

Single-Atom Catalysts: A New Frontier in Heterogeneous Catalysis

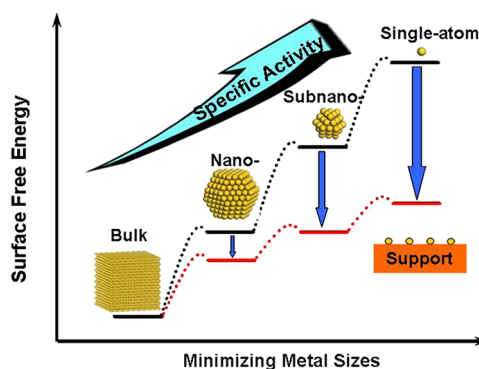
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CONSPECTUS

Supported metal nanostructures are the most widely used type of heterogeneous catalyst in industrial processes. The size of metal particles is a key factor in determining the performance of such catalysts. In particular, because low-coordinated metal atoms often function as the catalytically active sites, the specific activity per metal atom usually increases with decreasing size of the metal particles. However, the surface free energy of metals increases significantly with decreasing particle size, promoting aggregation of small clusters. Using an appropriate support material that strongly interacts with the metal species prevents this aggregation, creating stable, finely dispersed metal clusters with a high catalytic activity, an approach industry has used for a long time. Nevertheless, practical supported metal catalysts are inhomogeneous and usually consist of a mixture of sizes from nanoparticles to subnanometer clusters. Such heterogeneity not only reduces the metal atom efficiency but also frequently leads to undesired side reactions. It also makes it extremely difficult, if not impossible, to uniquely identify and control the active sites of interest.



The ultimate small-size limit for metal particles is the single-atom catalyst (SAC), which contains isolated metal atoms singly dispersed on supports. SACs maximize the efficiency of metal atom use, which is particularly important for supported noble metal catalysts. Moreover, with well-defined and uniform single-atom dispersion, SACs offer great potential for achieving high activity and selectivity.

In this Account, we highlight recent advances in preparation, characterization, and catalytic performance of SACs, with a focus on single atoms anchored to metal oxides, metal surfaces, and graphene. We discuss experimental and theoretical studies for a variety of reactions, including oxidation, water gas shift, and hydrogenation. We describe advances in understanding the spatial arrangements and electronic properties of single atoms, as well as their interactions with the support. Single metal atoms on support surfaces provide a unique opportunity to tune active sites and optimize the activity, selectivity, and stability of heterogeneous catalysts, offering the potential for applications in a variety of industrial chemical reactions.

1. Introduction

There is strength in numbers. This old saying has been widespread for thousands of years; however, not everything fits such a case. In heterogeneous catalysis by supported metal nanostructures, enormous efforts have been devoted toward improving the performance of supported metal catalysts by downsizing the metal particles. In such catalysts, metal components are generally finely dispersed on a high-surface-area support, and only a small portion is

actually involved in catalysis, with some of them acting as the active centers in the catalytic process. The supported metal catalysts usually consist of an assembly of metal particles with broad size distributions and irregular morphology, and each metal particle may possess multiple active sites with different performances. Such heterogeneity affects the efficient utilization of metal active sites and thus reduces selectivity toward a specific product. The size of metal particles therefore becomes one of the most

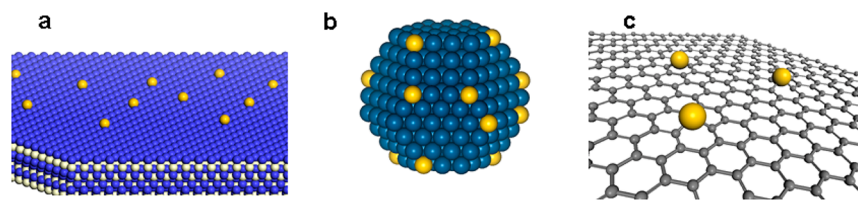


FIGURE 1. Schematic diagrams illustrate different types of SACs: Metal single atoms anchored to (a) metal oxide, (b) metal surfaces, and (c) graphene.

critical factors determining the reactivity and specificity of supported metal catalysts.

Size reduction of metal particles also benefits the performance of catalysts in other aspects: (1) low-coordination environment of metal centers, which is ascribed to the unsaturated metal atoms exposed on the small-sized particles;^{1,2} (2) quantum size effects, where confinement of electrons leads to a discrete energy level distributions and a distinctive HOMO–LUMO gap;^{3,4} (3) metal–support interactions, which originate from the chemical bonding effect between metal and supports and the associated interface, as well as the charge transfer between metal species and supports.^{5,6} As a result, nanoclusters of metals usually show a distinct size effect on their reactivities.^{7–9} Recent theoretical and experimental studies have demonstrated that subnanometer-sized metal clusters can sometimes have better catalytic activity or selectivity than the nanometer-sized counterparts.^{10–16} An example of such size effect is that the chemically inert gold exhibits extraordinary catalytic performance in many heterogeneous reactions upon downsizing bulk gold to nanoparticles or even to subnanoclusters.^{7,10}

Despite their small sizes, subnanoclusters still contain multiple active centers and are not always the most desirable active sites for specific catalytic processes. Searching for catalysts with well-defined single active centers is necessary for improving the performance and understanding catalytic mechanisms.¹⁷ Accordingly, the most effective way to make use of each and every metal atom of supported metal catalysts is to downsize the metal nanostructures to well-defined, atomically distributed metal active centers, that is, single-atom catalysts (SACs), which is the ultimate goal of fine dispersion.^{18–21} We have for the first time prepared a practical Pt single atom catalyst supported on iron oxide, which we named as Pt₁/FeO_x.¹⁸ The excellent performance of the above catalyst demonstrates that heterogeneous catalysis with SACs is no longer a dream.

