Abstract: In the past few decades, metal nanoparticles applied in heterogeneous catalysis have attracted extensive attention. The term nanocatalysis is broadly referred to as the unique catalytic effect of this series of materials. Although considerable progress has been made in nanocatalysis, it still remains a great challenge to fully understand the nature of active sites in the nanoscale. Many concepts and models have been put forward to describe the properties and performances of nano- and subnanoparticles in catalysis. In this review, we propose our perspective on the active sites of heterogeneous catalysis from the aspects of electronic structure and geometric structure of nanoclusters and consider briefly how these clusters function in catalysis. The challenge in nanocatalysis research methods is also discussed.

Keywords: active site; electronic structure; geometric structure; heterogeneous catalysis; nanocluster.

1 Introduction

The controlling of chemical reactions has always been the central tasks of chemists. Heterogeneous catalysis is just the science of altering the reaction pathways through functional materials [1–6]. The progresses of experimental methods and theoretical simulations facilitated the catalysis [6] researches at the molecular level [7–13]. Researchers now design the catalysts through reaction mechanisms and in situ characterizations [10, 13–19]. Catalysis is a complex multidisciplinary science. Theoretical chemistry, surface science, and nanoscience are bringing catalysis new research topics and methods, and catalysis has, in turn, provided abundant research background to these areas. Nanoscience, especially, has always been associated closely to catalysis [7, 15, 20–24]. In fact, researchers and chemical industries had tried to reduce the size of catalysts since very early [2, 7]. Hence, we could see the initial type of nanocatalysis from the early researches of noble metal catalysis in organic reactions. In 1940, Nord [25, 26] had applied polymer-decorated Pt and Pd colloidal in the catalysis of nitrobenzene reductions. From the year 1970, reduction and oxidation catalyzed by noble metal nanoparticles were reported widely, especially the hydrogenation of unsaturated C–C bonds and the oxidation of alkyl, alkene, and ethanol. In the first place, the main goal of reducing the size of catalysis materials was to enhance the surface area of catalysts; therefore, the catalysis efficiency could be improved, and cost would decrease [7]. In this regard, catalysis is just the earliest and largest application of nanoscience. Besides the catalysis researched based on functional materials, the catalysis theory and mechanisms have also been deeply developed [11, 16, 27–35]. In the past two decades, the activation of reactants attracted much attention. From the activation of N≡N triple bond, O=O bond, to C–H bond, C–C bond activation researchers are approaching to the importance of the active sites [1, 6–9, 11, 29, 36–44].

In 1989, M. Haruta [45] reported that the Au nanoparticles supported on TiO2 performed excellent catalytic activities in a series of reactions. The following researches showed that the activities of the supported Au nanoparticles reached maximum when the size was in the range of 3–5 nm, especially for CO oxidation [46]. As a result, the chemical properties of metals, even the well-known inert metal Au, would drastically change when their sizes reduce to a certain range. Although it is well known that the nanoparticles would maintain different properties from the corresponding bulk materials, such a difference is especially remarkable on Au because the nanoparticle and bulk Pt, Pd have similar catalytic properties in many reactions [21, 47]. Such an important finding inspired people to investigate the structures and states of catalysts of the nanometer and reconsider how the active sites could activate reactants and accelerate reactions.
Such is the milestone of nanocatalysis. Today, nanocatalysis has become the science of nanoscale synthesis and the control, characterization of the catalysis center and catalysis dynamics. Therefore, implanting nanoscience to catalysis research could advance the synthesis of catalysts, deepen the understanding of the catalysis processes, and open a new area for the catalysis researches.

However, there are still arguments on several fundamental questions of Au catalysis, for example, the essence of the active sites of Au nanoparticle in a series of reactions, the relationship between the electronic states, microstructure Au NPs and their catalysis performances [12], or the state of the catalysts during the reactions [12, 17]. Apparently, these questions are associated with each other. At present, several interpretations of the activities of the supported Au catalysts include: (1) the defects of the support surface, (2) cation Au atoms or clusters on the support surface, (3) unsaturated-coordinating Au atoms, (4) neutral atoms on Au NPs, (5) the strain in the Au NPs, and (6) metal-nonmetal transitions of Au NPs [5, 21, 46, 48–54].

