OPERANDO DYNAMIC ELECTROCATALYSIS

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1.Introduction

Catalysis serves as the cornerstone of modern industrial processes, underpinning everything from large-scale ammonia production via the Haber-Bosch process to petroleum refining and the emerging field of renewable energy conversion. The efficiency and selectivity of heterogeneous catalysts, particularly those based on metal nanoparticles, are governed by a complex interplay of factors including particle size, morphology, chemical composition, and—critically—their dynamic structural evolution under operating conditions [1-3]. Recent breakthroughs in operando characterization techniques have fundamentally changed our understanding of catalytic systems, revealing that far from being static, catalysts undergo continuous and often dramatic transformations during electrochemical reactions such as CO_2 reduction (CO_2RR) [4-10]. Rather than viewing these structural changes as undesirable, a new paradigm is emerging where such dynamic behavior is recognized as an opportunity to enhance catalytic performance. This perspective examines the latest advances in understanding structural evolution across various catalytic systems, with a particular emphasis on Cu-based and bimetallic nanocatalysts, such as Pt_3Ni nanoframes [11]. We explore how dynamic surface reconstruction, nanoparticle coalescence, and microenvironment engineering can be leveraged to optimize electrocatalytic processes. Furthermore, we discuss cutting-edge operando characterization techniques that are revolutionizing our ability to observe these transformations in real time, and outline future directions for designing next-generation dynamic catalysts for sustainable energy applications.

Traditional approaches to catalyst design have largely treated catalytic materials as static entities, with the implicit assumption that the structure characterized before and after reactions remains unchanged during operation. However, a growing body of evidence from advanced in situ and operando characterization techniques has fundamentally challenged this notion. It is now clear that most catalytic systems undergo significant structural evolution under reaction conditions, with changes occurring across multiple length and time scales.

This dynamic behavior is not merely an academic curiosity; it has profound implications for catalytic performance. In some cases, structural evolution leads to catalyst deactivation, as in the well-known sintering of supported metal nanoparticles at high temperatures. However, there are increasing examples where structural changes actually create more active catalytic sites. The Pt_3Ni nanoframe catalysts, for instance, develop highly active Pt-skin surfaces through electrochemical leaching of nickel [11]. Similarly, copper catalysts for CO_2 reduction often require an "activation" period where

the initial structure transforms into a more active configuration. These observations suggest that the traditional distinction between catalyst "activation" and "deactivation" may be overly simplistic—what matters is not whether the catalyst changes, but how it changes.

This realization has given rise to the concept of "dynamic catalysis," where structural evolution is not merely tolerated but actively engineered to enhance performance. This paradigm shift necessitates new approaches to catalyst design, where materials are optimized not only for their initial state but also for their evolutionary trajectory under operating conditions. It also requires advanced characterization tools capable of tracking these transformations in real-time, under realistic reaction environments. The following sections explore these concepts in detail, focusing first on fundamental mechanisms of structural evolution, then on specific catalytic systems, and finally on emerging strategies to harness dynamic behavior for improved catalytic performance.

2. Structural Evolution of Nanocatalysts Under Operando Conditions

The restructuring of catalyst surfaces under reaction conditions can be understood through the lens of surface thermodynamics. In vacuum or inert environments, surfaces tend to minimize their free energy by forming close-packed planes with the lowest surface energy. However, under catalytic conditions, the presence of adsorbates can dramatically alter this balance. The adsorption energy of reaction intermediates often varies significantly between different surface sites—for example, step edges typically bind adsorbates more strongly than terraces. When the energy gained from stronger adsorption outweighs the energy cost of creating undercoordinated sites, the surface will reconstruct to maximize the number of favorable binding sites.

This phenomenon is particularly pronounced in electrocatalysis, where the applied potential provides an additional thermodynamic driving force. The Nernst equation relates the electrode potential to the surface free energy, indicating that changes in potential can directly induce surface reconstruction. This is clearly illustrated by Pourbaix diagrams, which map the stable phases of metals as a function of potential and pH. For instance, copper is known to form various oxide and hydroxide phases at oxidizing potentials, while reducing conditions favor metallic copper with reconstructed surfaces.

While thermodynamics determines the equilibrium state, kinetics governs how quickly a catalyst can reach that state. Surface diffusion plays a critical role—metal atoms must be able to migrate across the surface for reconstruction to occur. This mobility is highly temperature-dependent, following an Arrhenius relationship, but can also be strongly influenced by the presence of adsorbates. Some species, like carbon monoxide, are known to dramatically increase surface mobility through the so-called "adsorbate-induced surface diffusion" mechanism. In electrochemical systems, an additional kinetic factor comes into play: the potential-dependent strength of metal-metal bonds.