As shown in Figure 1, there are different types of SACs according to the chemical interactions between the mononuclear metal atom and supports, including single metal atoms anchored to metal oxides, metal surfaces, graphene,

etc. Ion-exchanged metals supported on porous materials such as metal–organic frameworks (MOFs) and zeolites, as well as organometallic complexes anchored to supports, in principle could also be viewed as SACs.^{17,20,21} In this Account, we will focus on investigations of single metal atoms anchored to metal oxides, metal surfaces, and graphene.

2. Experimental Findings about SACs

While SACs are of great interest and potential in heterogeneous catalysis, experimental preparation and characterization of SACs are challenging. It was not clear for a long time whether SACs could be experimentally attainable, catalytically active, or stable in chemical processes. Recent technological advances have made it possible to prepare and unambiguously characterize SACs.^{12,16,18,22–45}

2.1. Preparation of SACs. A prerequisite for the application of SACs is to prepare highly dispersed single atoms of a defined species on appropriate supports. However, fabrication of such SACs is a major challenge because of the tendency of aggregation of single metal atoms. Previously, by using mass-selected soft-landing techniques or improved wet chemistry methods, atomic dispersion of the metal species on supports had been achieved, as shown in Figure 2.

The mass-selected soft-landing technique is powerful in preparing supported metal clusters or even SACs, because of its exact control of the size of metal species by using mass-selected molecular or atom beams and precise regulation of the surface structure of the support by combining these with ultrahigh vacuum surface science procedures.^{12,16,22} This technique provides excellent model catalysts for fundamental studies, on the atomic level, of metal–support interactions and cluster size effects. A number of experimental and theoretical studies based on the soft-landing method have addressed the catalytic properties of metal species on supports.^{5,12,13,16,22} However, such an expensive and low-yield fabrication method limits its wide application and is clearly not suitable for practical industrial applications of heterogeneous catalysis. Other alternatives for preparing SACs are urgently needed.

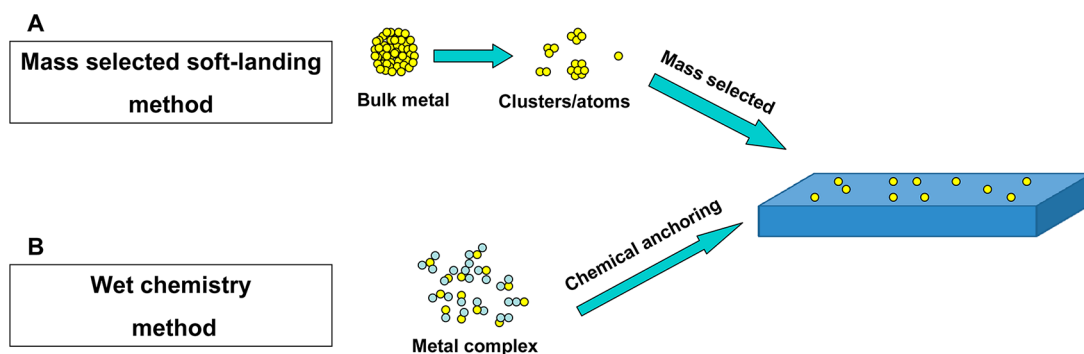


FIGURE 2. Methods for preparing SACs: mass-selected soft-landing (A) and wet chemistry (B).

In the wet-chemistry approach, because the precursor materials already contain single-atom metal species, the objective is to anchor metal species on the supports through a chemical reaction and to avoid their aggregation during the post-treatment processes. Experimentally, anchoring mononuclear organometallic complexes on supports can be achieved by utilization of the coordination between the ligands of the complex and the surface groups of the support materials.^{17,23,25,26} In many heterogeneously catalytic processes, more accessible metal active sites are needed for activation of reactants, which requires pretreatment of catalyst to remove useless or even poisonous ligands. As a result, it runs the risk for the single-atom metal species to aggregate to larger particles.²⁵ Therefore a strong metal–support interaction is the key to prevent aggregation of single atoms on the surface. In this case, the anchoring sites with surface species of the support as ligands, such as surface uncapped sites or other aggregation inhibitors on supports like alkali-ion contaminants or residual organic ligands during chemical preparations, will play an essential role in stabilizing single-atom metal species.^{18,24,25,38,39} Inasmuch as the anchoring sites on the support are not always abundant, low loadings of metal with high-surface-area supports are generally required to achieve SACs.^{18,24,26,31}

2.2. Characterizations of SACs. The characterization of practical single-atom species is another important factor that hinders the development of SACs. Recent advances in atomic resolution characterization techniques, such as subangstrom-resolution aberration-corrected scanning transmission electron microscopy (AC-STEM), can precisely locate the individual metal atoms in such SACs thus providing direct local structural information about the metal species on supports.^{18,23,24,27,28,35} In addition, with the combination of state-of-the-art experimental techniques such as X-ray absorption spectroscopy and advanced modeling and simulation methods in computational chemistry, more in-depth

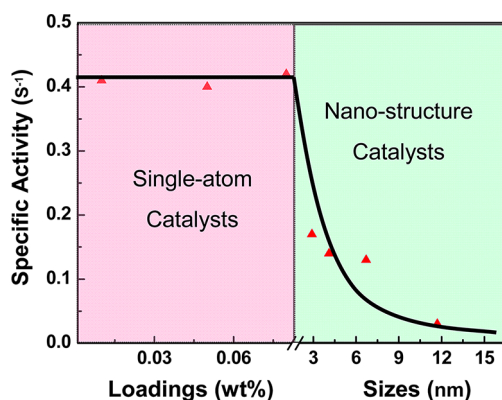


FIGURE 3. Specific activity as a function of metal loadings/sizes. Data points from ref 26.