These factors have different emphasis and are strongly related to each other. At the atomic level, the active sites of Au NPs could be reduced to the following three parameters: the Au-Au distance, the coordination of Au atom, and the binding energy of Au electrons. The first two parameters describe the geometric structure of Au and, the latter, the electronic structure. Although several new concepts have been proposed based on the special activities and properties of the nanocatalysts, this two fundamental approaches, the geometric structures and electronic structures, would still be indispensable and instructive. Herein, we start from Au catalysis and try to connect the catalytic performances of metal nanomaterials with the geometric structures and electronic structures. In this way, we briefly discuss the essences of the active sites in heterogeneous catalysis. Finally, we would present our perspectives on the challenges of the catalysis research methods.

2 Electronic structure of active component

The metal nanoclusters display different properties from the bulk metal because of the quantum size effect [7, 21, 23, 55, 56]. The electronic transition between the support and metal further strengthen the change of the electronic structure of the nanoclusters [5, 57–59]. Such an electronic transition is just the essence of the metal support strong interaction. Most reports discuss the difference of the electronic structure between the metal nanoclusters and the bulk materials from these two factors. The important topic is how the change of the electronic structure influences the catalytic performances.

In heterogeneous catalysis, it is complicated to figure out whether the changes of the activities resulted from the electronic effects or the structural effects. In 2009, Scott L. Anderson [60] applied the mass selected technique to prepare Pd (Pdₙ, n=1, 2, 4, 7, 10, 16, 20, 25) supported on TiO₂(110) and study their CO oxidation activities. The key result is that, the cluster size did not vary monotonically with CO oxidation activities, while the Pd 3d binding energy variation correlated with that change (as shown in Figure 1). The author thus attributed the CO oxidation activities of Pdₙ/TiO₂ to the electronic structures.

![Figure 1](image-url)  
**Figure 1** Left: CO oxidation activity compared with the shifts in the Pd 3d binding energy, relative to the expectations from the smooth bulk scaling (right axis, open circles), as a function of cluster size. Right: Shifts in the observed Pd 3d peak position relative to the bulk Pd limit as a function of cluster size. For details, see Ref. [60]; reprinted with permission from AAAS.
The question is what the strong correlation between the Pd 3d binding energy and activities tell us about the chemistry. The key point is that the CO oxidation activities enhanced as the Pd 3d binding energy of the clusters close to the bulk metal. The XPS spectra of Pd20/TiO2 with the best activity were quite similar with that of the bulk metal. The ISS results show that Pd20 was deposited as a bilayer structure. The author believed that the structure of Pd20 is significantly different from that of the bulk Pd; thus, their electronic properties could hardly be the same. In addition, the binding energy of both Pd16 and Pd25 are higher than that of the bulk Pd. This indicates that the initial state effect and final state effect may cancel each other for Pd20. The electronic confinement and the lesser shielding effect of the metal nanoparticles would shift the BE to a higher energy (final state effect). However, an initial state effect decreases the BE, which was proposed to be the electron transfer from the support to the Pd20.

The differences between the Pd3d and Pd 3d binding energy probably revealed the extent of the support-metal electron transfer. Because of this electron transfer, the metal nanoparticles would form stronger dissociative adsorption with O2 and enhance the activation of O2, which is the rate-controlling step of CO oxidation. The Pd3d maintains a higher BE than the bulk Pd due to its electronic confinement effect. The electron transfer in Pd20/TiO2 was the strongest; thus, its apparent BE was quite close to that of the bulk Pd. As a result, its CO oxidation activity reached the maximum.

A research on Ag3/Al2O3 discussed the electron transfer from a different aspect. S. Vajda [61] and coworkers studied the propylene epoxidation on the size-selected Ag3 clusters and the 3.5-nm Ag nanoparticles supported on Al2O3. The DFT calculations showed that their high activities and selectivity was related with the open-shell electronic structure. As shown in Figure 2, O2 dissociate on Ag3, and Ag3O clusters were formed. The Ag3O/Al2O3 has great net spin density on Ag and O in the cluster. If an oxygen atom was adsorbed on the Ag3 cluster, the net spin density would be zero. To some extent, a high net spin density is an indication of a partly occupied s-d hybridized energy level in Ag3O. Such an open-shell electronic structure made the clusters very reactive toward the double bond. To conclude, there are electron transfers between the support and metal nanoclusters. It was found in many kinds of metal that the electron transfers become stronger as the number of atoms in the clusters increase. However, the catalytic activities do not always vary monotonically with the extent of the electron transfer. On the one hand, the metal cluster may show a stronger O2 activation as the electron transfers enhance. On the other hand, if the close-shell electronic structure is formed, the O2 activation would, instead, be prevented. Therefore, the electron transfer is an intrinsic property between the support and metal, and its influence on the catalytic performances is indirect; many other factors should be taken into account.

