxidation state near surface	Low atomic-resolution	<i>In situ</i>
Mössbauer spectroscopy	Coordination symmetry, Chemical state, Spin state	“Selected” elements (Fe, Sn, Au, Ru, Ir, etc.)	-

3. Summary and Outlook

In summary, recent studies have clearly highlighted the advantages of *in situ/operando* techniques

accompanied with SACs as model platforms for capturing the reaction intermediates, identifying the active sites, and even monitoring the dynamic behaviors of both the geometric structure and electronic environment of catalytic sites. For instance, *in situ* TEM and STM with real time atomic resolution is powerful for directly probing the single atom dynamics under operational conditions, *in situ* FTIR is highly sensitive to study the vibration mode of the adsorbed CO molecule on the active single atom site, and *in situ* AP-XPS could provide the information of surface elemental composition and oxidation state of SACs. However, up to now, most of these *in situ* techniques are performed only for the characterization of SACs without simultaneous catalytic activity/selectivity measurement. Although *operando* XAS technique have been performed to monitor the evolution of catalytic sites at atomic scale, results from these recently emerged *operando* techniques for characterization of SACs appear to highlight the complexity of the mechanisms for various catalytic reactions, which are still far from enough to clearly understand the nature of catalytic sites and the structure-performance relationship. Moreover, the reactive intermediates, reaction pathways, real active sites, stepwise elementary reaction mechanisms, and etc. for most catalytic processes are still indistinct.

To this end, efforts are urgently needed toward the development of special reaction cells that allow integrating *in situ* characterization with activity/selectivity measurement. In addition, as shown in Table 1, each technique has strengths and limitations, the integrated utilization of multiple *in situ/operando* techniques is highly desired in studying SACs under dynamic conditions for revealing the structure-activity/selectivity relationships and underlying stepwise elementary reaction mechanisms. For instance, the combined use of *in situ/operando* FTIR, XPS and XAS might obtain surface-specific chemical information including local coordination environment, structure and

oxidation state of SACs during catalytic processes. With the further integration of *in situ* MS, the evolution of intermediates produced over SACs could be provided.

In addition, the exploration of novel synthetic strategies to realize controllable synthesis of SACs with definite coordination environment as model systems and the development of novel *operando* techniques with high atomic-resolution are highly desired. Moreover, the further combination of theoretical calculations should offer the most effective way to give deeper insights into both the stepwise elementary reaction mechanism and the electronic environment of the smallest catalytic blocks. The insights thus obtained will contribute as the stepping-stone toward the clear identification of the nature of catalytic sites and benefit for the further design of highly active heterogeneous catalysts for practical applications.

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References

1. Qiao, B.; Wang, A.; Yang, X.; Allard, L. F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T., Single-Atom Catalysis of CO Oxidation Using Pt₁/FeO_x, *Nat. Chem.* **2011**, 3, 634-641.
2. Wang, A.; Li, J.; Zhang, T., Heterogeneous Single-Atom Catalysis, *Nat. Rev. Chem.* **2018**, 2, 65-81.
3. Zhang, L.; Ren, Y.; Liu, W.; Wang, A.; Zhang, T., Single-Atom Catalyst: A Rising Star for Green Synthesis of Fine Chemicals, *National Science Review* **2018**, 5, 653-672.
4. Liu, J., Catalysis by Supported Single Metal Atoms, *ACS Catal.* **2017**, 7, 34-59.
5. Yang, X. F.; Wang, A. Q.; Qiao, B. T.; Li, J.; Liu, J. Y.; Zhang, T., Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis, *Acc. Chem. Res.* **2013**, 46, 1740-1748.
6. Zhu, C. Z.; Fu, S. F.; Shi, Q. R.; Du, D.; Lin, Y. H., Single-Atom Electrocatalysts, *Angew. Chem. Int. Ed.* **2017**, 56, 13944-13960.
7. Zhang, H. B.; Liu, G. G.; Shi, L.; Ye, J. H., Single-Atom Catalysts: Emerging Multifunctional Materials in Heterogeneous Catalysis, *Adv. Energy Mater.* **2018**, 8, 1701343.
8. Liu, L.; Corma, A., Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles, *Chem. Rev.* **2018**, 118, 4981-5079.
9. Mitchell, S.; Vorobyeva, E.; Pérez-Ramírez, J., The Multifaceted Reactivity of Single-Atom Heterogeneous Catalysts, *Angew. Chem. Int. Ed.* **2018**, 57, 15316-15329.
10. Chen, Y.; Ji, S.; Chen, C.; Peng, Q.; Wang, D.; Li, Y., Single-Atom Catalysts: Synthetic Strategies and Electrochemical Applications, *Joule* **2018**, 2, 1242-1264.
11. Li, X.; Huang, X.; Xi, S.; Miao, S.; Ding, J.; Cai, W.; Liu, S.; Yang, X.; Yang, H.; Gao, J.; Wang, J.; Huang, Y.; Zhang, T.; Liu, B., Single Cobalt Atoms Anchored on Porous N-Doped Graphene with

Dual Reaction Sites for Efficient Fenton-like Catalysis, *J. Am. Chem. Soc.* **2018**, 140, 12469-12475.