characterizations about structures of SACs start to become accessible. For example, the detailed surface structure of Pt₁/FeO_x regarding the single-atom species on supports is obtained by the combination of a variety of spectral experiments and density functional theory (DFT) modeling.¹⁸ Similarly, Kwak et al. have reported that coordinatively unsaturated pentacoordinate Al³⁺ centers of γ -Al₂O₃ supports serve as the anchoring sites for platinum atoms by combinations of Al-NMR, AC-STEM, and computational methods.²⁹ It should be pointed out that the employment of in situ characterization techniques under pretreatment or reaction conditions, although with a reduced resolution, allows for a better structure–performance correlation.³⁴

2.3. Catalytic Performance of SACs. SACs aim at improving the utilization of metal active components. Experiments show that they can promote catalytic performance in a variety of heterogeneous reactions.^{18,22,24,26,30,31,38–42} An effective evaluation of the catalytic activity of SACs is to scale with the specific activity per atom. Figure 3 shows schematically the change of activity with metal loadings or sizes. When single atoms serve as the catalytically active sites, the activity will increase with reduced particle

sizes or loadings and arrive at a constant value until atomic dispersion is reached.²⁶ We will summarize here several key SAC systems.

(a) Oxidation. SACs have shown great potential in a variety of oxidation reactions, including CO oxidation or preferential oxidation (PROX),¹⁸ aerobic oxidation of alcohols,²⁴ formaldehyde oxidation,^{39,41} and methane oxidation,⁴³ among others. For both CO oxidation and PROX, experimental results indicate that Pt₁/FeO_x is 2–3 times more active than the subnanometer-sized counterpart and is stable during a long-term test.¹⁸ Similarly, Metiu and co-workers reported that the catalysts containing more isolated ionic Pt atoms are more active for methane oxidation.⁴³ Lee et al. observed a decrease of activity with an increase of the metal particle size and that single-atom catalysts were most active in the alcohol oxidation with Pd/meso-Al₂O₃ catalysts.²⁴ (b) Water–gas shift (WGS). By comparing the catalytic performance of supported metal nanostructured catalysts with or without leaching of its metallic components, Flytzani-Stephanopoulos and co-workers found that the leached catalysts exhibited comparable or even higher activities than the parent catalysts, indicating that metallic components do not participate in the reactions and metal cations conjugated with support are responsible for their activity. Meanwhile, such ionic metal species show similar TOF values irrespective of their loadings and do not seem to migrate to form metal particles even after long-time reactions.^{30,31} In terms of its atomic active sites, we consider it another example of a SAC in practical catalytic processes. (c) Hydrogenation. Xu et al. investigated Au/ZrO₂ catalysts with various loadings of Au for the selective hydrogenation of 1,3-butadiene, observed a trend that can be well fitted with the curve in Figure 3, and thus proposed that isolated surface-type Au³⁺ ions serve as the active sites.²⁶ This is also an example of a SAC that shows better catalytic performance than the nanostructures.

2.4. SACs over Other Supports. Most of the SACs we reviewed so far are composed of metal single atoms anchored on oxide surfaces. The metal active sites can also be supported on metals, graphene, or other materials, forming unique ensembles that exhibit excellent performance.^{32,36,44–46} For example, Toshima et al. prepared crown-jewel-structured Au/Pd nanocatalysts by a galvanic replacement reaction method, where gold atoms were atomically dispersed on Pd clusters. This single-atom gold species showed unprecedentedly high activity in glucose oxidation.³² Kyriakou et al. reported that individual, isolated Pd atoms dispersed onto Cu surfaces dissociated hydrogen and facilitated the spillover of H, resulting in selective hydrogenation of styrene and acetylene.⁴⁴

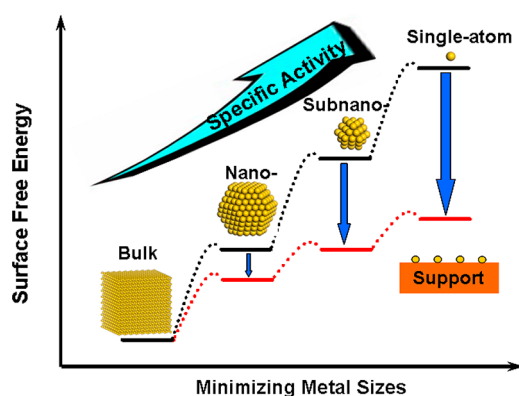


FIGURE 4. Schematic illustrate the changes of surface free energy and specific activity per metal atom with metal particle size and the support effects on stabilizing single atoms.

Sun and co-workers synthesized isolated Pt atoms anchored to graphene using the ALD technique. Such Pt SACs exhibited significantly improved catalytic activity in methanol electro-oxidation reactions.³⁶

3. Understanding the SACs

As illustrated in Figure 4, the bulk materials can be turned into nanoparticles, subnanoclusters, and finally single metal atoms. The size reduction generates an increase of unsaturated coordination environment of the metal species. Accordingly, the surface free energy of the metal components increases, and the metal sites become more and more active for chemical interactions with the support and adsorbates, which accounts for the size effects of metal nanocatalysts. In the extreme case of SACs, because of the highly active valence electrons, the quantum confinement of electrons, and the sparse quantum level of metal atoms, the surface free energy of metal species reaches a maximum, which then leads to promoted chemical interactions with the support and unique chemical properties of SACs.

