CHEMCATCHEM
Concepts

The Power of Single-Atom Catalysis

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Single-atom catalysts (SACs) with individual and isolated metal atoms anchored to supports can act as active centers. Single-atom catalysis is powerful and attractive because SACs have demonstrated distinguishing performances, such as drastic cost-reduction, notable catalytic activity, and selectivity. Herein, we firstly introduce SAC, including the concept and some key issues in synthesis and catalysis. Then, the power of single-atom catalysis is highlighted and the most recent advances are summarized. It is very encouraging that in recent years our understanding of SACs has increased, owing to substantial studies regarding sample preparation, characterization, evaluation, and also mechanistic interpretation. On the other hand, great challenges still remain for SACs.

1. Introduction

Among various catalytic reactions, catalysis that occurs at the interface between solid catalysts and reactants dispersed within fluids is known as heterogeneous catalysis. Noble metals, such as Pt, Pd, Ru, Rh, and Ir, are superior heterogeneous catalysts and have been widely used in the petrochemical industry, medicine production, environmental protection, and new energy. However, owing to the high price and low natural abundance of such noble metals, they cannot meet the increasing demand. For example, a brick with the dimensions $20 \times 10 \times 5$ cm, made of pure gold with a price of \$38.1 per gram, is worth approximately \$736 000. If a common brick worth 20 cents is coated with an atomic thin layer of gold, the cost of the gold layer is 1 cent and the total value is just 21 cents (Figure 1). The gold-coated brick, despite only having an extremely thin layer containing gold, is capable of accelerating and controlling the overall chemical reaction because only the surface atoms of the catalyst are necessary for heterogeneous catalysis. Thus, the key to cost reduction is to maximize the acquisition of surface atoms of noble metals. Presently, how to maximize the atom utilization efficiency of the supported noble metals is becoming increasingly stringent for heterogeneous catalysis.

The development of nanoscience has triggered technological innovation and industrial revolution, and has also provided good opportunities and strategies for the design of novel heterogeneous catalysts. The amazing properties of nanomaterials, such as huge surface area and quantum size effect, result in excellent catalytic activity and selectivity when serving as catalysts. The biggest difference between surface atoms and those in the bulk is that the former are in an unsaturated coordination environment and have higher reactivity. When the particle size of a catalyst is reduced to nanoscale, the ratio of surface atoms is substantially increased. Meanwhile, as the catalyst size is further reduced, the surface atomic structure, electronic structure, and defects will change significantly. As a consequence, the catalytic activity of the catalyst will be further improved. The use of specific nanosized catalysts has brought about breakthroughs in some heterogeneous catalysis by providing abundant and well-designed active sites. What would be the consequence of solid catalysts being reduced to their ultimate limit? The answer is single-atom catalysis (SAC), an innovative concept that, especially in recent years, has attracted increasing attention in the field of heterogeneous catalysis.[1]

Research on single-atom catalysts (SACs) is thriving and our understanding of SAC has been further promoted in recent years, including better understanding of sample preparation and characterization, the role of support, the strong metal–support interactions (SMSIs), and the catalytic mechanism. Single-atom catalysis offers fascinating prospects, such as drastic cost-reduction, high activity, and selectivity. On the other hand, the synthesis of SACs with densely dispersed and isolated single atoms, the robust stabilization of these surface single-metal atoms, as well as some other issues remain to be great challenges and are in urgent need of experimental and theoretical investigations. Herein, we introduce the concept of SAC and synthesis of the catalysts, we elaborate the key issues and challenges, and finally we summarize the most recent advances, especially the use in electrocatalysis.
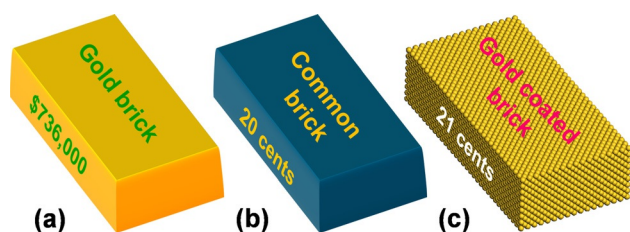

Figure 1. Prices of different bricks with a size of $20 \times 10 \times 5$ cm; a) gold brick; b) common brick; c) common brick coated with a single atomic layer of gold atoms.

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2. Concept, Synthesis, and Key Issues

2.1. Background and concept

As the size of one supported metal particle is reduced, more and more surface atoms appear and locate in a low-coordination environment, together with quantum-size effect and the reinforced metal–support interaction, these surface atoms become increasingly active to specific reactions.[1c] In 1991, Basset and co-workers reported a silica-supported zirconium hydride that was extremely electron deficient and gave rise to unusual catalytic activity for the hydrogenolysis of neopentane, isobutane, and propane at 50 °C.[2] In 1996 they synthesized a silica-supported tantalum(III) monohydride complex, which was characterized by infrared spectroscopy, extended X-ray absorption fine structure (EXAFS) analysis, microanalysis, and quantitative chemical reactions.[3] Despite the absence of direct electron microscopy images for the $(\equiv SiO)_2ZrH$ and $(\equiv SiO)_2Ta^{III}H$ species, single-atom catalysis may have been in operation. In 2000, Abbet et al. reported the cyclotrimerization of acetylene on size-selected Pd_n clusters $(1 \leq n \leq 30)$ supported on thin MgO (100) films and found that a single palladium atom was enough for the production of benzene at 300 K, whereas for larger clusters $(7 \leq n \leq 30)$ benzene was produced at the higher temperature of 430 K.[4] In 2005, Böhme and Schwarz reviewed gas reactions catalyzed by atomic and cluster metal ions and regarded such catalysts as the ultimate single-site catalysts.[1b] In the meantime, Thomas et al. reviewed heterogeneous catalysts with single active sites, in which a catalyst with individual atoms was listed as one of four representative cases.[1a] In 2011, Thomas et al. published another article in which the issue of whether a single atom could serve as the active site in some heterogeneous catalysis was discussed again.[5] In the same year Zhang and co-workers reported the practical fabrication of a novel catalyst with single Pt atoms supported on iron oxide (Pt_1/FeO_x) and proved that the single Pt atoms served as active sites for CO oxidation.[6] More importantly, in this work they formally introduced the concept of "single-atom catalysts" and "single-atom catalysis".