12. Lang, R.; Li, T.; Matsumura, D.; Miao, S.; Ren, Y.; Cui, Y.-T.; Tan, Y.; Qiao, B.; Li, L.; Wang, A.; Wang, X.; Zhang, T., Hydroformylation of Olefins by a Rhodium Single-Atom Catalyst with Activity Comparable to $\text{RhCl}(\text{PPh}_3)_3$, *Angew. Chem. Int. Ed.* **2016**, 55, 16054-16058.

13. Li, X.; Wang, H. Y.; Yang, H.; Cai, W.; Liu, S.; Liu, B., In Situ/Operando Characterization Techniques to Probe the Electrochemical Reactions for Energy Conversion, *Small Methods* **2018**, 2, 1700395.

14. Weishen, Y.; Kaiyue, Z.; Xuefeng, Z., Application of In Situ Techniques for the Characterization of NiFe based Oxygen Evolution Reaction (OER) Electrocatalysts, *Angew. Chem. Int. Ed.* **2018**, 57, 2-16.

15. Yuan, Y.; Li, M.; Bai, Z.; Jiang, G.; Liu, B.; Wu, T.; Chen, Z.; Amine, K.; Lu, J., The Absence and Importance of Operando Techniques for Metal-Free Catalysts, *Adv. Mater.* **2018**, 30, 1805609.

16. Lukashuk, L.; Foettinger, K., In Situ and Operando Spectroscopy: A Powerful Approach Towards Understanding Catalysts, *Johnson Matthey Tech.* **2018**, 62, 316-331.

17. Jodłowski, P.; Łojewska, J. In *Molecular Spectroscopy—Experiment and Theory: From Molecules to Functional Materials*, Koleżyński, A., Król, M., Eds. Springer International Publishing: Cham, **2019**; pp 333-359.

18. Bañares, M. A., Operando Methodology: Combination of In Situ Spectroscopy and Simultaneous Activity Measurements under Catalytic Reaction Conditions, *Catal. Today* **2005**, 100, 71-77.

19. Bañares, M. A., Operando Spectroscopy: the Knowledge Bridge to Assessing Structure–Performance Relationships in Catalyst Nanoparticles, *Adv. Mater.* **2011**, 23, 5293-5301.

20. Jinschek, J. R., Advances In the Environmental Transmission Electron Microscope (ETEM) for

Nanoscale In Situ Studies of Gas–Solid Interactions, *Chem. Commun.* **2014**, 50, 2696-2706.

21. Gai, P. L.; Boyes, E. D., Advances in Atomic Resolution In Situ Environmental Transmission Electron Microscopy and 1 Å Aberration Corrected In Situ Electron Microscopy, *Microsc. Res. Tech.* **2009**, 72, 153-164.

22. Gai, P. L.; Boyes, E. D., In-situ Environmental (Scanning) Transmission Electron Microscopy of Catalysts at the Atomic Level, *J. Phys. Conf. Ser.* **2014**, 522, 012002.

23. Gai, P. L.; Lari, L.; Ward, M. R.; Boyes, E. D., Visualisation of Single Atom Dynamics and Their Role in Nanocatalysts under Controlled Reaction Environments, *Chem. Phys. Lett.* **2014**, 592, 355-359.

24. Liu, L. C.; Zakharov, D. N.; Arenal, R.; Concepcion, P.; Stach, E. A.; Corma, A., Evolution and Stabilization of Subnanometric Metal Species in Confined Space by In Situ TEM, *Nat. Commun.* **2018**, 9, 574.

25. Wei, S.; Li, A.; Liu, J.-C.; Li, Z.; Chen, W.; Gong, Y.; Zhang, Q.; Cheong, W.-C.; Wang, Y.; Zheng, L.; Xiao, H.; Chen, C.; Wang, D.; Peng, Q.; Gu, L.; Han, X.; Li, J.; Li, Y., Direct Observation of Noble Metal Nanoparticles Transforming to Thermally Stable Single Atoms, *Nat. Nanotech.* **2018**, 13, 856–861.

