

Catalytic Reaction Processes Revealed by Scanning Probe Microscopy

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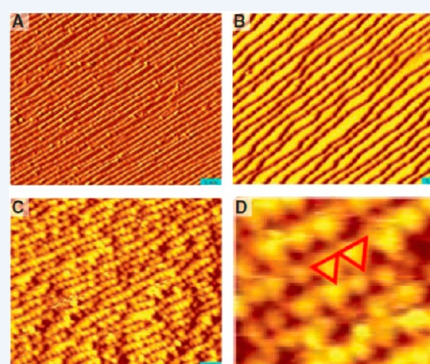
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CONSPECTUS: Heterogeneous catalysis is of great importance for modern society. About 80% of the chemicals are produced by catalytic reactions. Green energy production and utilization as well as environmental protection also need efficient catalysts. Understanding the reaction mechanisms is crucial to improve the existing catalysts and develop new ones with better activity, selectivity, and stability. Three components are involved in one catalytic reaction: reactant, product, and catalyst. The catalytic reaction process consists of a series of elementary steps: adsorption, diffusion, reaction, and desorption. During reaction, the catalyst surface can change at the atomic level, with roughening, sintering, and segregation processes occurring dynamically in response to the reaction conditions. Therefore, it is imperative to obtain atomic-scale information for understanding catalytic reactions.

Scanning probe microscopy (SPM) is a very appropriate tool for catalytic research at the atomic scale because of its unique atomic-resolution capability. A distinguishing feature of SPM, compared to other surface characterization techniques, such as X-ray photoelectron spectroscopy, is that there is no intrinsic limitation for SPM to work under realistic reaction conditions (usually high temperature and high pressure). Therefore, since it was introduced in 1981, scanning tunneling microscopy (STM) has been widely used to investigate the adsorption, diffusion, reaction, and desorption processes on solid catalyst surfaces at the atomic level. STM can also monitor dynamic changes of catalyst surfaces during reactions. These invaluable microscopic insights have not only deepened the understanding of catalytic processes, but also provided important guidance for the development of new catalysts.

This Account will focus on elementary reaction processes revealed by SPM. First, we will demonstrate the power of SPM to investigate the adsorption and diffusion process of reactants on catalyst surfaces at the atomic level. Then the dynamic processes, including surface reconstruction, roughening, sintering, and phase separation, studied by SPM will be discussed. Furthermore, SPM provides valuable insights toward identifying the active sites and understanding the reaction mechanisms. We also illustrate here how both ultrahigh vacuum STM and high pressure STM provide valuable information, expanding the understanding provided by traditional surface science. We conclude with highlighting remarkable recent progress in noncontact atomic force microscopy (NC-AFM) and inelastic electron tunneling spectroscopy (IETS), and their impact on single-chemical-bond level characterization for catalytic reaction processes in the future.



1. INTRODUCTION

Catalytic reactions play an important role for the global economic development and environmental sustainability. Ammonia synthesis and vehicle exhaust conversion are two representative examples. A molecular level understanding of the reaction mechanism is crucial for the rational design of smart catalysts with high performance, low cost, and long durability. In the last half-century, surface science studies have accumulated a vast amount of knowledge toward understanding the fundamental mechanisms of numerous catalytic reactions¹ and culminated with the Nobel Prize in Chemistry to Prof. Gerhard Ertl in 2007.² Among various surface characterization techniques, scanning probe microscopy (SPM) has played a

crucial role since it was introduced in the 1980s, because of its unique power to provide valuable atomic-scale information about chemical elementary processes, including adsorption, diffusion, and reconstruction. The scanning probe techniques have since then continued to develop and improve, giving rise to variations such as low temperature scanning tunneling microscopy (LT-STM), high-pressure scanning tunneling microscopy (HP-STM),^{3,4} noncontact atomic force microscopy (NC-AFM),⁵ and STM-based inelastic electron tunneling spectroscopy (STM-IETS).⁶ Among these, HP-STM, which

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can operate in realistic reaction environments, is attracting increasing attention because it allows researchers to bridge the pressure gap between traditional surface science research and realistic catalytic reactions. Traditional surface science studies, which mostly rely on electron or photon detection, are performed under ultrahigh vacuum (UHV) conditions, while industrial reactions occur at high pressure and high temperature environments.⁷ SPM techniques are not limited to UHV conditions because the working principles are based on the electron tunneling process, or in the measurement of atomic interaction forces between tip and sample. The gap between tip and sample is usually less than 1 nm; thus, even in the presence of gas or liquid, the tunneling process is not strongly modified and atomic forces can still be detected. It needs to be emphasized that the information provided by surface science studies under UHV conditions continues to be irreplaceable.