3.1. Location and Geometric Effects of Single Atoms on Supports. The locations of metal single atoms are correlated with the anchor sites of the support, for instance, through the architectural structure of metal–oxygen–cation–(support) or even occupying the position for the cations in the cases of oxide supports.^{18,24,27,47} For example, our previous subangstrom-resolution HAADF image of Pt₁/FeO_x reveals that individual Pt atoms (indicated by the white circles in Figure 5a) locate exactly at the positions of the Fe atoms. Further DFT calculations (Figure 5b) confirm that the most probable sites for single Pt atoms are the 3-fold hollow sites on the O₃-terminated surface, where each Pt atom is coordinated by three surface oxygen atoms and can be viewed as the surface Fe atoms being

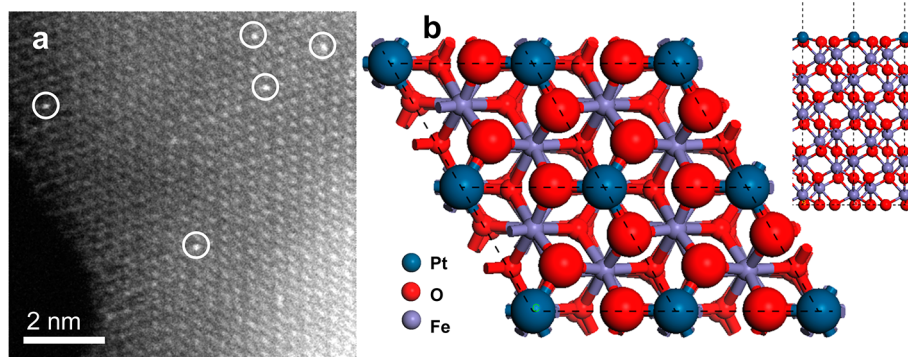


FIGURE 5. (a) HAADF-STEM image and (b) density functional modeling of Pt_1/FeO_x .¹⁸

replaced by single Pt atoms.¹⁸ An intensive investigation of the model catalyst of Au adatoms on the (111) surface of single-crystal magnetite has also indicated that Au single atoms are attached atop an uncapped O atom in the position that would be occupied by Fe tetrahedral ions in a bulk iron oxide crystal.⁴⁷ For single-atom metals supported on $\gamma\text{-Al}_2\text{O}_3$, the atomically dispersed metal species on supports are found to be on the defects of the support with metal–O–Al bonding contributions.^{24,27,29,48} Correspondingly, for a hollandite-type manganese oxide support with its tunnels composed of oxygen with lone-pair dangling electrons and a proper diameter for Ag–O–Mn bonding, single-atom Ag chains can be formed in the tunnels.⁴¹ For SACs with metals as support, the location of single atoms depends on the chemical potential of the constituent metals. For example, because of the higher chemical potential of gold than palladium, gold atoms prefer to stay on the corner sites of Pd clusters.³² For SACs with graphene as support, the single atoms were located on the defects with carbon vacancies serving as anchoring sites.^{36,49,50}

A straightforward geometric effect of such locations of single atoms is that SACs make full use of all active metal atoms. This is the primary motivation for downsizing metal nanostructures to single atoms, especially for the noble metals. Another geometric effect of the SAC is its homogenized active site for catalytic reactions. For the practically prepared catalysts of metal nanostructures, the broad size distribution and irregular morphology of metal particles generally leads to a wide variety of metal active sites. In contrast, the SAC has a substantial merit of structural simplicity compared with the heterogeneity of nanostructured catalysts. The single-atom active sites are all well-defined and atomically distributed on the supports, resulting in an identical geometric structure of each active center, analogous to that of a homogeneous catalyst. Meanwhile, since only single-atom metal active sites are available in SACs, the catalytic pathway involving multiatoms of

nanostructured catalysts will be inhibited accordingly, and a modified or different catalytic mechanism might take place. For example, contiguously located Pd sites function as the active sites for the elementary step of N_2O decomposition, while the rate-determining step was found to have been changed by forming Pd single-atoms on a Au surface.⁵¹ Similarly, a double-site activation of acetylene and ethylene was found on gold nanoclusters, while they exhibit single-site π -bonding with single-atom gold species.⁵² These findings reveal vast opportunities in tuning the catalytic performance by the geometric effects of SACs.

3.2. Electronic Effects. The special locations and chemical bonding on supports also lead to unique electronic properties of metal single atoms different from those of metal nanocatalysts. Their electronic structures are much more volatile according to their coordinated environments. In fact, the coordination to the surface atoms of the support is so critical that it is not quite suitable to discuss an isolated single metal atom without the support. The bonding of metal atoms with the uncapped sites on the supports leads to charge transfer between metal atoms and the support due to different chemical potentials. As a result, the anchored metal atoms usually carry some charge, which was verified by various spectral measurements and computational modeling.^{18,24,26,30,47,48,53–55} For Pt_1/FeO_x catalysts, the white line intensity in the X-ray absorption spectra reflects the increased oxidation state of Pt atoms, consistent with the blue shift of the vibrational frequency of CO on $\text{Pt}^{\delta+}$ (Figure 6). The calculated Bader charges show that Pt single atoms are positively charged when anchored on FeO_x .¹⁸ On the other hand, the conjunction of metal atom with the surface groups of supports also leads to the bonding or coupling of quantum levels of single metal atoms with surface species.⁴⁶ In our previous study of Pt_1/FeO_x catalyst, it was found that the discrete 5d-orbitals of Pt single-atom

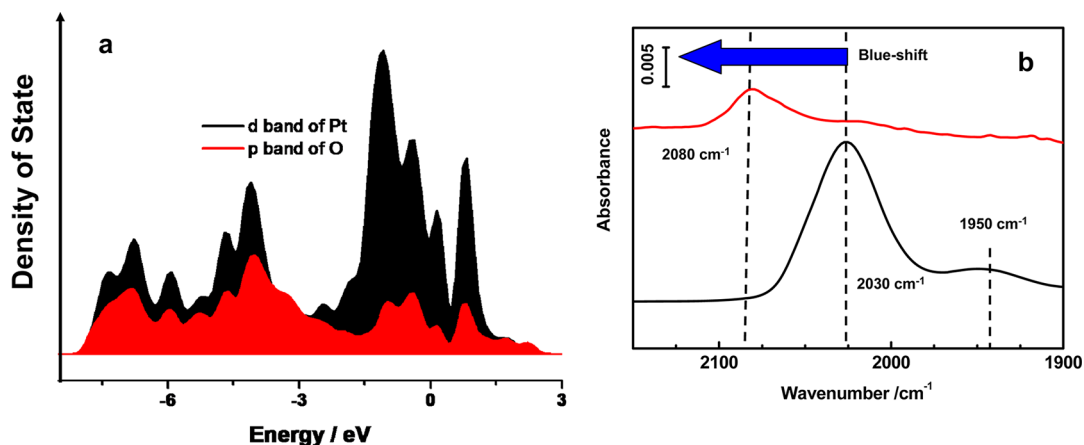


FIGURE 6. (a) Density of states of the Pt-5d and O-2p bands of Pt₁/FeO_x catalyst. (b) The blue shift of the CO vibration frequency on Pt single atom compared with the Pt clusters on hematite.¹⁸