Another research on Au55 induced a different respect to consider the relation between the electronic effects and sterical effects in catalysis [62]. The authors discovered that the redox properties of Au clusters (1–8 nm) are closely related to size. The Au clusters of 1.4 nm (Au55) specifically showed a complete resistance to oxidation, which is different from all the other Au clusters of different sizes. The XPS valence electron spectra results suggested that
the valence electron binding energy is similar in Au55 and bulk Au. Their binding energies at the Fermi level are almost the same and maintain a large difference from Au2O3 (Figure 3). The author, thus, proposed that the oxidation resistance is independent of the electronic structure. D. W. Goodman have pointed that the Au clusters that are inert to the oxygen atom usually display a high activity for CO oxidation [46]. Some other studies on the Au55 also support this claim. Hence, this work is similar to the first research, namely, the clusters that showed a close XPS to the bulk metal have excellent catalytic activity for CO oxidation. However, the redox property of Au55 is considered to be not influenced by the electronic structure because the binding energy at the Fermi level is close in Au55 and bulk Au. After all, there are possibly charge transfers between Au55 and the substrate. More importantly, it is incomplete to describe the electronic structure of a system simply by electron binding energy.

The relationship between the electronic structure and adsorption properties are described more clearly by the studies of density of states. Uzi Landman et al. [48] prepared Au8 and Au8Sr supported on MgO(100) by the mass-selected technique. As shown in Figure 4, Au8 was the reactive cluster toward CO oxidation. In addition, Au4 showed no activity, while the doped cluster Au4Sr was active (n ≥ 8 for Au8n and n ≥ 3 for Au4Sr clusters were active). The density of states calculations showed that the states of adsorbed O2 overlap with the entire d band of the Au8 cluster (-7 eV - E_F). More importantly, the antibonding 2π* states were located below the E_F, which led to the strong O2 activation. Yet, O2 was adsorbed on Au4 with only one oxygen atom attached to Au4. In this case, the molecular oxygen was binding weakly to the cluster. Also, the narrower d band of Au4 compared with Au8 made its states fail to overlap with the O2 states. Thus, the doping of Sr alters the electronic structure of Au8. The spin-down states of O2 antibonding 2π* orbit could be occupied, and the superoxide-like state of adsorbate was formed.

### 3 Geometric structure of active component

The active component could be viewed as the assembly of the active sites. The active site could be a single atom or a local shot-range structure containing several atoms. This shot-range structure could be described by two parameters: the distances between the atoms and the coordination of the atoms. When it is extended to a long-range structure, the crystal planes, a commonly used concept in catalysis, are formed. Therefore, there are two kinds of geometric structure here. The first refers to an individual active site itself, namely, the topology of multiple atoms. The second means the positional relationships between the several active sites on a crystal plane. The former one
is associated with the fundamental nature of the active sites. As indicated in many researches, the geometrical structure and the electronic structure of an active site are strongly related to each other, and it is difficult to investigate them separately. As a result, the relationship between the topological structures and their effects of molecular activation is also unclear. Therefore, it is necessary to discuss the connection between the geometrical structure and the electronic structure. Later, we would see that this is critical for understanding the catalytic properties of the active sites.

3.1 Connections between geometrical structure and electronic structure

As discussed in the former section, the researchers attempted to correlate the electronic effect and the catalytic activity via comparing the adsorption behavior of the different active sites. However, one problem is still puzzling. Namely, the electronic effect and geometric effect cannot be separately analyzed. Some researchers study the metal clusters in the gas phase in order to avoid the influence of the support-metal interaction. In 2008, Andre Fielicke [50, 63] studied the vibrational spectra of the gold nanocluster in the gas phase between 47 and 220 wavenumbers (Figure 5).