SACs have individual and isolated metal atoms that are anchored to a specific support and can behave as active centers for heterogeneous catalysis.[1] In addition, ion-exchanged metals supported on porous materials, as well as organometallic complexes anchored to supports, in principle, could also be viewed as SACs.[1c, 7] The concept of SAC is novel and the catalysts are totally different from conventional heterogeneous catalysts, which consist of various metal nanostructures and supports with huge specific areas. SACs have high activities and enable the utmost utilization of supported metals, and they also provide single active sites, which offers superior selectivity as homogeneous catalysts.[1a] SACs bridge the gap between homogeneous and heterogeneous catalysis and can perhaps be regarded as the limit of heterogeneous catalysis; the limit in dimension and the limit in precise design of catalytic active sites at the atomic level. Investigation of SACs will facilitate our understanding of the catalytic mechanisms and also offer some rational strategies for the design of novel catalysts. There

are a number of scientific issues regarding the preparation of high-quality SACs and the understanding of their catalytic performance. For example, the support must have a large surface area, but more importantly, it must be able to provide some specific anchoring sites to tightly "grasp" the guest atoms.[8] Furthermore, there are many factors to be taken into account when designing and understanding single-atom catalysis, such as the species of supported atoms, the surface atomic and electronic structures of the supports, the solvent effect, the interaction between single atoms and the support as well as their synergistic effect, among others.[1c] To date, some examples of single-atom catalysts using metal oxides,[6, 9] metal nanoparticles,[10] and carbon materials[11] as supports have been reported. These examples open a new domain for more precise design of efficient and specific catalysts in the future.

2.2. Synthesis

Synthesis of SACs can be realized through high-vacuum physical deposition techniques, such as sputtering and atomic-layer deposition (ALD).[12] Although vacuum depositions of single atoms are easier to control, this route can only offer model SACs for fundamental research because of the high cost and low yield.[1c] Taking advantage of gas-phase reactions, another route, similar to chemical vapor deposition, was reported by Dong and co-workers.[11b] Within an enclosed chamber, high-purity niobium was evaporated through arc-discharge and then promptly reacted with pyrolytic carbon (the source was methane), by which single niobium atoms finally were well dispersed within the layer structures of graphite. So far, SACs have been synthesized mainly by wet-chemical routes,[6, 13] among which co-precipitation is very facile and cost-effective, quite suitable for future mass production and applications. In recent years, Zhang and co-workers have successfully prepared a series of SACs, in which single atoms could be tuned from Pt, Ir, to Au.[6, 13b, 14] Presently, the great challenge for SAC is how to prepare catalysts with isolated single atoms finely, densely, and tightly anchored to the support. Firstly, owing to the huge surface-free-energy of single atoms, aggregation seems to be inevitable, especially when the enhancement of surface-loading densities of single atoms is desired. On the other hand, even when dispersed finely as single atoms on the support, stabilization of these surface single atoms remains to be a challenge owing to high mobility and easy sintering.[15] These single atoms are, therefore, not capable of withstanding practical use, especially at higher temperatures. Therefore, obtaining robust anchoring sites through SMSIs are the key to resolving these issues.[16] However, on a flat and common surface an individual guest atom is usually in contact with only three or four host atoms, resulting in very weak bonding and easy mobilization. For example, the activation energy for self-diffusion of gold atoms on a gold surface was found to be only ≈ 30 kJ mol^{-1}.[17] For some supports the surface vacancies or defects can be good anchoring sites for single atoms, for example, the cation vacancies on FeO_x or γ-Al_2O_3 for Pt atoms.[6, 18] In a similar manner to organics ligand, the nonmetallic elements on the support surface, such as C, O, N, can

also be used to tightly anchor single metal atoms, as proposed by Schüth.[19] For instance, metal–carbon bonds are in the order of ≈ 200–$300\ kJ\,mol^{-1}$, which is sufficient to keep them stable under many catalytic reaction conditions.[19, 20] Also, anchoring single atoms through spatial confinement has been proven to be effective. In 2012, Tang and co-workers reported the fabrication of single-atom silver chains inserted in the tunnels of Hollandite-type manganese, as shown in Figure 2.[13a] Additionally, Wang and co-workers, in 2014, reported the stabilization of single Ni atoms on a 2D titania structure with periodic six- and ten-membered nanopores, which was stable even at room temperature, as shown in Figure 3.[21] Investigations devoted to the theoretical analysis or prediction of robust anchoring sites for single atoms, with respect to graphene, θ-Al_2O_3, TiN, CeO_2, and graphyne as supports, have also been reported elsewhere.[22] Moreover, Basset and co-workers have obtained a single-metal catalyst through precise design of the grafting strategy. For instance, they prepared a catalyst of surface tantalum(III) monohydride ($\equiv SiO)_2Ta^{III}H$, which is similar to a single-atom catalyst, through sublimation of $Ta[CH_2C(CH_3)_3]_3[=CHC(CH_3)_3]$ under vacuum (10^{-5} mmHg) at $80\,°C$ onto pre-processed silica, followed by post-treatment under 1 atm of hydrogen up to $200\,°C$.[3] This strategy could be transferred to the preparation of other types of SACs.