are mixed considerably with the oxygen-2p band and evolved to d-band (Figure 6).

Similarly, the electronic properties of single atoms on metal or graphene are also modified through the electron donation between single-atom centers and the supports. For example, the more electropositive element Pd on a Au–Pd surface will have more d-vacancies, and the Pt single atoms on graphene contain high unoccupied 5d densities of states, akin to the metal atoms anchored on oxide surfaces.^{32,36}

3.3. Activation of Supports. Strong interaction between metal atoms and the support will unavoidably affect the supports. Generally, different single metal atoms on the support potentially modify the properties of support differently.^{11,18,27} For example, stabilization of the support to prevent degradation of the catalysts can be achieved by isolated La atoms on the surface of γ -Al₂O₃, because the strong binding and mutual repulsion of La atoms pin the surface and inhibit both sintering and the transformation of supports.²⁷ For noble metals on reducible supports (Pt/FeO_x, Ir/CeO₂, etc.), metal single atoms or small subnanoclusters are found to facilitate the reduction of supports.^{11,18} Subsequently, this type of SAC exhibits an excellent ability to activate the lattice oxygen on the support surface.^{18,43,53–55} Our previous DFT calculations indicated that the formation of oxygen vacancies on the hematite with the presence of single-Pt atoms is more thermodynamically favored than on the pure supports because of the promotion effect of Pt single atoms.¹⁸ Such a promotional effect on the creation of vacancies on the support surface adjacent to the metal single atoms was also suggested by Metiu and co-workers and has been intensively studied in various single-atom-based catalysts.^{43,53,54}

4. The Correlations between the Properties and Reactivities of SACs

Attributed to their unique properties, SACs serve as a new type of catalyst with great potential applications. Establishment of the structure–performance relationship of the SACs in different reactions will provide guidance to the design of more efficient SACs for different targeted reactions. (a) Activity. As seen in Figure 7, the superior performance of Pt₁/FeO_x originates from the following aspects: (i) the activation of O₂ is improved because of the promotion of oxygen-vacancy formation; (ii) the chance of poisoning by CO adsorption is reduced due to the Pt^{δ+} active center on the support. As a result, all the elementary steps in the catalytic cycle are exothermic, and the barriers are low enough for CO oxidation.¹⁸ Such promotional effects of vacancy creation on the activity as well as its superior CO tolerance was also observed in other oxidation reactions.^{36,43,53–55} Besides, the modified electronic properties of metal single active sites are suggested to be the origin of high activity of SACs in some other catalytic processes.^{26,30} (b) Selectivity. SACs also improve selectivity in various reactions because of their well-defined, single site features. In the hydrogenation of styrene or acetylene, the Pd single atoms on a Cu surface serve as the active sites to activate hydrogen for hydrogenation meanwhile avoiding the decomposition of reactants occurring on multimetal active sites, which then leads to a high hydrogenation selectivity.⁴⁴ In the selective hydrogenation of unsaturated aldehydes, the hydrogenation reaction follows an Eley–Rideal mechanism on single gold atoms on a ZrO₂ support because only single-atom sites are available for intermediate adsorption. Therefore, a high selectivity toward allyl-alcohol with lower deep hydrogenation products was achieved.⁵⁶ (c) Stability. Because of the

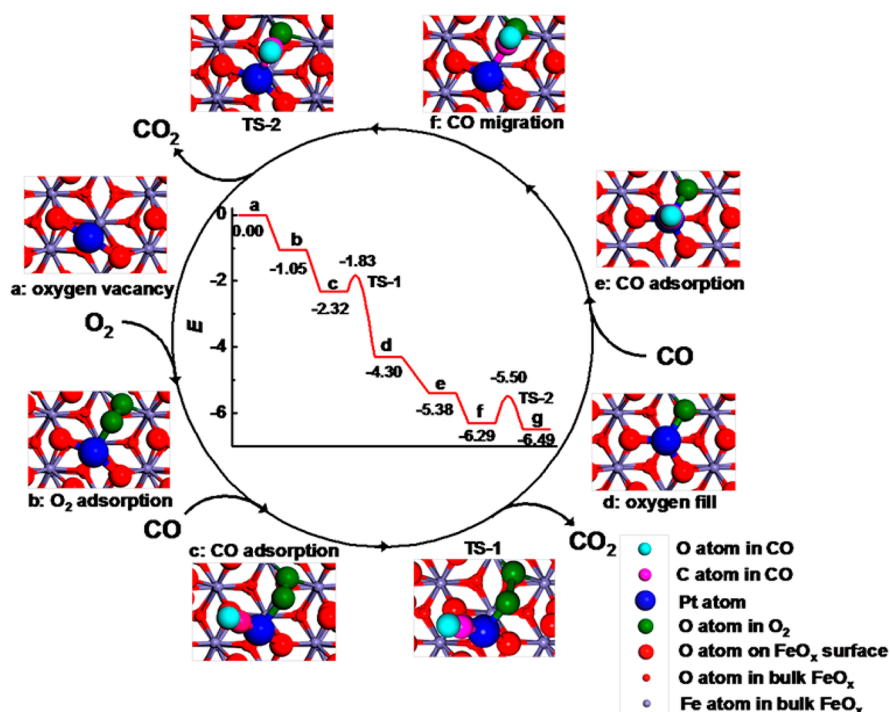


FIGURE 7. The proposed reaction pathways and energy profile (in eV) for CO oxidation on the single-atom catalyst Pt_1/FeO_x .¹⁸