The experimental vibrational spectrum and the DFT calculations revealed that the Au$_7$ cluster would change its geometries for the different charge states, so that Au$_7^-$, Au$_7^0$, and Au$_7^+$ could be assigned. When the tetrahedral Au$_{20}$ cluster lost its corner atom, it could be reflected in the spectrum of Au$_{19}$ because of the reduction of symmetry. The clusters tend to lessen the average coordination and transform to a more open structure when the electron density increases. As we all know, the electronic structure of the nanoparticle is the transition between the split level of the molecule and continuous energy band of the solid. This could be especially reflected by the variation of DOS along with energy [56]. Theoretically, the metal nanoparticle would lose the energy band structure when it is smaller than the de Broglie wavelength of the electron, and the quantum confinement effect presents. In such case, the subnano clusters would have a series of isomers, which is similar to the molecules. These isomers maintain different molecular orbitals, and their structure would vary along with their electronic states. Then, are the geometric structure and the electronic structure just the different sides of the same property? In other words, if all of the positions of the atoms of a chemical system, such as a metal atom cluster, are given, is the energy or the electronic states of the system uniquely determined? Or, if the electronic states of all the atoms in a cluster is given, are the relative positions of the atoms uniquely determined? The basic theoretical chemistry would give positive answers. Therefore, it will be difficult to discuss solely the relation of the electronic structure or geometric structure of an individual active site with its chemical properties.

It is important to realize that the geometrically particular clusters do not necessarily have special electronic structures. Au$_{55}$ is regarded to be icosahedron [2, 64]. The Au$_{55}$ surface atoms have the largest coordination number compared to the clusters with about the same atom number. Although Au$_{55}$ is a close-packed structure, it is not really stable because its valence electrons are not the close-shell structure. The valence electrons at the surface could make the cluster chemically reactive. According to the Jellium model [65], the atom number that could make a close-shell electronic structure is 57, not 55. In this regard, the electronic effects and the geometric effects could be separately discussed because the close-packed structure is very different from the electronically close shell. Previous studies have shown that the chemical properties of the nanoclusters with relatively small size are mainly controlled by the electronic effects, while in larger clusters, the geometric effects dominate [66]. How the stability of
the cluster controlled by these two effects determine the catalytic activity of the cluster is really a compelling topic. This remains to be addressed in further researches. In the following, we will discuss how the variations of the electronic structure along with the geometric structure are associated with the catalytic properties of the metal clusters.

### 3.2 What makes an active site?

Figure 6 presented another example about the Au clusters supported on MgO. The DFT calculations showed that the isomers of Au$_8$ on MgO(100) would reach an equilibrium and that the isomers are catalytically different [48]. This structural flexibility enables the Au clusters to alter the steric condition to catalyze the reaction through the path that is energetically favored. For the bilayer Au$_8$, the O$_2$ molecules were adsorbed at the interface of the clusters and support. After the interaction with O$_2$, the structure of the cluster dramatically changed, which is very important to the activation adsorption because the calculation also showed that the activation adsorption would be blocked if the clusters maintain their structure. The metal oxide films grown on metal substrate are another kind of support. Gianfranco Pacchioni et al. [67, 68] explored how the metal clusters are related to the metal oxide film. For MgO/Mo(100), the structure of Au$_{20}$ on the thin film is very different from that on the thick film. Au$_{20}$ is of a tetrahedron shape in the gas phase, and it would maintain this structure when grown on thick film, while the planar isomer would form on the thin film. The structural change is caused by the electron transfer from the metal substrate, namely, transforming the structure to reach the most stable condition in that charge state. The STM results elucidated that the Au cluster on the three-layer-thick MgO could still form a planar structure, while it would totally become a 3d structure on an eight-layer-thick MgO. The early EXAFS studies also provided representative cases. One important research is about the CO adsorption on 0.6% Rh/γ-Al$_2$O$_3$. The Rh-Rh peak would disappear after CO adsorption, indicating that the Rh-Rh bonds were broken by CO [69]. Thus, the adsorption of the reactant molecules may alter the structure of the metal clusters. While for relatively large Rh particles, like on 1% Rh/γ-Al$_2$O$_3$, the Rh-Rh signs would still be present in the EXAFS spectra. The coordination analysis also showed that the Rh-Rh bonds would not be influenced on the large Rh particles. Therefore, the metal clusters of various sizes will interact with the reactant differently.