2.1 Case Study: Bimetallic Pt_3Ni Nanoframes

Bimetallic nanocatalysts offer a compelling example of how structural evolution can be engineered to achieve superior performance. The synthesis of Pt_3Ni nanoframes begins with $PtNi_3$ rhombic dodecahedra, which undergo phase segregation to form Pt-rich edges and Ni-rich cores [11]. Subsequent corrosion of the Ni-rich interior yields hollow Pt_3Ni nanoframes. These structures exhibit a mass activity 36 times higher than

conventional Pt/C catalysts in the oxygen reduction reaction (ORR), attributed to the formation of Pt-skin surfaces with optimized binding energies for oxygen intermediates. Remarkably, these nanoframes retain their activity even after 4,000 electrochemical cycles, demonstrating the durability of dynamically evolved structures.

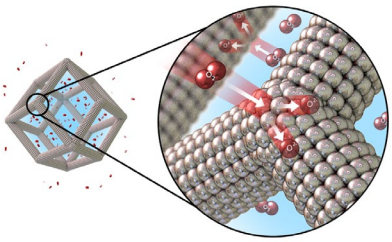

Figure 1: Illustration of the catalytic oxygen reduction reaction on the surface of platinum-nickel nanoframes with an in situ evolved multilayered platinum skin structure [Adapted from Ref 11].

2.2 Case Study: Cu Nanocatalysts in CO_2RR

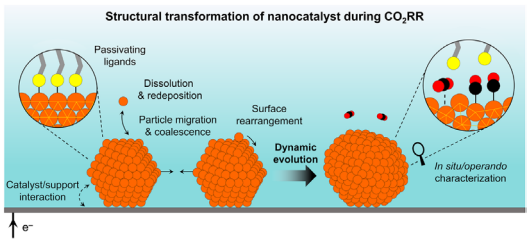

Figure 2. Schematic illustration of the structural transformation of the nanocatalyst occurring under CO_2-reducing conditions [Adapted from Ref 10].

Copper stands out as the only known electrocatalyst capable of producing multicarbon (C_2^+) products from CO_2. In situ microscopy and spectroscopy techniques have revealed that Cu nanoparticles often coalesce into nanograins with undercoordinated sites, which are believed to enhance C-C coupling [4-9, 12]. The relationship between structural evolution and catalytic performance remains debated, due to the lack of nanoscale, time-resolved *operando*/*in situ* methods. While some studies associate nanoclustering with competitive hydrogen evolution (HER), others link undercoordinated sites to higher C_2^+ selectivity, highlighting the complexity of dynamic catalyst behavior. Recently our team provided the first definitive picture of copper active sites as metallic Cu nanograins through a comprehensive *operando* study on the dynamic structural evolution over the life cycle of a family of Cu nanocatalysts from (i) their initial nanoparticle (NP) ensemble, through (ii) their catalytically active structure under CO_2RR conditions, to (iii) their post-electrolysis structure after air exposure [4,5]. Correlative electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM) and high-energy-resolution X-ray spectroscopy probe the dynamic evolution of a Cu NP ensemble under CO_2-reducing conditions. The rich nanograin boundaries bear

undercoordinated Cu sites as probable active sites for selective CO_2RR. *Operando* four-dimensional STEM (4D-STEM) reveals the structural evolution of the NP ensemble, with a spatial resolution of approximately 1 nm, transitioning from the initial stage of loosely connected nanograins to the steady-state, closely packed nanograins as the applied potentials approach the optimal condition for CO_2RR. This collection of Operando tools can serve as a general platform to resolve electrocatalytic interfaces under real-time operating conditions across multiple spatiotemporal scales (Figure 2).

3. The Catalytic Microenvironment: Beyond Static Surfaces

The local environment surrounding a catalyst plays a crucial role in determining reaction pathways. Alkali metal cations, such as Cs^+, have been shown to stabilize $*CO_2$ intermediates through electrostatic interactions, thereby influencing product selectivity. Local pH gradients also significantly impact catalytic behavior (Figure 3). Understanding and controlling these microenvironmental factors are essential for optimizing CO_2RR performance. An emerging strategy for tailoring catalytic microenvironments involves the use of organic ligands to create structured interlayers around nanoparticles. For instance, Ag nanoparticles functionalized with alkylphosphonic ligands form a Nanoparticle-Ordered Ligand Interlayer (NOLI) under reductive bias [6, 13]. This unique structure acts as a catalytic pocket, significantly enhancing CO selectivity with Faradaic efficiencies reaching 99%. Spectroscopic and computational studies reveal that dehydrated cations intercalated within the NOLI stabilize reaction intermediates through strong electrostatic interactions.