26. Zhao, J.; Deng, Q. M.; Avdoshenko, S. M.; Fu, L.; Eckert, J.; Ruemmeli, M. H., Direct In Situ Observations of Single Fe Atom Catalytic Processes and Anomalous Diffusion at Graphene Edges, *Proc. Natl. Acad. Sci. U. S. A.* **2014**, 111, 15641-15646.

27. Patera, L. L.; Bianchini, F.; Africh, C.; Dri, C.; Soldano, G.; Mariscal, M. M.; Peressi, M.; Comelli, G., Real-Time Imaging of Adatom-Promoted Graphene Growth on Nickel, *Science* **2018**, 359, 1243-1246.

28. Yang, S.; Tak, Y. J.; Kim, J.; Soon, A.; Lee, H., Support Effects in Single-Atom Platinum Catalysts for Electrochemical Oxygen Reduction, *ACS Catal.* **2017**, *7*, 1301-1307.
29. Pei, G. X.; Liu, X. Y.; Wang, A. Q.; Lee, A. F.; Isaacs, M. A.; Li, L.; Pan, X. L.; Yang, X. F.; Wang, X. D.; Tai, Z. J.; Wilson, K.; Zhang, T., Ag Alloyed Pd Single-Atom Catalysts for Efficient Selective Hydrogenation of Acetylene to Ethylene in Excess Ethylene, *ACS Catal.* **2015**, *5*, 3717-3725.
30. Yang, C. J.; Miao, Z. L.; Zhang, F.; Li, L.; Liu, Y. T.; Wang, A. Q.; Zhang, T., Hydrogenolysis of Methyl Glycolate to Ethanol Over a Pt-Cu/SiO₂ Single-Atom Alloy Catalyst: A Further Step from Cellulose to Ethanol, *Green Chem.* **2018**, *20*, 2142-2150.
31. Giannakakis, G.; Trimpalis, A.; Shan, J. J.; Qi, Z.; Cao, S. F.; Liu, J. L.; Ye, J. C.; Biener, J.; Flytzani-Stephanopoulos, M., NiAu Single Atom Alloys for the Non-oxidative Dehydrogenation of Ethanol to Acetaldehyde and Hydrogen, *Top. Catal.* **2018**, *61*, 475-486.
32. Zhang, S. R.; Tang, Y.; Nguyen, L.; Zhao, Y. F.; Wu, Z. L.; Goh, T. W.; Liu, J. J. Y.; Li, Y. Y.; Zhu, T.; Huang, W. Y.; Frenkel, A. I.; Li, J.; Tao, F. F., Catalysis on Singly Dispersed Rh Atoms Anchored on an Inert Support, *ACS Catal.* **2018**, *8*, 110-121.
33. Shan, J. J.; Liu, J. L.; Li, M. W.; Lustig, S.; Lee, S.; Flytzani-Stephanopoulos, M., NiCu Single Atom Alloys Catalyze the C-H Bond Activation in the Selective Non-Oxidative Ethanol Dehydrogenation Reaction, *Appl. Catal. B* **2018**, *226*, 534-543.
34. Yang, H. B.; Hung, S.-F.; Liu, S.; Yuan, K.; Miao, S.; Zhang, L.; Huang, X.; Wang, H.-Y.; Cai, W.; Chen, R.; Gao, J.; Yang, X.; Chen, W.; Huang, Y.; Chen, H. M.; Li, C. M.; Zhang, T.; Liu, B., Atomically Dispersed Ni(i) as the Active Site For Electrochemical CO₂ Reduction, *Nat. Energy* **2018**, *3*, 140-147.