It is reasonable to propose that the subnano cluster may be the essential active site. The quantum confinement effect and discrete energy levels of the cluster enable its isomerizations. In the reaction coordinate, a series of different active site-transition state reactant complexes are able to form. The structure of the cluster could evolve along with the structural changes of the reactant reaching its “transition state” as well (Figure 7). Therefore, the transition states are stabilized, and the activation barriers are reduced. The theoretical calculations suggest that the vibrational densities of the states of Au, Ag, Cu, and Ni nanoparticles in the low-frequency region are higher compared with the bulk metals [55]. These properties are related to the increased ratio of the surface atoms in the nanoparticles. As the coordination number of the surface atoms decrease, the force fields around the surface atoms would be more flexible; this is also indicated by the change of lattice force constant. Thus, the subnano metal cluster could reduce the energy of a system through adjusting the geometric structure when the electronic structure

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**Figure 6** The optimized atomic structures of the model catalysts: (A) and (B) Au$_8$; (C) Au$_4$; (D) Au$_{20}$Sr; (E), (F), (G), (H): (A), (B), (C), (D) after O$_2$ adsorption. For details, see Ref. [48]; reprinted with permission from John Wiley and Sons.
or charge states are changed. This is very important for the subnano clusters to serve as the active sites. These subnano clusters are metastable species and are similar to the reactant molecules in size. The molecules adsorbed on the active sites could undergo a series of transition states in an energetically favored way, and the activation energies are, thus, greatly reduced. The conventionally mentioned active sites, such as the coordination unsaturated sites, surface defects, could all be viewed as subnano clusters embedded in crystal planes. It is worth noting that the size of the active sites is of the same order as the reactant molecules in enzyme catalysis and homogeneous catalysis [70]. The conformation variations of the enzyme, especially, enable its ultrahigh selectivity and activity in catalysis. The structural variability of the subnano metal clusters may probably be the essential condition for high activity.

3.3 Positional relationship between multiple active sites

In the following, we mainly talk about the latter geometric structure, which is also an important property of the crystal plane. The catalytic properties of the nanoparticles with various shape mainly originate from their differently exposed crystal planes [15, 71]. Our group has investigated the crystal plane-dependent catalytic properties of a series of metal oxide nanocrystals. In 2005, we discovered that (111) planes on the CeO₂ nanocrystals were more reactive than the (001) and (110) planes for CO oxidation [72]. Such phenomenon was also found on the CuO nanocrystals with different morphologies and preferentially exposed crystal planes [71, 73]. The MnO₂ nanocrystals with different phases also exhibited different activities for CO oxidation [74]. This is originated from the different Mn-O bond in α- and β-MnO₂. The cleavage of Mn-O bond in α-MnO₂ is easier because β-MnO₂ has a denser structure. We also demonstrated the crystal-facet-dependent activities of the Co₃O₄ nanocrystals in the different kinds of reactions [75, 76]. For methane combustion, the activities were: (112)>(011)>(001). Afterwards, we began to investigate the hydrogenation reaction of the bimetallic nanocrystals. Among a series of PtNi nanocrystals, the sample with a larger percentage of (111) facets displayed better activity for benzalacetone hydrogenation [77]. The adsorption of the reactant molecules, at least for the same catalytic species, would not vary significantly among the different crystal planes. Then, what property makes the crystal planes perform differently in catalysis? One of the basic steps in catalysis is the contact of the electron cloud, the part that reacts, in the reactant molecules. If the distance between the active sites is in a certain range or other particular conditions, the contact efficiency of the reactants reaches its maximum. In other words, the overlaps of the molecular orbital could be influenced. Therefore, the distances between the surface atoms or active sites would determine the contiguity of the reactants. The catalytic reaction would be the most favored when such distances lie in a certain range.