Figure 3. a) STM image ($30 \times 30\ nm^2$, $V_{sample} = +2.0$ V, $I_{tunnel} = 0.3$ nA) of the $SrTiO_3$ (110)-(4×1) surface. Sr adatoms are labelled as well as stripes that form the (5×1) reconstruction. b) Top view of the $SrTiO_3$ (110)-(4×1) surface. Ti and O atoms are shown in blue and red, respectively. Positions (I–III) for Ni adatoms (gray), attached to surface O atoms, have the most favorable adsorption energies according to DFT calculations. Reprinted with permission from Ref. [21a]. Copyright 2014 American Chemical Society.

2.3. Strong metal–support interactions (SMSIs)

SMSIs arising from interfacial bonding are crucial to the understanding of SAC, this not only determines whether guest metal atoms in SACs can be tightly anchored onto the support, but also plays a significant role on the subsequent catalysis. As proposed by Tauster and co-workers in 1978,[23] the notion of SMSIs was first used to describe the drastic suppression in chemisorption properties as group VIII noble metals were supported on titanium oxide after hydrogen reduction at high temperature. Early research preferred to understand SMSIs as electronic effects, namely electron transfer from cations in transition-metal oxides to supported metallic components, possibly because of mutual *d*-orbital overlap.[16] Gradually, it became clear why hydrogen reductions were a prerequisite in terms of producing SMSIs: The need for low-valence surface cations to take part in interfacial bonding with guest metal atoms.[24] Also in early research, surface scientists found that, for heterogeneous catalysts, SMSIs had an effect not only on chemisorption or catalytic dynamics, but also on the morphology of the supported metals.[8] For example, in 1987 Tauster reported that Pt particles on reduced TiO_2 (the surface had been reduced into Ti_4O_7) were much smaller than those supported on SiO_2, which showed no strong SMSIs with Pt, as illus-
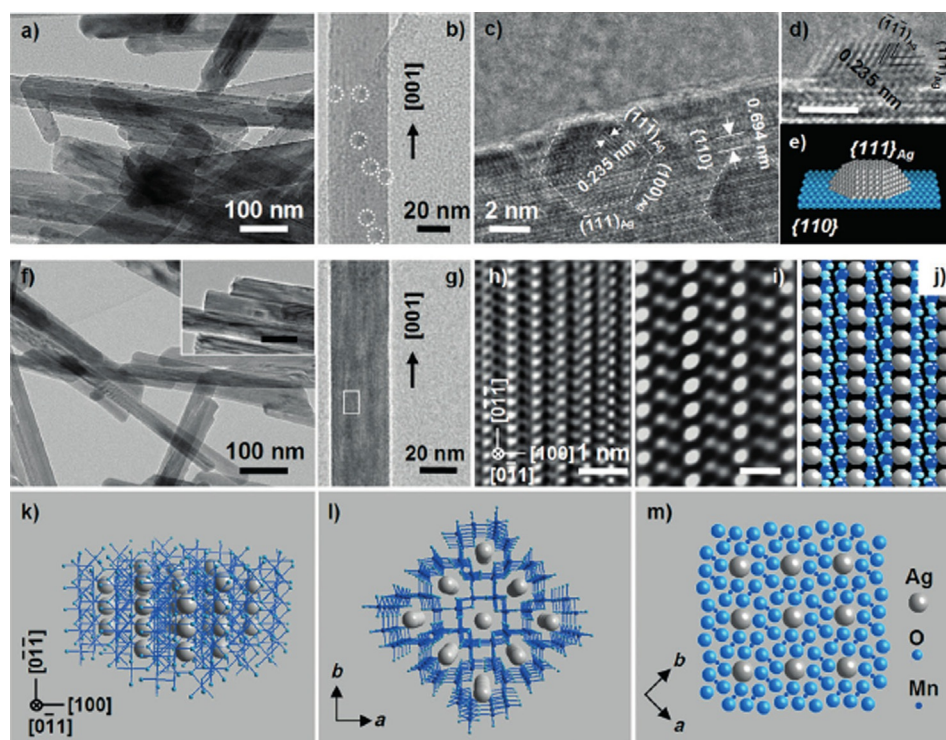

Figure 2. a) TEM image of Ag/HMO. b) TEM image of the supported silver nanoparticles (SNP; white dotted circles) supported on a typical HMO nanorod with a [001] growth direction. c) HRTEM image of the Ag/HMO showing a hexagonal SNP. d) HRTEM image of the Ag particle of Ag/HMO. e) Structural model of the Ag particle supported on the {110} side-facet of the HMO. f) TEM images of Ag-HMO. g) TEM image and h) HRTEM image of a Ag-HMO nanorod with a [001] growth direction, indicating the Ag atom chains. i) Auto-correlation function analysis and j) simulated images of the panel (h) showing Ag single-atom chains. Scale bar: 0.5 nm in panel (i). k,l) Single-atom Ag chains inside the tunnels of the HMO viewed from the [011] and [001] directions, respectively. m) Atom arrangement on the {001} facet of Ag-HMO. Adapted from Ref. [13a]. Copyright 2012 Wiley-VCH Co. KGaA, Weinheim.
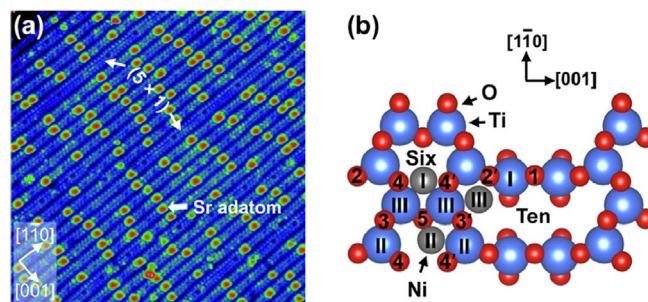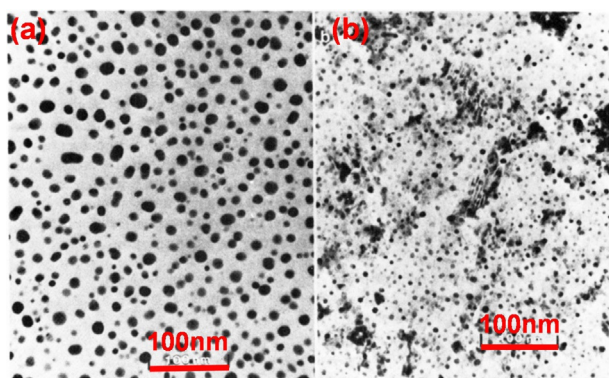
Figure 4. Electron micrograph of Pt supported on a) SiO_2 and b) TiO_2 after treatment in H_2 at 800 °C for 1 h. Reprinted with permission from Ref. [16]. Copyright 1987 American Chemical Society.