chemical-bonding trait of metal single atoms on the supports, SACs also present satisfactory stability under many chemical processes. As shown in the Pt_1/FeO_x catalyst, Pt single atoms are located on hematite with Pt–O–Fe architectures, which explain its catalytic stability in CO oxidation reactions.¹⁸ Such metal–oxygen–support structures are also suggested to be the origin of the stability of SACs in various catalytic processes.^{30,33,47} In addition, the property of charged single atoms on supports also contributes to its stability. For example, the cationic species coordinated with supports could not be removed whereas metallic species were leached by CN^- .^{26,30,31}

5. Conclusions and Prospects

Size does matter in heterogeneous catalysis by supported metal nanostructures. As the size of metal nanostructures is decreased from nanometer to subnanometer scale and ultimately to single atoms, the catalytic performance may change significantly due to the low-coordination environment, quantum size effect, and improved metal–support interactions. In particular, SACs with well-defined and atomically dispersed metal sites on supports can maximize the efficiency of metal utilization. Although SACs for a long time seemed an unrealistic dream in supported metal catalysts, recent experimental and theoretical studies, especially our recent work on Pt_1/FeO_x , have provided unambiguous evidence that SACs can have higher activity, selectivity, or both

than their nanostructured counterparts with satisfying stability in various reactions. Furthermore, SACs can act as ideal and simplified model systems to make a direct comparison of experimental results with theoretical calculations. Inasmuch as supports act in a similar way as ligands for the metal active sites, SACs also serve as a bridge to connect the hetero- and homogeneous catalysis.

Single atoms anchored on appropriate supports might have existed for a long time and played significant roles in many catalytic processes, but they have rarely been recognized as active sites. With the emergence of new characterization and computational modeling techniques, single-atom active sites become accessible. The development of Pt_1/FeO_x has exclusively proven that supported single atoms can be excellent heterogeneous catalysts.

It should be pointed out that SACs must not be considered to be superior to the conventional nanostructured catalysts in every circumstance; the single-site feature likely limits its application in catalytic processes requiring multimetal active sites. However, utilization of the novel properties derived from SACs seems to provide vast opportunities for applications in heterogeneous catalysis. With the establishment of SACs as a new concept and a thorough elucidation of the nature of single-atom catalysis, we believe that development and understanding of SACs might be a new frontier in heterogeneous catalysis. The current findings about SACs

are only an iceberg in catalysis science, and an even more exciting world of single-atom catalysis is yet to come.

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BIOGRAPHICAL INFORMATION

Xiao-Feng Yang received his Ph.D. degree in 2010 from DICP under the supervision of Prof. Tao Zhang. After 2 years as a postdoctoral fellow in Prof. Jun Li's group at Tsinghua University for theoretical and computational catalysis, he went back to join Prof. Tao Zhang's group. His current research interests involve computational catalysis and nanocatalysis.

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Botao Qiao received his Ph.D. degree in 2008 from Lanzhou Institute of Chemical Physics under the supervision of Prof. Youquan Deng. After 3 years' postdoctoral research in Prof. Tao Zhang's group at DICP, he joined this group in 2011. His research interests are focused on energy and environment-related catalysis and on the design and development of highly dispersed catalysts with new structures and high performance.

Jun Li received a Ph.D. in 1992 from the Chinese Academy of Sciences. He did a postdoctoral research at University of Siegen (Germany) and The Ohio State University (USA) and then worked as a Chief Scientist at Pacific Northwest National Laboratory, USA. He is now a Chang Jiang Professor at Tsinghua University, China, and an elected AAAS Fellow. He has published more than 180 peer-reviewed papers and six book chapters. His research interests include theoretical actinide chemistry, computational catalysis, nanocluster chemistry, and theoretical heavy-element chemistry.

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Tao Zhang received his Ph.D. degree in 1989 from Dalian Institute of Chemical Physics (DICP) under the supervision of Profs. Liwu Lin and Jingling Zang. After one year at the University of Birmingham as a postdoctoral fellow with Prof. Frank Berry, he