Catalytic reaction includes three participants: reactant, catalyst, and product. The reaction process consists of adsorption, diffusion, reaction, and product desorption. Equally important and not so easily controlled is the simultaneous dynamic evolution of the catalyst itself during and induced by the reaction. Identifying the active sites and phases of the catalyst, and correlating the reaction processes with the local electronic structures is crucial for explaining reaction mechanisms, which will allow for the designing of novel catalysts. There are numerous reviews on SPM itself and in situ characterization using SPM.^{4,8,9} Here we will focus on basic catalytic processes that have been revealed by SPM, including both in UHV and under reactant gases.

2. CATALYTIC PROCESSES REVEALED BY SPM

2.1. Adsorption

The adsorption of reactants on catalyst surfaces is the first step for chemical reactions. There are two kinds of adsorption: molecular adsorption and dissociative adsorption. For some catalytic reactions, the dissociation of adsorbed molecules is regarded as the rate-limiting step for the whole reaction. For example, the dissociations of N₂ and H₂ are the rate limiting processes for ammonia synthesis and hydrogenation reactions, respectively. Gas adsorption is actually a complex chemical process, which is not homogeneous and includes charge and spin redistribution and energy dissipation. From the atomic-resolution STM images, very useful information on the adsorption process has been obtained. First, the adsorption site and adsorption state of reactants can be precisely determined from atomic-resolution STM images.^{10,11} This information is the foundation for the following discussions. Second, the mutual interaction between adsorbates is revealed by high-resolution STM images. It was observed that the gas adsorption on solid surfaces is not random. Instead, the adsorption and dissociation of molecules can be affected by previously chemisorbed species.¹⁰ Figure 1 shows STM images of dissociated oxygen atoms on Pt(111) surface at different temperatures. The adsorption heterogeneity is evident from these STM images and is attributed to the interaction between adsorbate molecules or to local electronic changes, modified by the adsorbates. These atomic-scale observations are important for understanding the adsorption of gas molecules on solid catalyst surfaces.

An important question arises as to whether UHV studies, such as the one described above, capture the key steps and structures that form under practical reactions, under high gas

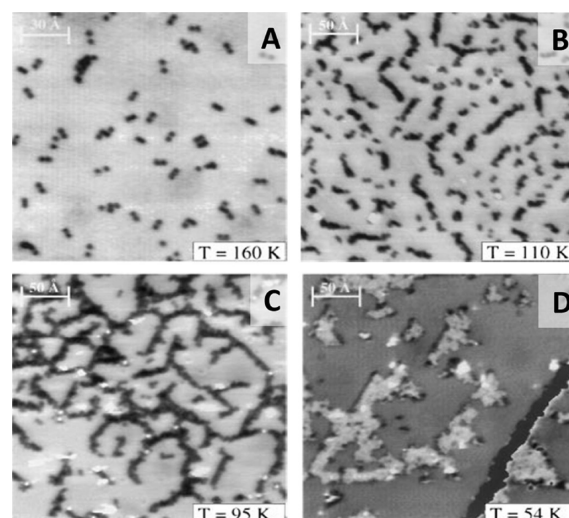


Figure 1. STM images illustrating the temperature dependence of oxygen adsorption (10^{-6} Torr s of O₂ dosing) on Pt(111) surface. The dark spots correspond to O atoms, in pairs in A (from the dissociation of O₂), and forming clusters at higher coverage (B–D). Adapted with permission from ref 10. Copyright 1997 Nature Publishing Group.