35. Genovese, C.; Schuster, M. E.; Gibson, E. K.; Gianolio, D.; Posligua, V.; Grau-Crespo, R.; Cibir, G.; Wells, P. P.; Garai, D.; Solokha, V.; Calderon, S. K.; Velasco-Velez, J. J.; Ampelli, C.; Perathoner, S.; Held, G.; Centi, G.; Arrigo, R., Operando Spectroscopy Study of the Carbon Dioxide Electro-Reduction by Iron Species on Nitrogen-Doped Carbon, *Nat. Commun.* **2018**, 9, 935.
36. Jiang, K.; Siahrostami, S.; Zheng, T. T.; Hu, Y. F.; Hwang, S.; Stavitski, E.; Peng, Y. D.; Dynes, J.; Gangisetty, M.; Su, D.; Attenkofer, K.; Wang, H. T., Isolated Ni Single Atoms in Graphene Nanosheets for High-Performance CO₂ Reduction, *Energy Environ. Sci.* **2018**, 11, 893-903.
37. Zhang, Z.; Xiao, J.; Chen, X.-J.; Yu, S.; Yu, L.; Si, R.; Wang, Y.; Wang, S.; Meng, X.; Wang, Y.; Tian, Z.-Q.; Deng, D., Understanding the Reaction Mechanisms of Well-Defined Metal-N₄ Sites in Electrocatalytic CO₂ Reduction, *Angew. Chem. Int. Ed.* **2018**, 57, 16339–16342.
38. Zitolo, A.; Ranjbar-Sahraie, N.; Mineva, T.; Li, J.; Jia, Q.; Stamatini, S.; Harrington, G. F.; Lyth, S. M.; Krttil, P.; Mukerjee, S.; Fonda, E.; Jaouen, F., Identification of Catalytic Sites in Cobalt-Nitrogen-Carbon Materials for the Oxygen Reduction Reaction, *Nat. Commun.* **2017**, 8, 957.
39. Peterson, E. J.; Delariva, A. T.; Lin, S.; Johnson, R. S.; Guo, H.; Miller, J. T.; Kwak, J. H.; Peden, C. H. F.; Kiefer, B.; Allard, L. F.; Ribeiro, F. H.; Datye, A. K., Low-Temperature Carbon Monoxide Oxidation Catalysed by Regenerable Atomically Dispersed Palladium on Alumina, *Nat. Commun.* **2014**, 5, 4885.
40. Piernavieja-Hermida, M.; Lu, Z.; White, A.; Low, K. B.; Wu, T. P.; Elam, J. W.; Wu, Z. L.; Lei, Y., Towards ALD Thin Film Stabilized Single-Atom Pd-1 Catalysts, *Nanoscale* **2016**, 8, 15348-15356.
41. Nakatsuka, K.; Yoshii, T.; Kuwahara, Y.; Mori, K.; Yamashita, H., Controlled Synthesis of Carbon-Supported Co Catalysts from Single-Steps to Nanoparticles: Characterization of the Structural

Transformation and Investigation of their Oxidation Catalysis, *Phys. Chem. Chem. Phys.* **2017**, 19, 4967-4974.

42. Nakamura, M. In *Compendium of Surface and Interface Analysis*, The Surface Science Society of, J., Ed. Springer Singapore: Singapore, **2018**; pp 833-842.

43. Favaro, M.; Drisdell, W. S.; Marcus, M. A.; Gregoire, J. M.; Crumlin, E. J.; Haber, J. A.; Yano, J., An Operando Investigation of (Ni-Fe-Co-Ce)O_x System as Highly Efficient Electrocatalyst for Oxygen Evolution Reaction, *ACS Catal.* **2017**, 7, 1248-1258.

44. Nguyen, L.; Zhang, S. R.; Wang, L.; Li, Y. Y.; Yoshida, H.; Patlolla, A.; Takeda, S.; Frenkel, A. I.; Tao, F., Reduction of Nitric Oxide with Hydrogen on Catalysts of Singly Dispersed Bimetallic Sites Pt₁Co and Pd₁Co, *ACS Catal.* **2016**, 6, 840-850.

45. Simonovis, J. P.; Hunt, A.; Palomino, R. M.; Senanayake, S. D.; Waluyo, I., Enhanced Stability of Pt-Cu Single-Atom Alloy Catalysts: In Situ Characterization of the Pt/Cu(111) Surface in an Ambient Pressure of CO, *J. Phys. Chem. C* **2018**, 122, 4488-4495.

46. Kwon, H. C.; Kim, M.; Grote, J. P.; Cho, S. J.; Chung, M. W.; Kim, H.; Won, D. H.; Zeradjanin, A. R.; Mayrhofer, K. J. J.; Choi, M.; Kim, H.; Choi, C. H., Carbon Monoxide as a Promoter of Atomically Dispersed Platinum Catalyst in Electrochemical Hydrogen Evolution Reaction, *J. Am. Chem. Soc.* **2018**, 140, 16198-16205.

47. Cui, X. J.; Li, H. B.; Wang, Y.; Hu, Y. L.; Hua, L.; Li, H. Y.; Han, X. W.; Liu, Q. F.; Yang, F.; He, L. M.; Chen, X. Q.; Li, Q. Y.; Xiao, J. P.; Deng, D. H.; Bao, X. H., Room-Temperature Methane Conversion by Graphene-Confined Single Iron Atoms, *Chem* **2018**, 4, 1902-1910.