trated in Figure 4.[16] In addition, owing to SMSIs, the spreading of TiO_x on metals and the spreading of metals on TiO_x were both observed.[16]

As demonstrated above, SMSIs in the early stages were somewhat constrained within the scope of using transition-metal oxides as supports. With the rapid development of research methods, especially with the help of advanced electron microscopy techniques, various interactions have been found between metals and other types of supports, such as non-transition metal oxides,[18] metals,[14,25] and 2D carbon materials.[11] Therefore, the scope of SMSIs has been largely extended, involving all strong interactions between any supported metallic components and any support. In Figure 5, twelve types of interaction between metal and support are illustrated, in which only a fraction can be considered as a SMSI.[8] According to the nature of the interaction, SMSIs can be mainly divided into two types, one stemming from electronic defects and the other one mainly caused by surface structural defects.[8,18,26] Around this term, there are many important issues to understand, for example, effects of SMSIs on the sintering and shaping of metal particles, on electron transfer, on formation of interfacial phase, or new compounds.

Surface organometallic chemistry can construct active sites on the surface by a true molecular engineering approach, on which a great deal of excellent work has been performed.[27] For example, metathesis of alkanes catalyzed by silica-supported transition-metal hydrides was reported by Basset and co-workers. A possible reaction pathway was speculated, which might involve a four-centered transition state between a tantalum–alkyl intermediate and a C—C bond of a second molecule of alkane.(Scheme 1)[28] As for SAC, in principle, all uncapped sites on the support surface could probably be used to bond with specific foreign species. SMSIs of electronic defects have been proven to be capable of anchoring individual atoms tightly, either through direct M_2–M_1 bonding or through the formation of M_2–O–M_1, in which M_1 and M_2 represent the supported metal atom and the metal cation of the support, respectively.[18,25,29] The second type of SMSI, namely structural defects, can be surface steps,[8] coordinatively unsaturated sites,[18] surface vacancies,[30] or other types of surface defects, such as F centers that are able to anchor the supported metal
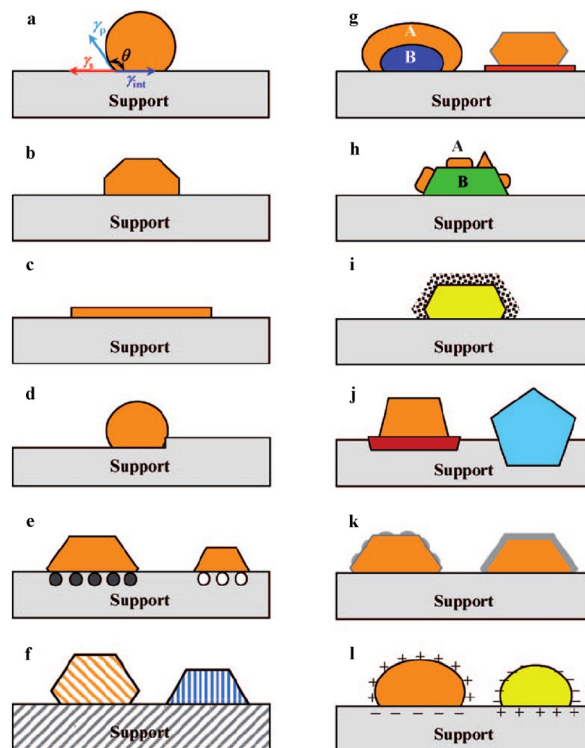

Figure 5. Illustration of metal–support interactions: a) weak metal–support interaction; b) intermediate metal–support interaction; c) strong metal–support interaction; d) anchoring of metal nanoparticles by nanofacets or steps; e) anchoring of nanoparticles or clusters by surface vacancies or impurities; f) anchoring of nanoparticles by epitaxial growth; g) anchoring of metal nanoparticles by "pinning" (left) or by the use of "nanoglue" (right); h) anchoring of nanoparticles by "configuring"; i) anchoring of nanoparticles by "caging"; j) formation of interfacial interphases (left) or compounds (right); k) partial coverage (left) or encapsulation (right) of nanoparticles by support materials; and l) electron transfer from metal particle to support (left) or from support to metal particle (right). Adapted from Ref. [8]. Copyright 2011 Wiley-VCH Co. KGaA, Weinheim.
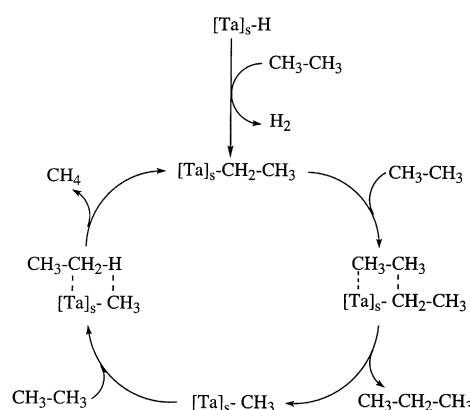
Scheme 1. One possible reaction mechanism for ethane metathesis. Adapted from Ref. [28]. Copyright 1997 American Association for the Advancement of Science.