pressures. This is a fundamental question because the high surface coverage characteristic of high pressure conditions can only be achieved in UHV by cooling the surface to low temperature, which may prevent reaching thermodynamic equilibrium and produce kinetically frozen structures. The possibility of resolving this issue is provided by the development of HP-STM.³ With it, the structures of many model catalysts formed after adsorption of several important reactants have been studied under ambient conditions, including H/Cu(110),¹² CO/Pt(110),¹³ CO/Pt(111),¹⁴ and NO/Pd(111).¹⁵ Interestingly, many results indicate that there is no real pressure gap in the structure, as the surface structures obtained under high pressures were similar to those obtained under UHV conditions, indicating that in these cases the activation energy for any surface structuring is low enough. For example, for CO adsorption on Pt(111) surface, the coverage of CO was found to vary continuously over the entire pressure range from 10^{-6} to 760 Torr. At 760 Torr and room temperature, a $\sqrt{19} \times \sqrt{19}R23.4^\circ - 13\text{CO}$ moiré structure, which corresponds to 0.68 monolayer (ML) surface coverage, was observed by HP-STM.¹⁴ The exactly same structure can be obtained at low pressure and temperature conditions (170 K), which is a sufficiently high temperature to overcome the CO diffusion barrier. This is however not always the case. For NO on Rh(111), it is well-known that a (2×2) structure with a coverage of 0.75 ML can be formed on the surface after dosing NO. By using HP-STM, a new phase (3×3) structure with a coverage of 0.778 ML was observed only at pressure higher than 0.01 Torr.¹⁶ These observations and comparisons suggest that it is important to combine traditional surface science studies under UHV conditions and high pressure in situ measurements for understanding the fundamental surface processes of heterogeneous catalysis. As we will discuss below, however, there are other cases where the activation barriers for surface reconstruction are high, and there only HP-STM at higher temperatures can reveal the real catalyst structure.

2.2. Diffusion

After adsorption, the molecules diffuse on the surface to meet reaction partners or to reach an active site.¹⁷ Using STM, the diffusion process can be monitored at the single-molecule/atom scale and the diffusion constant and the energy barriers can be obtained quantitatively. There are several interesting diffusion phenomena resolved by STM at the molecular level. For example, CO molecules on Cu(110), and H₂O molecules on Pd(111) surface, were seen to form clusters (dimers or trimers), which surprisingly diffused faster than the isolated molecules.^{18,19} Figure 2 shows some snap-shots of an STM

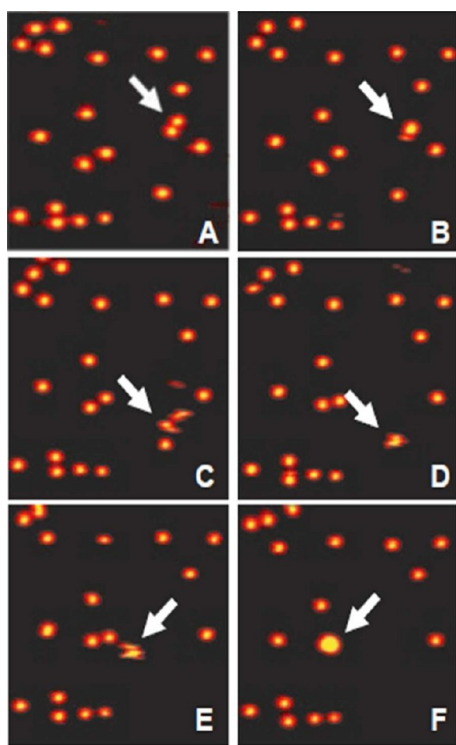


Figure 2. Sequence of STM images (18 nm × 18 nm) showing water molecules (bright spots) adsorbed and diffusing on Pd(111) at 40 K. The arrows point to the formation of dimers, trimers and pentamers. Adapted with permission from ref 19. Copyright 2002 American Association for the Advancement of Science.

movie of H₂O molecules diffusing on the Pd(111) surface.¹⁹ The diffusion of monomers was measured to be more than 4 orders of magnitude slower than dimers and 500 times slower than trimers and tetramers. This was first attributed to the combination of strong H bonding between H₂O molecules and the misfit between the O–O distance in the H₂O dimer and the lattice constant of Pd(111). Later, new theoretical work explained the rapid diffusion of dimers as a result of H-tunneling between two dimer configurations that change the site of the dimer by one lattice constant.²⁰

Another interesting diffusion phenomenon revealed by STM was the water assisted proton hopping on TiO₂(110)²¹ and FeO(111)²² surfaces. Water and proton diffusion on solid oxide surfaces is of great scientific significance because the process is closely related to several important catalytic reactions, like water splitting to obtain H₂. On the TiO₂(110) surface, using STM, Besenbacher et al. observed that protons are carried in paired hydroxyl groups, which could split into two single OH groups when interacting with water molecules. Through this

process, the proton was transferred to an adjacent, bare O_{br} row.²¹ On a hydrogenated oxygen-terminated FeO(111) monolayer film on Pt(111), in the presence of water molecules, the rapid movement of H atoms was captured as irregular streaks in the atom-resolved STM images.²² The difference between the proton transfer mechanisms on the two oxide surfaces is a consequence of the fact that on TiO₂(110) surface, water dissociation is required for proton transfer, while on FeO(111) surface, the proton-transfer proceeds via an H₃O⁺-like transition state without water dissociation. Obviously, these water-assisted proton transfer processes identified by STM are of significance for understanding water and proton related catalytic reactions.