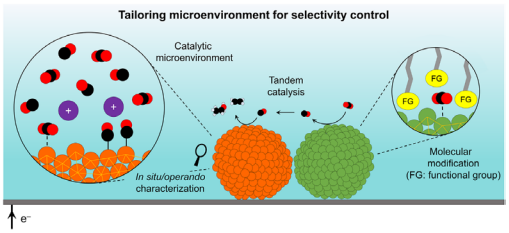

Figure 3. Schematic illustration of catalytic microenvironment of nanocatalysts during CO_2 electrolysis and approaches to tuning microenvironment [Adapted from Ref. 10].

4. Correlative and Multimodal Operando Techniques: Capturing Catalysis in Action

Advancements in operando characterization techniques have revolutionized our understanding of dynamic catalysis under working conditions. X-ray absorption spectroscopy (XAS) and small-angle X-ray scattering (SAXS) provide ensemble-averaged chemical and structural insights, while electrochemical resonant soft X-ray scattering (EC-RSoXS) combines scattering and spectroscopy to probe valence states under applied bias. The most powerful insights come from combining multiple techniques. For instance, correlating EC-TEM with XAS allows researchers to link structural changes observed microscopically with ensemble-averaged electronic structure changes. Similarly, combining vibrational spectroscopy (like IR or Raman) with electrochemical measurements connects surface adsorbates to reaction rates. These

multimodal approaches are facilitated by specialized electrochemical cells designed to work across multiple techniques. These multimodal techniques aim to understand how to activate and sustain catalytic activity and selectivity over extended time periods with the ultimate goal of directly capturing real-time "movies" of reaction dynamics under operating conditions, *i.e.,* "*watching chemistry in action*" (Figure 4) [7]. In general, electron probes provide nanometer-to-atomic scale information on individual nanoparticles in a localized environment, while synchrotron-based X-rays interrogate a large ensemble of nanoparticles to provide statistical analysis. Mutimodal *operando* methods can now offer a comprehensive atomic/molecular-level picture of structures and compositions of multisite tandem catalysts under reaction conditions at gas-liquid-solid interfaces, which serve as accurate input for collaborating with theory groups to identify activity descriptors and establish structure-property relationships required for designing cooperative and/or evolving catalysts that affect complex catalytic processes.

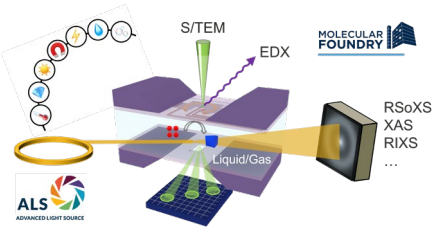

Figure 4. A powerful and complementary toolbox of multimodal operando STEM and X-ray methods. The upper left schematic includes a variety of stimuli (temperature, pressure, optical, magnetic, biasing, liquid or gas environment) [Adapted from Ref. 7].

5. Future Perspectives and Conclusions

Future catalyst design must embrace structural evolution as an integral feature rather than an obstacle. Pre-catalysts should be engineered to transform into active states under operando conditions, leveraging reconstruction processes to generate optimal active sites. Furthermore, tailoring local microenvironments—through ligand engineering, cation modulation, and pH control—can enhance selectivity and activity. The integration of advanced characterization, computational modeling, and innovative material design will drive the next generation of dynamic electrocatalysts, paving the way for sustainable energy technologies.

The field of electrocatalysis is undergoing a profound transformation as we recognize that catalyst materials are not static, but dynamic entities that evolve under reaction conditions. This shift in perspective—from resisting structural change to understanding and harnessing it—opens new avenues for catalyst design. Key insights from recent research include: 1). Structural evolution is ubiquitous in electrocatalysis, occurring across multiple length and time scales. 2). These changes can create highly active sites that would be difficult to synthesize directly. 3). The local microenvironment (double layer, pH, cations) interacts strongly with dynamic surfaces to determine performance. 4). Advanced operando techniques are revealing these processes with unprecedented detail.

Looking ahead, the most significant opportunities lie in developing predictive theories of catalyst evolution, creating design rules for dynamic materials, and translating

these concepts to industrial-scale processes. As we meet these challenges, dynamic electrocatalysis will play an increasingly important role in sustainable energy conversion and chemical production.

Acknowledgments

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