strongly.[31] If the bond strength with some sites on the support surface is weak, for example, owing to polarization and dispersion with little mixing with the support orbitals, single atoms cannot be anchored. Owing to the advantage of multi-

ple bonding with more than one adjacent oxygen atom, some vacancies on specific supports have been found to be superior anchoring sites for single atoms, such as the aluminum vacancies of γ-Al_2O_3[18] and the iron vacancies on Fe_2O_3 for Pt,[6] and the zinc vacancies of ZnO for Au,[8] as shown in Figure 6.
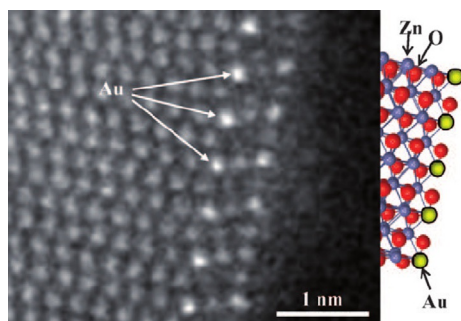

Figure 6. Sub-angstrom resolution, high-angle annular dark-field image of a ZnO nanobelt decorated with individual Au atoms. The right-hand side diagram illustrates the relative positional relationship between the Au atoms and the Zn and O columns of atoms. Adapted from Ref. [8]. Copyright 2011 Wiley-VCH Co. KGaA, Weinheim.

Carbon materials, in some cases, can tightly bond with metals, especially after some treatment; attempts of using such support for SACs have been carried out both experimentally and theoretically. For instance, on graphene the isolated Pt atoms could be anchored directly by surface carbon atoms. Hollow sites, each missing three carbon atoms, on graphene were thought to be ideal anchoring sites for single Ni atoms after calculation.[11b] Recently, theoretical screening with the aim of finding robust anchoring sites for SACs have been reported intensively, for example, for graphene,[22e] TiN,[22c] BN,[32] θ-Al_2O_3,[22b] TiO_2,[9b] and various metal nanoparticles.[10] In fact, robust anchoring of the single atom to the support is not enough to achieve the potential of SACs. These single atoms still need stabilization, careful design of the active sites, and understanding of the role of the support.

# 3. The Power of Single-Atom Catalysis and Recent Advances

Generally, three principal indicators are considered during the performance evaluation of industrial heterogeneous catalysts: activity, selectivity, and long-term stability, which strongly depend on many factors, such as the nature of each component, particle size, surface structure and atomic composition, and the physical/chemical interactions among the various components.[8] As a type of novel heterogeneous catalyst, SACs have unique interfacial configurations that offer maximum atomic utilization and single, highly active sites. As mentioned above, before the advent of the formal concept of SAC, Abbet et al. reported that by using a single-atom catalyst (Pd supported on MgO) or with very small Pd clusters ($n \leq 7$), the temperature for the cyclotrimerization of acetylene into benzene could be largely decreased from 430 to 300 K.[4] Subsequent theoretical calculations showed that free inert Pd atoms

were activated by charge transfer from defect sites of the MgO substrate upon deposition. For some other reactions, such as oxidation, the water–gas shift reaction, and hydrogenation, SACs have proven to be powerful catalysts with high activity, excellent selectivity, and stability. In recent years, SACs have also demonstrated notable catalytic performances in some other fields, such as hydrogen evolution, methane conversion, and electrolysis. Below, some representative research, as well as the advances of single-atom catalysis, is summarized.

3.1. Oxidation, hydrogenation, and other reactions

Oxidation and hydrogenation reactions are often used as probe reactions for the evaluation of the catalytic performance of SACs. In a variety of oxidations, such as CO oxidation,[6] HCHO oxidation,[13a] and that of small organic molecules,[14a] SACs have been shown to be better than their counterparts (supported nanoparticles or clusters). For example, SAC of Pt_1/FeO_x could provide isolated and positively charged Pt atoms, in turn capable of largely lowering the CO adsorption energy. This single-atom catalyst exhibited excellent stability and high activity for both CO oxidation and preferential oxidation, several times more active than subnanometer-sized Pt clusters.[6] One may wonder how single Pt atoms could act as active sites because at least one Pt—Pt bond is necessary for CO oxidation according to the conventional Langmuir–Hinshelwood scheme (L–H scheme). Narula and co-workers studied CO oxidation on single Pt atoms supported on θ-Al_2O_3 and proposed another pathway based on their experimental results and theoretical calculations.[33] First of all, the supported Pt single atom preferred to bond to O_2 rather than CO. Then, CO bonded with the oxygenated Pt atom and formed a carbonate, which dissociates to liberate CO_2, leaving an oxygen atom on Pt. Finally, the catalyst was regenerated through subsequent reaction with another CO molecule, as shown in Scheme 2.[33] The pathway proposed was convincing because strong evidence of CO_3 coverage that ought to occur was found. Notable performances of SACs in methane, alcohol, and some other oxidations have also been reported.[29a, b, 34] In 2014, Zhang and co-workers reported the preparation of colloidal Au/Pd SACs. In glucose oxidation, this SAC exhibited a significantly improved catalytic activity (up to 17 times) compared with that of Au nanoclusters (NCs) with a similar size.[14a] In addition, theoretical studies revealed that the 2D graphene or graphyne could tightly anchor metal atoms and the corresponding SACs have the potential to effectively catalyze CO oxidation.[22a, e]