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FOOTNOTES

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REFERENCES

- 1 Vanharde, R.; Hartog, F. Statistics of surface atoms and surface sites on metal crystals. *Surf. Sci.* **1969**, *15*, 189–230.
- 2 Lopez, N.; Janssens, T. V. W.; Clausen, B. S.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; Nørskov, J. K. On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation. *J. Catal.* **2004**, *223*, 232–235.
- 3 Valden, M.; Lai, X.; Goodman, D. W. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science* **1998**, *281*, 1647–1650.
- 4 Li, J.; Li, X.; Zhai, H. J.; Wang, L. S. Au₂₀: A tetrahedral cluster. *Science* **2003**, *299*, 864–867.
- 5 Yoon, B.; Häkkinen, H.; Landman, U.; Wörz, A. S.; Antonietti, J.-M.; Abbet, S.; Judai, K.; Heiz, U. Charging Effects on bonding and catalyzed oxidation of CO on Au₈ clusters on MgO. *Science* **2005**, *307*, 403–407.
- 6 Campbell, C. T. Catalyst-support interactions: Electronic perturbations. *Nat. Chem.* **2012**, *4*, 597–598.
- 7 Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel gold catalysts for the oxidation of carbon-monoxide at a temperature far below 0 °C. *Chem. Lett.* **1987**, 405–408.
- 8 Somorjai, G. A.; Park, J. Y. Molecular surface chemistry by metal single crystals and nanoparticles from vacuum to high pressure. *Chem. Soc. Rev.* **2008**, *37*, 2155–2162.
- 9 Crespo-Quesada, M.; Yarulin, A.; Jin, M.; Xia, Y.; Kiwi-Minsker, L. Structure sensitivity of alkyne hydrogenation on shape- and size-controlled palladium nanocrystals: Which sites are most active and selective? *J. Am. Chem. Soc.* **2011**, *133*, 12787–12794.
- 10 Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. Identification of active gold nanoclusters on iron oxide supports for CO oxidation. *Science* **2008**, *321*, 1331–1335.
- 11 Lin, J.; Qiao, B.; Liu, J.; Huang, Y.; Wang, A.; Li, L.; Zhang, W.; Allard, L. F.; Wang, X.; Zhang, T. Design of a highly active Ir/Fe(OH)_x catalyst: versatile application of Pt-group metals for the preferential oxidation of carbon monoxide. *Angew. Chem., Int. Ed.* **2012**, *51*, 2920–2924.
- 12 Heiz, U.; Sanchez, A.; Abbet, S.; Schneider, W. D. Catalytic oxidation of carbon monoxide on monodispersed platinum clusters: Each atom counts. *J. Am. Chem. Soc.* **1999**, *121*, 3214–3217.
- 13 Lei, Y.; Mehmood, F.; Lee, S.; Greeley, J.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Meyer, R. J.; Redfern, P. C.; Teschner, D.; Schlögl, R.; Pellin, M. J.; Curtiss, L. A.; Vajda, S. Increased silver activity for direct propylene epoxidation via subnanometer size effects. *Science* **2010**, *328*, 224–228.
- 14 Qiao, B.; Liu, L.; Zhang, J.; Deng, Y. Preparation of highly effective ferric hydroxide supported noble metal catalysts for CO oxidations: From gold to palladium. *J. Catal.* **2009**, *261*, 241–244.
- 15 Turner, M.; Golovko, V. B.; Vaughan, O. P. H.; Abdulkhan, P.; Berenguer-Murcia, A.; Tikhov, M. S.; Johnson, B. F. G.; Lambert, R. M. Selective oxidation with dioxygen by gold nanoparticle catalysts derived from 55-atom clusters. *Nature* **2008**, *454*, 981–983.
- 16 Kaden, W. E.; Wu, T.; Kunkel, W. A.; Anderson, S. L. Electronic structure controls reactivity of size-selected Pd clusters adsorbed on TiO₂ surfaces. *Science* **2009**, *326*, 826–829.
- 17 Thomas, J. M.; Raja, R.; Lewis, D. W. Single-site heterogeneous catalysts. *Angew. Chem., Int. Ed.* **2005**, *44*, 6456–6482.
- 18 Qiao, B.; Wang, A.; Yang, X.; Allard, L. F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt₁/FeO_x. *Nat. Chem.* **2011**, *3*, 634–641.
- 19 Thomas, J.; Saghi, Z.; Gai, P. Can a single atom serve as the active site in some heterogeneous catalysts? *Top. Catal.* **2011**, *54*, 588–594.
- 20 Ranocchiari, M.; Lothschütz, C.; Grolmund, D.; van Bokhoven, J. A. Single-atom active sites on metal-organic frameworks. *Proc. R. Soc. A* **2012**, *468*, 1985–1999.