Spillover, which involves the movement of activated reactants from one active site to another for the subsequent reaction, is an important diffusion process in heterogeneous catalysis.^{23,24} Microscopic insights obtained by STM are crucial for understanding the spillover process. Using STM, Bowker and co-workers suggested that O₂ dissociatively adsorbs at 673 K on Pd nanoparticles supported on TiO₂(110) substrate and then spills over to the TiO₂(110) surface.²⁵ Recently, high-resolution LT-STM results demonstrated that individual isolated Pd atoms can promote H₂ dissociation and allow the dissociated H atom to spill over onto Cu(111) host support.²⁶ Temperature-programmed desorption data revealed that single Pd atoms not only lower the activation barrier to H₂ dissociation, but also weaken the bonding energy of H on Cu(111) surface. The synergistic effect between Pd and Cu leads to very selective hydrogenation of styrene and acetylene as compared with pure Cu or Pd metal alone.

A related dynamic process is that of fluctuations in the local density of adsorbates. While dense coverage of adsorbates can poison the catalyst for further adsorption, fluctuations can expose substrate sites, liberating catalyst atoms from bonding with other adsorbates and making them active for further dissociation of reactants. That was shown to be the case on Pd(111) covered with H atoms at a coverage close to 1. STM revealed that clusters of three or more hydrogen vacancies produces Pd atoms not bound to H atoms and only these Pd atoms are active for dissociation of incoming H₂ molecules.^{27,28}

2.3. Surface Reconstruction

As mentioned above, HP-STM can reveal the occurrence of surface reconstructions, roughening, sintering, phase separation, segregation, and many other phenomena that may require high adsorbate density together with thermal activation. These processes need to be understood at the atomic level because of their relevance for the activity, selectivity, and stability of catalysts. For example, in the CO/Pt(110) system, it was shown that CO, which binds strongly to low-coordinated Pt atoms at step edges, can break Pt–Pt bonds and restructure the step structure formation, even at low pressure (10^{−7} Torr CO) and room temperature.¹³ Recently, more pronounced surface changes were observed on Pt(557) and (332) surfaces by CO adsorption at pressures about 1 Torr, as shown in Figure 3. HP-STM results demonstrated that, as the surface coverage of CO increases to near 1 ML at high pressure, the originally flat terraces break up into nanometer-sized clusters. After pumping out the CO, the surfaces return back to initially flat ones.²⁹ Only in situ measurements can observe such dramatic and reversible structural changes, which are important because such adsorbate-induced nanoclusters might play a significant role in the catalytic reactivity.

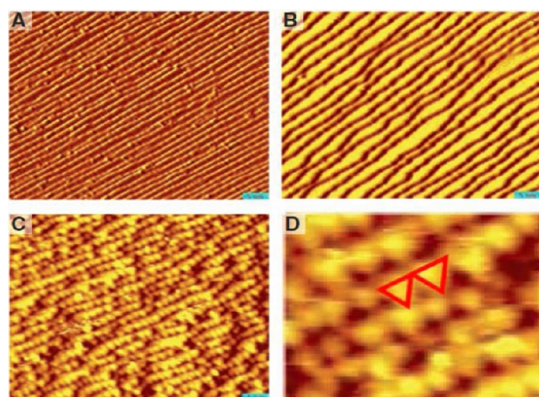


Figure 3. STM images of Pt(557) under different CO environment. (A) 1×10^{-10} Torr (UHV); (B) 5×10^{-8} Torr; (C) 1 Torr; (D) enlarged view of (C) at 1 Torr CO. Adapted with permission from ref 29. Copyright 2010 American Association for the Advancement of Science.