In addition to oxidations, SACs have been widely used in various hydrogenation reactions and have exhibited impressive catalytic performances. For example, in 2012, Sykes and co-workers reported that single Pd atoms on a Cu surface were capable of substantially lowering the energy barriers of both hydrogen uptake and subsequent desorption, which in turn exhibited very selective hydrogenation of styrene and acetylene compared with pure Cu or Pd metal alone, as shown in Figure 7.[25] In 2013, Wang et al. synthesized Co_3O_4 with singly dispersed Rh atoms, Rh_1/Co_3O_4, which were used for the reduction of nitric oxide with hydrogen.[9a] Extended X-ray absorp-
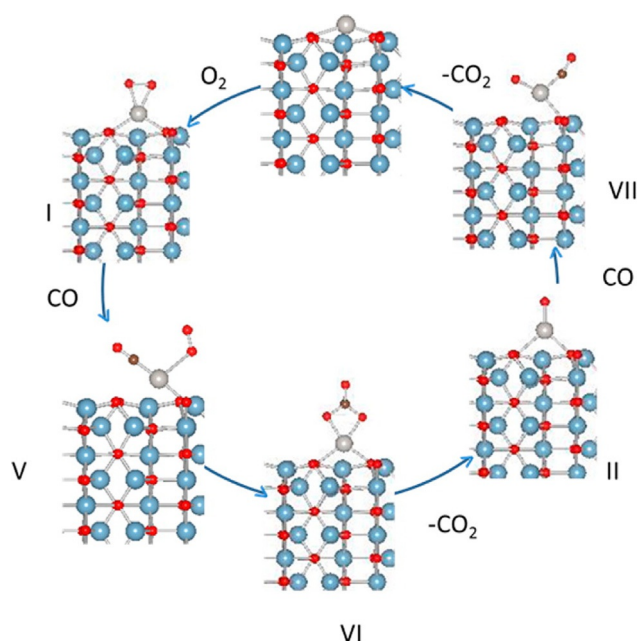
Scheme 2. Pathway for CO Oxidation on single Pt atoms supported on the (010) surface of θ-Al₂O₃. Reprinted with permission from Ref. [33]. Copyright 2013 American Chemical Society.
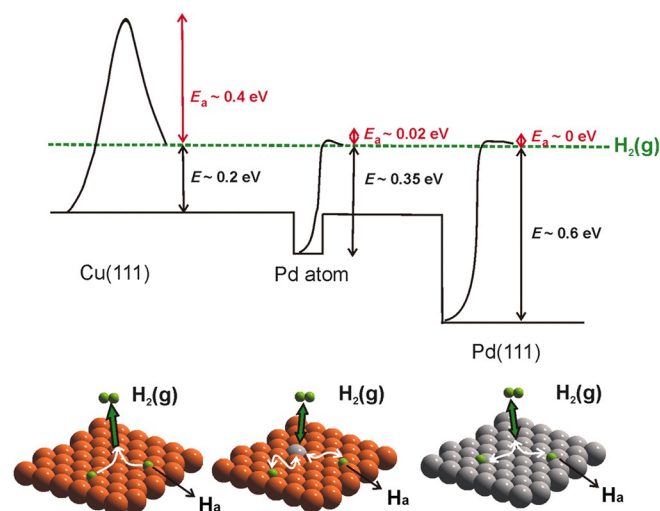

Figure 7. Potential energy diagram depicting the mode of action of a Pd SAA surface compared with those of pure Cu (111) and Pd (111). Adapted from Ref. [25]. Copyright 2012 American Association for the Advancement of Science.

tion fine structure (EXAFS) analysis showed that the singly dispersed Rh atoms are bonded to surface oxygen atoms before catalysis. Then, the surface of Rh_1/Co_3O_4 with singly dispersed Rh atoms was restructured into a new geometry at 220 °C in a mixture of reactant gases (NO and H_2). $RhCo_n$ nanoclusters were formed singly dispersed in the surface layer of Co_3O_4, and exhibited a much better catalytic performance compared with Rh_1/Co_3O_4 that had not undergone the restructuring procedure.[9a] In 2014, Wei et al. reported that FeO_x-supported single Pt

atoms and pseudo-single-atom structures could serve as highly active, chemoselective, and reusable catalysts for the hydrogenation of various nitroarenes.[35] For the hydrogenation of 3-nitrostyrene, this catalyst gave a turnover frequency (TOF) of ≈ 1500 h^{-1}, almost 20 fold higher than the best result reported previously. Furthermore, a selectivity towards 3-aminostyrene of almost 99 % was achieved, another substantial breakthrough of this work. The superior performance could be ascribed to the presence of positively charged platinum centers and the absence of Pt–Pt metallic bonding, both of which facilitated the preferential adsorption of nitro groups. In addition, this research team also prepared a Pd single-atom alloy (SAA) by alloying Pd with Au supported on silica.[36] Compared with monometallic Au or Pd systems, this Pd SAA structure exhibited a much better catalytic performance for the selective hydrogenation of acetylene in excess ethylene.