D. W. Goodman et al. [78] have prepared Pd/Au(100) and Pd/Au(111) by depositing the Pd atoms on a clean Au surfaces. The activities of acetoxylation of ethylene to vinyl acetate on the two catalysts (453 K) were compared. The results showed that the TOF was much lower on the Pd/Au(111) than on the Pd/Au(100) (Figure 8). The distances between the Pd monomers were thought to play an important role because they affect the coupling of the two reactant molecules, which is just the rate-limiting step of this reaction. As displayed in Figure 9, the calculations based on the bond lengths indicated that the most ideal distance between the active sites is 3.3 a. The space of the two neighboring Pd monomers is 4.08 on Au(100), while it is 4.99 on Au(111). The former distance makes it possible for the coupling of ethylene and acetate species. Instead, the spacing between the two nearest Pd sites is much longer than 3.3, the reaction is, thus, very difficult.

The remaining question is to rule out the electronic effects. By comparing the work function of Pd and Au as well as the XPS, the CO adsorption results of Pd on the two surfaces, the influences of the electronic properties were eventually excluded. More importantly, for the cyclization of acetylene to benzene, Pd/Au(100) and Pd/Au(111) presented identical activities. Similarly, according to a
research on dehydrogenation of cyclohexene to benzene [79], the activities of the different Pt crystal planes followed the trend of Pt(654) > Pt(557) > Pt(111), but these facets exhibited the same activity for the hydrogenation of cyclohexane to hexane. In other words, different reactions could hardly have the same ideal contiguous distance, thus, a single catalytic system could not meet all kinds of reactions. In this regard, the bond lengths, ideal distances between the molecules and the active sites, could be strongly connected. Sometimes, the relative positions of the active sites need to match the different reactive parts in a single reactant molecule.

The nanoclusters are different from the bulk particles in this term of geometric property. On the one hand, the atomic distances would change when the metal particle becomes smaller. Generally, the lattice in the metal clusters prepared by deposition or other physical methods would shrink [55, 80, 81], which is revealed in the EXAFS results and the lattice phonon frequency. The metal bond contractions in Ag, Cu, Ni nanoparticles could reach 1.6–2.0%, and the internal part could shrink more intensively than the surface atoms [55]. Therefore, the molecular orbitals in the adsorbed reactants overlap differently on the nanoclusters or the bulk metal. On the other hand, complex dynamic changes would occur on the nanoclusters in reaction conditions. In addition, there are strong lattice relaxations in metals like Au, Pd, and Pt [2, 71]. The melting point of Au is 1336 K, while it is less than 600 K when Au is of 1–2.5 nm in size. The lattice is less stable in these nanocrystals. It is just these metals that display remarkable catalytic activities. How could the nanoclusters of these metals catalyze many types of reactions? It is possible that the instability of nanocrystals enables the metal bond lengths and coordination to vary in a certain range. This variation makes the active sites match several types of reactions.

Similarly, the change of support could induce alterations in the shape and distribution of the loaded species. The EXAFS studies provided many valuable examples. When Rh and Ir are supported on SiO$_2$, Ir would segregate on the Ir core. However, Ir and Rh choose to homogeneously distribute when loaded on Al$_2$O$_3$, and the coordination unsaturation was higher because the planar structure was formed [69]. Also, Pt was of particle shape on $\eta$-Al$_2$O$_3$ (1% loading amount), while raft structure was generated when supported on $\gamma$-Al$_2$O$_3$ [69]. As been speculated, when the spacing between the tetrahedron centers or octahedron centers increase, the formations of the metal bonds are unfavorable, and thus, the planar structure with higher unsaturation is generated. At present, there are still many attentions on how the supports and crystal planes contribute in catalysis. The above discussions suggest possible approaches for this investigation. The electronic properties of active component control the activation adsorption of reactants, and the positional geometric properties determine the coupling of reactants.

4 Characterization: the challenge

The knowledge of the active component as well as the catalytic processes comes from the physicochemical characterizations. The researchers’ understandings of catalysis are directly defined by the developments of the characterization methods. A long time after 1989, it was demonstrated by many researches that the Au nanoparticles...
with sizes of 3–5 nm showed excellent activities in various reactions, especially CO oxidation. The activity for CO oxidation vanished when the Au particles were larger than 8 nm. Many experimental and theoretical studies attempted to explain the size dependence of the activities.