Sintering is one of the most challenging problems for catalyst stability because it can reduce the active surface area of catalysts and cause catalyst deactivation. In order to design novel catalysts with longevity, it is important to understand the sintering mechanisms at the atomic level. Sintering occurs via two mechanisms: cluster aggregation or Ostwald ripening. Recently, by combining STM and density functional theory (DFT) calculations, Diebold and co-workers revealed that in the Pd–Fe₃O₄ model system, the Pd-carbonyl species play a critical role for the sintering of Pd adatoms.³⁰ By weakening the Pd–O bonds between Pd adatoms and Fe₃O₄ support, the CO molecules enhance the mobility of Pd adatoms at room temperature. After reaching a critical density, clusters nucleate and subsequent sintering occurs through cluster diffusion. The adsorbate-enhanced mass transport at surfaces is a general phenomenon. Besides metal–carbonyl species, metal–hydrogen³¹ and metal–sulfur³² complexes have been identified as carriers accelerating mass transport. Searching for the ideal complexes or processing procedures to slow down the sintering/deactivating or redispersing of the catalysts is one way to prevent the catalyst deactivation.³³

Because of their remarkable catalytic properties, alloy catalysts attract increasing attention in heterogeneous catalysis, for example, in steam reforming³⁴ and in electrocatalysis in fuel cells.³⁵ The stability of alloy catalysts under realistic reactive conditions is critical for large-scale industrial applications. Phase separation and surface segregation are two important adsorbate-induced surface modification processes, which directly relate to the stability of alloy catalysts. Surface segregation process of Pd–Pt and Rh–Pd nanoparticles under oxidizing or reducing conditions has been studied using surface characterization techniques, like low-energy ion scattering³⁶ and ambient pressure X-ray photoelectron spectroscopy (AP-XPS).³⁷ Recently, phase separation of Au/Ni(111) surface alloy upon exposure to CO was revealed at the atomic level using HP-STM at room temperature.³⁸ By lowering the CO pressure to several mbar, to slow down the separation process, the morphological changes were monitored in real-time STM movies. Using DFT, it was further proposed that Ni-carbonyls are formed at the step edges and leave the surface while Au atoms are left behind.

2.4. Active Sites

The active site, defined as atoms or groups of atoms where the chemical reactions occur, is an important concept in catalysis.³⁹ Only after determining the nature of the active sites, the reaction mechanism can be understood, allowing for the rational design of new catalysts. Step edges, uncoordinated sites, and defects are usually considered to be active sites. With its atomic resolution capability, STM is an ideal tool to identify active sites. For example, the low-coordinated, top metal atoms of atomic steps of Ru(0001) were observed to be the active sites for NO dissociation and the activity was attributed to the local changes in the electronic structure.⁴⁰

Not only limited to metal catalysts, the active step edges have been studied in semiconductor systems, like TiO₂⁴¹ and MoS₂.^{42–45} By combining atomic-scale STM images and DFT calculations, the atomic structure of MoS₂ clusters was determined, as shown in Figure 4A.⁴⁵ One-dimensional metallic

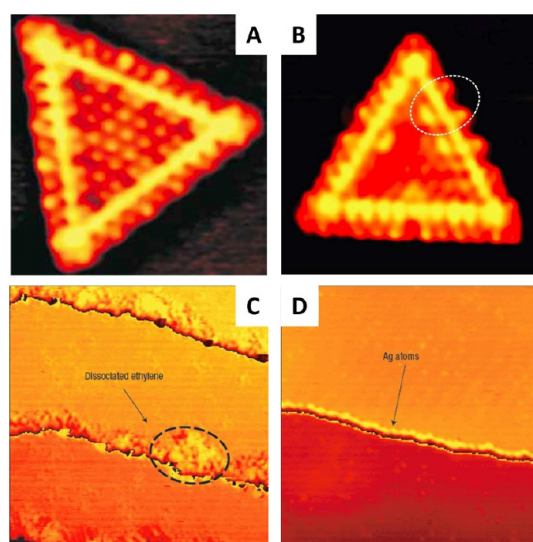


Figure 4. (A) Atomic-resolved STM image ($4.8 \text{ nm} \times 5.3 \text{ nm}$) of triangular, single-layer MoS₂ nanoclusters on Au(111). Adapted with permission from ref 45. Copyright 2001 American Physical Society. (B) STM image ($5.0 \text{ nm} \times 5.4 \text{ nm}$) of an atomic hydrogen pretreated MoS₂ cluster subsequently exposed to thiophene. The dashed circle indicates the features associated with individual adsorbed thiophene molecule. Adapted with permission from ref 42. Copyright 2006 Elsevier. (C) STM image ($20 \text{ nm} \times 20 \text{ nm}$) of a Ni(111) surface after exposure to ethylene (10^{-8} Torr; 100 s). (D) STM image ($40 \text{ nm} \times 40 \text{ nm}$) of a Ni(111) surface with the step edges blocked by Ag atoms. Adapted with permission from ref 47. Copyright 2005 Nature Publishing Group.