The research and applications of SACs are rapidly being extended. In 2014, Yang and co-workers for the first time reported the use of SACs of M_1/TiO_2 in photocatalytic hydrogen evolution,[9b] where M is an isolated atom of Pt, Pd, Rh, or Ru strongly anchored to the support. As novel photocatalysts, M_1/TiO_2 illustrated not only excellent stability for H_2 evolution, but also a 6–13 fold increase in photocatalytic activity compared with the metal clusters loaded onto TiO_2. In another field, Gu et al. reported SACs with single Pt and Au atoms anchored by lattice oxygen on ZnO{1 0 1 0} lattice plane for methanol steam reforming.[14b] Theoretical calculations revealed that the single metal atoms together with coordinated lattice oxygen resulted in stronger binding toward the intermediates, lowering the reaction barriers, changing the reaction pathway, and greatly enhancing the activity. The measured TOF of single Pt sites was more than 1000 times higher than the pristine ZnO. In addition, Bao and co-workers reported, in 2014, that single iron sites embedded in a silica matrix enabled direct nonoxidative conversion of methane exclusively to ethylene and aromatics.[37] At 1363 K, a maximum of 48.1 % of methane conversion was reached, whereas the total hydrocarbon selectivity exceeded 99 %, illustrating an atom-economical transformation of methane. Recently, Matsubu et al. quantified the fraction of Rh sites residing as atomically dispersed isolated sites (Rh_{iso}), as well as Rh sites on the surface of Rh nanoparticles (Rh_{NP}), for a series of TiO_2-supported Rh catalysts.[13d] They observed that isolated-metal active-site concentration and stability control the catalytic CO_2 reduction selectivity towards CO and CH_4 production. The relative fraction of these site types on TiO_2 changed dynamically under the reaction conditions through nanoparticle disintegration to form isolated sites; this process controlled the unstable reactivity of higher Rh weight loadings under H_2-lean conditions with time-on-stream.[13d]

3.2. Water–gas shift reaction

The water–gas shift (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) reaction is of great significance in producing H_2-rich gas streams for fuel cells and simultaneously removing CO contamination. The WGS reaction can be catalyzed by supported metals and Flytzani-Stephanopoulos and co-workers have devoted their inter-

ests to the development of catalysts and investigations into the catalytic mechanism of the WGS reaction.[38] The approach used for sample fabrication usually includes two steps, loading and subsequent cyanide leaching, by which the weakly bound metal clusters or nanoparticles can be removed from support, thus enabling better investigation and evaluation of the catalytic activities of metal clusters and nanoparticles with strong interactions to the support. In fact, Flytzani-Stephanopoulos and co-workers have reported many times that the catalytic activity was not affected after removal of metallic particles, and confirmed that metallic components actually did not participate in the reaction and only ionic metal components chemically bonded to support were responsible for the activity.[38] In recent years they have shown interest in the development and investigation of catalysts with isolated single sites for the WGS reaction. Through deposition/precipitation and UV irradiation, a catalyst was prepared with isolated gold atoms on titania.[38b] Studies revealed that dissociation of H_2O on the thus-created Au–O–TiO_x sites was facile and, at higher gold loadings, nanoparticles formed but gave no further enhancement to the activity. In 2014, it was reported that for gold supported on KLTL-zeolite and mesoporous MCM-41 silica, the addition of alkali ions (sodium or potassium) could stabilize the mononuclear gold in the form of Au–O(OH)$_x$–(Na or K) ensembles.[39] These ensembles actually acted as highly efficient active sites for the low-temperature ($< 200\,°C$) WGS reaction. Furthermore, it was found that the activity of the single-site gold species was the same on irreducible supports as on reducible ceria, iron oxide, and titania supports, indicating that the various supports in this work played the role of only a carrier. A very similar conclusion has also been reached recently when the isolated Au species were changed into Pt species on the same supports.[40] Although Flytzani-Stephanopoulos and co-workers usually describe these catalysts as one with isolated atoms or species, we believe the concept is the same as that of SACs.

Zhang and co-workers reported that Ir single atoms supported on FeO_x (Ir_1/FeO_x) exhibited remarkable activity for the WGS reaction, about one order of magnitude higher than clusters or nanoparticles.[13b] For the catalyst containing single atoms, subnanoclusters, and nanoparticles, single atoms acted as the most active sites and accounted for $\approx 70\%$ of the total activity because Ir single atoms could possibly enhance the reducibility of the FeO_x support and generation of oxygen vacancies. It was noted that the activity of this single-atom catalyst was even higher than those of the most active Au- or Pt-based catalysts.

3.3. Electrocatalysis

Electrocatalysis will undoubtedly be at the heart of energizing future transportation and technology, with the added importance of being able to create the necessary fuels required to do so in an environmentally friendly and cost-effective manner.[41] Electrocatalysis, as a branch of heterogeneous catalysis, mainly occurs at the solid–liquid interface, where reactants accept or lose electrons at the cathode or anode reac-

tion, respectively. In addition to surface configuration, chemical composition, and electronic structure, some other important issues, such as material conductivity, bi-continuity, and solvent effects must be taken into account when designing electrocatalysts. Also, practical electrocatalysts ought to be stable enough when continuously working in electrolyte solutions that usually contain acid, basic components, and a variety of additives that may corrode the electrode surface.