However, in a research on the WGS catalytic active sites of Au/CeO$_2$ and Pt/CeO$_2$ [49], the author discovered that the WGS activity was not affected even when the metal state Au or Pt was washed by NaCN (Figure 10). The XPS results suggested that Au$^{+}$, Au$^{3+}$ or Pt$^{2+}$, Pt$^{4+}$ were all presented on the surface of the catalysts before or after wash, namely, the positive charge state metal were not removed. According to the CO-TPR and calculation results, Au$^{+}$ was able to create more oxygen vacancies on the CeO$_2$ surface and increase the amount of the oxygen species.

From then on, the researches involving the removal of crystalline metal particle started to appear. Similar results have also been reported on Au/CeO$_2$ and Au/TiO$_2$ for CO oxidation. The nonmetallic Au$^{+}$ was then considered to play an important role in these reactions, not simply Au nanoparticles.

A research on Au/FeO$_x$ for CO oxidation elucidated more convincingly the nature of the active sites [53]. The great influence of the drying conditions on the catalytic performances induced the question. The two Au/FeO$_x$ samples were derived from drying in static air and flowing air. CO conversion of the latter sample reached 100% at 298 K, while the former had no activity at the same temperature. The aberration-corrected STEM-HAADF was then used to observe the two samples. The results (Figure 11) revealed four types of Au of the iron oxide surface: individual Au atom, monolayer Au clusters (0.2–0.3 nm), bilayer Au clusters (0.5 nm), and Au nanoparticles (3–5 nm). Further STEM studies showed that the Au single atom and Au nanoparticles existed under both drying conditions. The monolayer and bilayer Au were only found in the latter sample, which means that one or both of them determined the activity. Then, the author compared the changes after the thermal treatments of the catalysts. The bilayer Au clusters was eventually defined as the active species.

The bilayer Au clusters of 0.5 nm contain approximately 10 atoms, while there are 1900–2500 atoms in the 5- to 7-nm range of Au particles. Thus, the active component occupied a very small part (<1%). Because of this, the subnano Au clusters were very difficult to be detected by the traditional microscopic methods. As revealed in the STEM pictures, the bilayer clusters and individual atoms maintained similar contrast. Such a low contrast could neither be probed before the applications of the aberration-corrected STEM nor could these subnano structures be detected by the spectroscopic methods, for their signals were too weak to be observed. Because of the low percentage, these Au clusters may only be “seen” under advanced microscopy with enough resolution. Therefore, the generally accepted high activity of the Au nanoparticles among the 3- to 5-nm range may be insufficient and unrepresentative.

People attempt to investigate the process of CO oxidation, a simple reaction. However, the understandings and the interpretations of the results are shaped by the
research method applied. Currently, the Au-catalyzed CO oxidation is controversial in several important aspects, including the structure of the catalysts’ surface during the catalysis processes, the type of active oxygen species, or the reaction sites for CO and O₂. On active oxygen species, for example, atomic oxygen was formerly considered to react with CO. As reported afterwards, it was the superoxide intermediates $O_2^\cdot\cdot(0<x<1)$ that could react with CO [83]. Also, there were evidences that peroxide species have the highest activity. Some other researchers believed that the molecularly adsorbed oxygen, instead of the atomic ones, were the active species [51].

It is important to realize that catalysis is the process that go across several scales of space and time, which means that many factors are associated. From the restructures of the surface and nanoparticle catalysts, the air diffusions, to the transfers of heat and mass, all these processes would directly or indirectly affect the catalytic performances [12]. The understandings and explanations of the spectroscopic results depend on the spatial, temporal, and energetic resolution of the methods. The elementary reactions occur typically on ultrafast (femto- to picosecond) timescales [12]. The resolution of the most traditional spectroscopy is no more than the microsecond order. In other words, only the macroscopic and average information could be reflected. As discussed above, the active sites may have similar sizes with the reactant molecules. Thus, the elementary reaction kinetics information that correlated to the subnano structures of the catalysts is significant for further understandings of the
catalytic mechanisms. G. Ertl [16] had realized the potentials of the surface analysis techniques and had catalysis studies from surface chemistry aspects since the 1960s. By studying the interactions between the small molecules like O₂, CO, H₂, N₂, and NO with the surface of the metal and alloy, he founded the paradigm for the research of surface chemistry. Building up the relation between the catalysts surface species and catalytic performances has become a very important research method. However, more advanced analysis techniques are necessary for the further investigation of the catalysis. G. Ertl has done remarkable researches on the reaction mechanism of ammonia synthesis. A question which had been most concerned was whether nitrogen participates in the reaction in the molecular state or atomic state [16]. Nevertheless, for the molecules like N₂ and O₂, there could be many transition structures between the entirely molecular state and atomic state, which are two extreme conditions. The information about these transition structures could be essential in understanding the catalytic processes, which was impossible to be addressed at that time because of the temporal resolution of the techniques. Therefore, the properties and structures of the active sites, the dynamic of catalytic reactions, the activations of molecules, and the in situ conditions of the catalysts’ surface during the reactions, all these topics that have puzzled researchers for a long time, are still open to dispute.