step edges were identified as active sites for the hydrodesulfurization reaction⁴² and hydrogen evolution reactions.⁴³ Thiophene (C₄H₄S) molecules were observed to adsorb exclusively on edge sites, not on the inert basal plane of MoS₂ clusters (Figure 4B), confirming earlier results obtained by thermal desorption spectroscopy.⁴⁶ Similarly, the electrocatalytic activity of MoS₂ was revealed to correlate linearly with the number of edge sites, which was quantified from the STM measurements.⁴³ It is interesting to note that step edges not only can influence the catalytic activity, but also can affect the reaction selectivity. This important information was obtained from investigating the dissociation of ethylene (C₂H₄) on Ni(111) surface by STM.⁴⁷ Based on STM (Figure 4C) and DFT calculations, it was concluded that step-edges are more

effective for C–C bond breaking than for C–H bond breaking, which results in bond-breaking selectivity. Furthermore, it was demonstrated that the reactive step sites can be controlled by blocking the steps with Ag atoms, as shown in Figure 4D.

STM helped to reveal the active sites of several important inverse model systems, where the interfaces between oxide nanoparticles and metal supports were proposed to enhance dramatically the catalytic reactivity.^{48–50} Rodriguez et al. revealed that, for the water gas shift (WGS) reaction on $\text{TiO}_{2-x}/\text{Au}(111)$ and $\text{CeO}_{2-x}/\text{Au}(111)$, water dissociates on O vacancies along the edges of oxide nanoparticles while CO adsorbs on nearby Au sites. The subsequent reaction occurs at the metal-oxide interface.⁴⁸ Due to the interface effect between oxide nanoparticles and bulk Au surface, both $\text{TiO}_{2-x}/\text{Au}(111)$ and $\text{CeO}_{2-x}/\text{Au}(111)$ exhibit comparable activity as the well-studied WGS model systems, like $\text{Cu}(111)$ or $\text{Cu}(100)$. Recently, coordinatively unsaturated ferrous (CUF) sites confined at the interface between FeO island and $\text{Pt}(111)$ surface were revealed to be active sites for CO oxidation and CO preferential oxidation. An STM image from 0.25 ML $\text{FeO}_{1-x}/\text{Pt}(111)$ surface is shown in Figure 5A.⁴⁹ An interface-

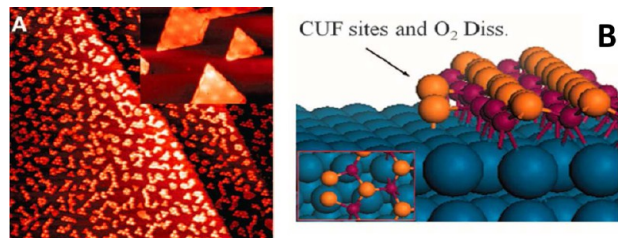


Figure 5. (A) STM image ($200 \text{ nm} \times 200 \text{ nm}$) of a $\text{Pt}(111)$ surface with 0.25 ML of FeO_{1-x} . The inset shows an atomic-resolution STM image ($25 \text{ nm} \times 20.8 \text{ nm}$) of FeO nanoislands. (B) Schematic structure of the CUF sites and the calculated transition states structure of O_2 dissociation (the inset shows the top view) at the interface boundary between FeO and $\text{Pt}(111)$. Adapted with permission from ref 49. Copyright 2010 American Association for the Advancement of Science.

confinement concept was proposed to explain the reaction mechanism. O_2 adsorbs and dissociates on the CUF sites on the $\text{FeO}_{1-x}/\text{Pt}(111)$ interface (schematic model of this process shown in Figure 5B), while CO adsorbs on the neighboring Pt surface. After removing the atomic oxygen by CO to form CO_2 , the coordinatively unsaturated state of Fe atoms at the boundary is restored for further O_2 adsorption and dissociation, closing the reaction cycle. The interface effect was also successfully applied to CeO_x/Cu system for methanol synthesis from CO_2 .⁵⁰ The rate of methanol production on CeO_x/Cu is ~ 200 times higher than on $\text{Cu}(111)$ and ~ 14 times faster than on Cu/ZnO . The ceria–copper interface was identified as the active site for the methanol synthesis.