SACs have been intensively studied for some heterogeneously catalyzed reactions, as mentioned above. However, only a few reports on the use of SACs in electrolysis have been published. The high activity and selectivity of SACs are desirable for electrocatalysis and, despite the relatively harsh reaction environment, instability issues could be alleviated when single atoms are tightly anchored to the host matrix. One example of the use of SAC in electrocatalysis was reported in 2013 by Sun et al. in which the single-atom catalyst sample was prepared by deposition (ALD) of Pt atoms on graphene.[12c] This SAC gave significantly improved catalytic activity up to 10 times greater than that of the state-of-the-art commercial Pt/C catalyst and exhibited superior CO tolerance for methanol oxidation. It was revealed that the low coordination and partially unoccupied densities of states of the 5 d orbital of Pt atoms were responsible for the excellent activity.[12c] Another example of SAC for use in electrolysis, oxygen reduction reaction (ORR), has also been mentioned briefly above.[11b] In this case, the single-atom catalyst had an advanced structure with single niobium atoms trapped within the graphitic layers, in turn capable of not only enhancing the overall conductivity for accelerating the exchange of ions and electrons, but also suppressing the chemical/thermal coarsening of the active particles. Experimental and theoretical studies revealed that the single niobium atoms produced a redistribution of d-band electrons, thus becoming surprisingly active for O_2 adsorption and dissociation, and exhibiting high stability. In electrocatalysis, the use of SACs in preferred H_2O_2 production has also been reported.[29d] SACs based on nanoalloys have been proposed by Jirkovský et al. through theoretical screening of the guest atoms for Au nanoparticles. Modeling indicated that isolated alloying atoms of Pd, Pt, or Rh placed within the Au surface should enhance the H_2O_2 production. Then, $Au_{1-x}Pd_x$ nanoalloys with various Pd contents were prepared. It was found that increasing the Pd concentration to 8% gave rise to an increase of the electrocatalytic H_2O_2 production selectivity up to almost 95%, whereas further increase of Pd content (to $x=0.5$) resulted in a drop in selectivity to below 10%. Finally, it was proposed that the enhancement in H_2O_2 selectivity was caused by the presence of individual surface Pd atoms surrounded by gold.

In 2014, we demonstrated the use of SAC of Pt_1/FeO_x in photovoltaics, as the counter electrode (CE) in dye-sensitized solar cells (DSCs).[42] Compared with a conventional Pt CE (a sputtering Pt CE with 350 nm thickness), the SAC-based CE exhibited much better activity and reversibility for the catalytic reduction of triiodide (I_3^-) into iodide(I^-), as shown in Figure 8. Notably, Pt_1/FeO_x-SAC with a Pt/Fe atomic ratio of only 1:3157 (Pt loading was 0.08%) exhibited the most effective atom utilization
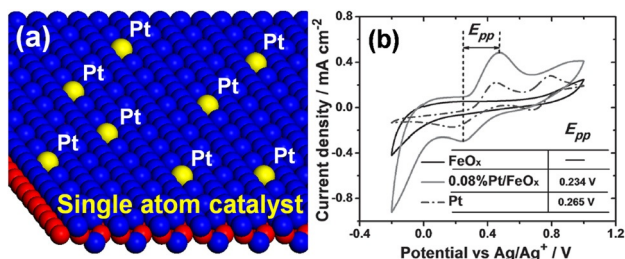
Figure 8. a) Schematic diagram of Pt_1/FeO_x SAC and b) the cyclic voltammetry (CV) curves demonstrating its superior electrocatalytic activity when compared to bare FeO_x and sputtering Pt. Adapted from Ref. [42]. Copyright 2014 Wiley-VCH Co. KGaA, Weinheim.

and doubled the power conversion efficiency of the DSCs based on bare FeO_x. We believe that there is great potential in terms of further improvement of the electrocatalytic performance of SAC in such mesoporous photovoltaics. For example, iron oxide (FeO_x), especially with small-sized nanoparticles, actually cannot guarantee a good conductivity for charge transport. Tailoring FeO_x nanostructures, or replacing it with superior conductors (such as graphene), might be a good idea. In addition, either by carefully collecting experimental information or through theoretical calculations, some important issues should be disclosed in the future to fully understand the inherent catalytic mechanism of SACs as the CE in DSCs, for example, the way in which supported single atoms are able to largely enhance the activity, and how to establish models to handle the issue of electron donating. Relevant research is on-going and will be reported in subsequent communications from our laboratory.

4. Summary and Outlook

By providing single active sites at the solid surface, SACs have established a bridge to link homogeneous and heterogeneous catalysis. Moreover, owing to low-coordination status, quantum size effect, and SMSIs, SACs exhibit many fascinating characteristics, such as high activity, selectivity, and maximum atomic utilization. So far, single-atom catalysis has proven to be very powerful in many typical heterogeneous catalysis including oxidation, the water-gas shift reaction, hydrogenation, hydrogen evolution, methane, and others. Meanwhile, the use of SAC in some other fields, such as electrocatalysis, has started. It is very encouraging that in recent years our understanding of SACs has been further promoted thanks to substantial studies regarding sample preparation, characterization, evaluation, and mechanism interpretation, among others.

Although single-atom catalysis has demonstrated attractive performance, great challenges still remain, including: (i) controllable, facile synthesis of SACs with finely and densely dispersed single atoms; (ii) robust stabilization of the single atoms on the support, especially confronting liquid reactants; (iii) comprehensive understanding and tuning of the strong metal–support interactions involved in SACs; (iv) rational and precise design of active sites in SACs at the atomic level. SAC also requires a combination of characterization and prepara-

tion technology at the atomic and molecular level, and closely related theoretical reasoning, on the basis of accumulated data, which summarizes the preparation regularity at the micro level.

Maybe single atoms have existed and functioned well for a very time, but during this time no advanced characterization techniques could be used to identify SAC. Recent works have provided significant insight into the physical chemical behavior of metals and supports as well as their interfaces, not only benefiting from fundamental studies, but also the design and synthesis of novel and highly efficient SACs. Single-atom catalysis opens up a very broad area for the design of catalysts and researchers may transfer this concept to other domains. It is speculated and expected that in the near future, large-scale applications of SACs will be developed.

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