5 Conclusions and perspectives

In this perspective, we have addressed the active sites from the electronic properties and geometric properties. In other words, it is from the catalytic materials’ viewpoint that we discuss catalysis. As has been proposed, there are still many problems on the catalytic effects of the active sites. On the one hand, the understandings of the electronic structure of the metals are not enough. Although there have been quantum mechanics methods that could analyze the larger metal clusters, comprehensive theoretical methods for describing the electronic structure of the nanostructures are still unknown. The calculation of the open-shell systems is a great difficulty of the current theoretical chemistry. On the other hand, the method for probing the short-range amorphous structure is insufficient. The in situ characterization of the active sites’ structures is one of the most difficult and important topics in catalysis [17]. In addition, the relationship between the electronic structure and the geometric structure of the metal nanoclusters calls for more clear elucidations. From current evidences, subnano clusters may be most close to the essence of the active sites. However, the exact type of these clusters and how they modulate among a series of transition states is unclear. Thus, the complete description of an active site is significant, which is also related to the boundary of the concept of nanocatalysis. Namely, how do these nano and subnano clusters be catalytically different from the coordination compounds or bulk particles? What are the catalytic properties of a perfectly flat surface without any defects? Further advances into nanocatalysis call for clear investigations to these questions. As another topic, it is important to note that metal nanoclusters may serve as the bridge that connects the heterogeneous catalysis and homogeneous catalysis. Our recent work (Figure 12) found that disordered Pd nanoparticles partly crystallized after the Miyaura-Suzuki reaction and that the bimetallic PdAu nanoparticles underwent phase segregation in the same reaction [84]. In other words, the assembly of Pd atoms or Pd subnano clusters may play a

Figure 12  Schematic illustrations of structural changes of Pd-based nanocatalysts in the Miyaura-Suzuki reaction. For details, see Ref. [84]; reprinted with permission from John Wiley and Sons.
significant role in this catalytic process. This result provides another important aspect to consider the nature of the active site in nanocatalysis.

Nanocatalysis is a young interdisciplinary study. Perhaps the future of such a relatively new science lies not in the proposal of new theories. Looking back to those important theories in the history of catalysis, such as the theory of active group, multiple sites theory, and semiconductor catalysis electron theory, although there were certain limitations, we could still glimpse on a prototype of the nanocatalysis. Especially, the theory of the active groups put forward in 1939 suggested that the amorphous phases of the catalysts were the active components, while the crystalline phases served as the inactive supports. For the reactions of the same type, the active site was a group containing a certain number of atoms, and for the other types, the atom number in the group altered. This was the first theory that regarded the noncrystalline phase as the active sites. Such a historic theory had been qualitatively similar with the present understandings of the active sites, only that the exact structure of the active sites and the bonds with the reactants were unable to be analyzed at that time. From the end of the 1960s to the 1990s, G. Ertl and Gabor A. Somorjai [16] induced research methods from surface science, the microscopic information could then be associated with the performances of the catalysts. However, a characterization method could only provide information under its time resolution, and the time resolution in catalysis research is far from being enough, even at present. In the 1900s, after the pulsed laser was applied in spectroscopy, more and more time-resolved techniques emerged [85–90]. Hopefully, the elementary reaction kinetics along with the dynamic changes may be revealed by these techniques. The reaction mechanisms could, in turn, instruct the designs of the catalysts with the specific structure and function. The future of the nanocatalysis lies in the development of research methods, which requires in situ, dynamic, high-resolution characterizations. The catalysis mechanisms could then be comprehended at the molecular level, and the catalysts will be constructed at the atomic level.

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