2.5. Reaction Mechanisms

Real-time monitoring the catalytic reactions at the atomic level can provide microscopic insights for understanding the reaction mechanisms and kinetics. It is generally accepted that under UHV conditions the reactions proceed via the Langmuir–Hinshelwood (LH) mechanism, where the reactant molecules first adsorb on the metal surface and then diffuse and meet and react. Using variable-temperature STM, the catalytic oxidation of CO on $\text{Pt}(111)$ surface was investigated systematically on a surface precovered with a submonolayer of oxygen.⁵¹ The STM images acquired during reaction demonstrated that the reaction occurs at the boundaries between oxygen domains ($(2 \times 2)\text{O}$ structure) and CO domains ($c(4 \times 2)$ structure), not randomly as traditionally expected, as shown in Figure 6.⁵¹ By measuring the changes of oxygen atom concentration from the images, the activation energy for $\text{CO}_{\text{ad}} + \text{O}_{\text{ad}} \rightarrow \text{CO}_2$ was derived to be 0.49 eV, consistent with macroscopic measurements.

It is important to note that the LH mechanism, where adsorption and dissociation of O_2 is the source of O atoms, is not the only mechanism for CO oxidation. In fact, the metal oxide surface might also be an active phase, known as Mars–van Krevelen (MvK) mechanism. Using STM and DFT, Over et al. proposed MvK as the mechanism for CO oxidation on Ru surface.⁵² They suggested that $\text{RuO}_2(110)$, which grows epitaxially on $\text{Ru}(0001)$ surface at high O_2 pressure and

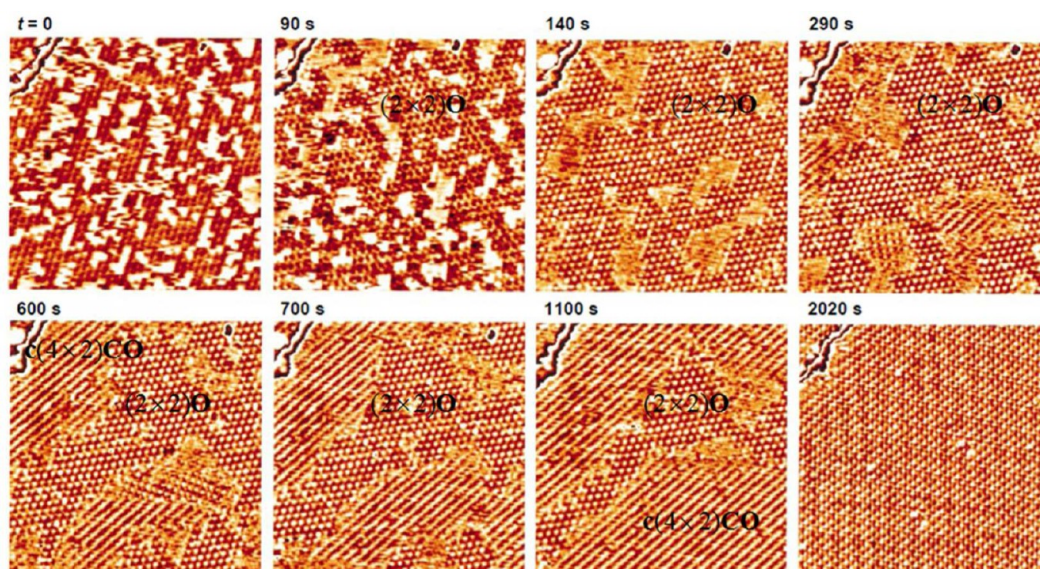


Figure 6. Sequence of STM images during reaction of adsorbed oxygen atoms with coadsorbed CO molecules at 247 K on a $\text{Pt}(111)$ surface. The evolution of $(2 \times 2)\text{O}$ structure and $c(4 \times 2)\text{CO}$ structure with reaction is evident from these atomic-resolved STM images. Image size: $18 \text{ nm} \times 17 \text{ nm}$. Adapted with permission from ref 51. Copyright 1997 American Association for the Advancement of Science.

temperatures (10^{-2} mbar and 700 K in this case), is the active phase for CO oxidation. The coordinatively unsaturated sites on RuO₂(110) are the active sites where CO chemisorbs and reacts with neighboring lattice-oxygen to form CO₂. The consumed lattice-oxygen is restored by oxygen uptake from the gas phase to complete the cycle.

Using high temperature HP-STM in a small flow reactor cell, Frenken et al. investigated the CO oxidation on Pt(110) surface under reaction conditions.⁵³ By switching from a CO-rich to an O₂-rich flow and vice versa, the Pt surface was reversibly oxidized or reduced. The authors observed that when the catalytic activity is higher, the surface becomes rougher and more oxidized. Based on these observations, the surface oxidized Pt was proposed to be the active phase for CO oxidation, thus showing that the MvK mechanism is also valid at high pressure. This was further extended to other Pt-group metal surfaces, like Pd(001) and Rh(111), and confirmed by other in situ techniques, such as XRD and AP-XPS.^{54–57} However, it should be pointed out that mass transfer limitations (MTL), where the turnover rate is limited by the flux of reactants reaching the catalytic surface rather than by the reactivity of the catalysts, can influence the identification of active phase and need special attention when explaining in situ experimental results.^{58,59}

One should also take into consideration, when utilizing synchrotron radiation for in situ characterization, that the high intensity X-ray beam irradiation might influence the experimental results. Proper checking and controlling potential beam damage is therefore crucial.⁶⁰

3. CONCLUSION AND OUTLOOK

We have shown how SPM techniques have provided unique and valuable insights for understanding the fundamental catalytic processes at the atomic level. The new understanding can further promote the improvement of existing catalysts and the development of new ones. Continuous technical advances promise that the power of SPM for revealing the catalytic mechanism has not reached the end. Instead, new developments of SPM with better spatial and time resolution show that there is plenty of room to further deepen our understanding on catalytic processes. For example, scanning tunneling spectroscopy (STS) can routinely probe the local electronic structure of surfaces, which directly relates to the activity of catalysts. It will be of importance to measure the local electronic structure of active sites and correlate it to the catalytic activity. At present, however, there are still few reports in this important area. As an encouraging example, recently, using STS, the close connection between catalytic properties of thin films and their local electronic structures modulated by quantum well states has been revealed.⁶¹

Another noteworthy development is NC-AFM. Because in AFM the signal originates from the local force between tip and sample surface, it can be used to study insulating surfaces, which is ubiquitous in catalysis. Surprisingly, AFM has not yet attracted enough attention from the catalysis community. Recently there are several remarkable achievements in NC-AFM, where submolecular resolution has been achieved, permitting to identify internal bond configurations and intermolecular hydrogen bonding structures.^{62,63} For example, the internal bond structure changes during thermally induced cyclization reactions of individual oligo-(phenylene-1,2-ethynylene)s on Ag(110) was investigated by NC-AFM, which shows much better resolution compared with standard LT-STM, as

shown in Figure 7.⁶² From these highly resolved NC-AFM images, the bonding geometries and bond length could be

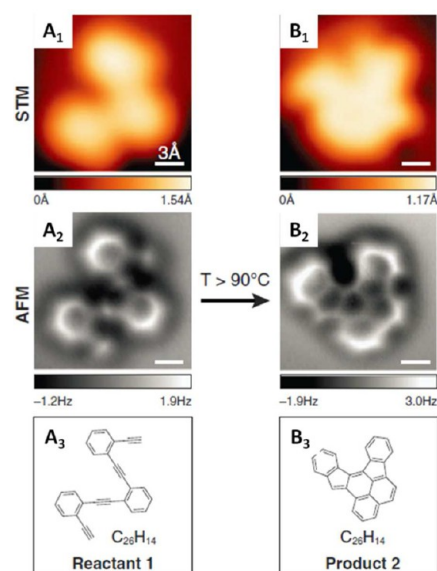


Figure 7. Comparison of STM images, NC-AFM images, and the structures for molecular reactant and product. (A) Reactant before cyclization reaction. (B) One kind of product after cyclization reaction. Adapted with permission from ref 62. Copyright 2013 American Association for the Advancement of Science.

extracted precisely and the detailed molecular structures could be established. Although these outstanding achievements require delicate tip modification and low temperature, it is possible that, with the further development of super-resolution SPM techniques, the understanding of catalytic processes at the single chemical bond level will advance substantially, which will promote the rational design of novel catalysts to meet the grand challenges of the 21st century on energy and environment.

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Notes

The authors declare no competing financial interest.

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In the title, the spelling of “Microscopy” was corrected. The revised version was published on the Web on June 25, 2015.