- 21 Flytzani-Stephanopoulos, M.; Gates, B. C. Atomically dispersed supported metal catalysts. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 545–574.
- 22 Abbet, S.; Sanchez, A.; Heiz, U.; Schneider, W. D.; Ferrari, A. M.; Pacchioni, G.; Rösch, N. Acetylene cyclotrimerization on supported size-selected Pd_n clusters (1 ≤ n ≤ 30): One atom is enough!. *J. Am. Chem. Soc.* **2000**, *122*, 3453–3457.
- 23 Lu, J.; Aydin, C.; Browning, N. D.; Gates, B. C. Imaging isolated gold atom catalytic sites in zeolite Naf. *Angew. Chem., Int. Ed.* **2012**, *51*, 5842–5846.
- 24 Hackett, S. F.; Brydson, R. M.; Gass, M. H.; Harvey, I.; Newman, A. D.; Wilson, K.; Lee, A. F. High-activity, single-site mesoporous Pd/Al₂O₃ catalysts for selective aerobic oxidation of allylic alcohols. *Angew. Chem., Int. Ed.* **2007**, *46*, 8593–8596.
- 25 Kim, Y.-T.; Ohshima, K.; Higashimine, K.; Uruga, T.; Takata, M.; Suematsu, H.; Mitani, T. Fine size control of platinum on carbon nanotubes: From single atoms to clusters. *Angew. Chem., Int. Ed.* **2006**, *118*, 421–425.
- 26 Zhang, X.; Shi, H.; Xu, B. Q. Catalysis by gold: Isolated surface Au³⁺ ions are active sites for selective hydrogenation of 1,3-butadiene over Au/ZrO₂ catalysts. *Angew. Chem., Int. Ed.* **2005**, *44*, 7132–7135.
- 27 Wang, S.; Borisevich, A. Y.; Rashkeev, S. N.; Glazoff, M. V.; Sohlberg, K.; Pennycook, S. J.; Pantelides, S. T. Dopants adsorbed as single atoms prevent degradation of catalysts. *Nat. Mater.* **2004**, *3*, 143–146.
- 28 Batson, P. E. Motion of gold atoms on carbon in the aberration-corrected STEM. *Microsc. Microanal.* **2008**, *14*, 89–97.
- 29 Kwak, J. H.; Hu, J.; Mei, D.; Yi, C. W.; Kim, D. H.; Peden, C. H.; Allard, L. F.; Szanyi, J. Coordinatively unsaturated Al³⁺ centers as binding sites for active catalyst phases of platinum on γ-Al₂O₃. *Science* **2009**, *325*, 1670–1673.
- 30 Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Active nonmetallic Au and Pt species on ceria-based water-gas shift catalysts. *Science* **2003**, *301*, 935–938.
- 31 Yang, M.; Allard, L. F.; Flytzani-Stephanopoulos, M. Atomically dispersed Au-(OH) species bound on titania catalyze the low-temperature water-gas shift reaction. *J. Am. Chem. Soc.* **2013**, *135*, 3768–3771.
- 32 Zhang, H.; Watanabe, T.; Okumura, M.; Haruta, M.; Toshima, N. Catalytically highly active top gold atom on palladium nanocluster. *Nat. Mater.* **2012**, *11*, 49–52.
- 33 Novotný, Z.; Argentero, G.; Wang, Z.; Schmid, M.; Diebold, U.; Parkinson, G. Ordered array of single adatoms with remarkable thermal stability: Au/Fe₃O₄(001). *Phys. Rev. Lett.* **2012**, *108*, No. 216103.
- 34 Hashimoto, A.; Takeguchi, M. In situ observation of Pt nanoparticles on graphene layers under high temperature using aberration-corrected transmission electron microscopy. *J. Electron Microsc.* **2012**, *61*, 409–413.
- 35 Bayram, E.; Lu, J.; Aydin, C.; Uzun, A.; Browning, N. D.; Gates, B. C.; Finke, R. G. Mononuclear zeolite-supported iridium: Kinetic, spectroscopic, electron microscopic, and size-selective poisoning evidence for an atomically dispersed true catalyst at 22 °C. *ACS Catal.* **2012**, *2*, 1947–1957.
- 36 Sun, S.; Zhang, G.; Gauquelin, N.; Chen, N.; Zhou, J.; Yang, S.; Chen, W.; Meng, X.; Geng, D.; Banis, M. N.; Li, R.; Ye, S.; Knights, S.; Botton, G. A.; Sham, T. K.; Sun, X. Single-atom catalysis using Pt/graphene achieved through atomic layer deposition. *Sci. Rep.* **2013**, *3*, 1775.
- 37 Wang, L.; Zhang, S.; Zhu, Y.; Patlolla, A.; Shan, J.; Yoshida, H.; Takeda, S.; Frenkel, A. I.; Tao, F. Catalysis and in situ studies of Rh₁/Co₃O₄ nanorods in reduction of NO with H₂. *ACS Catal.* **2013**, *3*, 1011–1019.
- 38 Zhai, Y.; Pierre, D.; Si, R.; Deng, W.; Ferrin, P.; Nilekar, A. U.; Peng, G.; Herron, J. A.; Bell, D. C.; Saltsburg, H.; Mavrikakis, M.; Flytzani-Stephanopoulos, M. Alkali-stabilized Pt-OH₂ species catalyze low-temperature water-gas shift reactions. *Science* **2010**, *329*, 1633–1636.
- 39 Zhang, C.; Liu, F.; Zhai, Y.; Ariga, H.; Yi, N.; Liu, Y.; Asakura, K.; Flytzani-Stephanopoulos, M.; He, H. Alkali-metal-promoted Pt/TiO₂ opens a more efficient pathway to formaldehyde oxidation at ambient temperatures. *Angew. Chem., Int. Ed.* **2012**, *51*, 9628–9632.
- 40 Wang, G.; Su, J.; Gong, Y.; Zhou, M.; Li, J. Chemistry on single atoms: Spontaneous hydrogen production from reactions of transition-metal atoms with methanol at cryogenic temperatures. *Angew. Chem., Int. Ed.* **2010**, *49*, 1302–1305.
- 41 Huang, Z.; Gu, X.; Cao, Q.; Hu, P.; Hao, J.; Li, J.; Tang, X. Catalytically active single-atom sites fabricated from silver particles. *Angew. Chem., Int. Ed.* **2012**, *51*, 4198–4203.
- 42 Wu, C.-T.; Yu, K. M. K.; Liao, F.; Young, N.; Nellist, P.; Dent, A.; Kroner, A.; Tsang, S. C. E. A non-syn-gas catalytic route to methanol production. *Nat. Commun.* **2012**, *3*, No. 1050.
- 43 Tang, W.; Hu, Z.; Wang, M.; Stucky, G. D.; Metiu, H.; McFarland, E. W. Methane complete and partial oxidation catalyzed by Pt-doped CeO₂. *J. Catal.* **2010**, *273*, 125–137.
- 44 Kyriakou, G.; Boucher, M. B.; Jewell, A. D.; Lewis, E. A.; Lawton, T. J.; Baber, A. E.; Tierney, H. L.; Flytzani-Stephanopoulos, M.; Sykes, E. C. Isolated metal atom geometries as a strategy for selective heterogeneous hydrogenations. *Science* **2012**, *335*, 1209–1212.
- 45 Jirkovsky, J. S.; Panas, I.; Ahlberg, E.; Halasa, M.; Romani, S.; Schiffrin, D. J. Single atom hot-spots at Au-Pd nanoalloys for electrocatalytic H₂O₂ production. *J. Am. Chem. Soc.* **2011**, *133*, 19432–19441.
- 46 Zhang, R. Q.; Lee, T. H.; Yu, B. D.; Stampfl, C.; Soon, A. The role of titanium nitride supports for single-atom platinum-based catalysts in fuel cell technology. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16552–16557.
- 47 Rim, K. T.; Eom, D.; Liu, L.; Stolyarova, E.; Raitano, J. M.; Chan, S. W.; Flytzani-Stephanopoulos, M.; Flynn, G. W. Charging and chemical reactivity of gold nanoparticles and adatoms on the (111) surface of single-crystal magnetite: A scanning tunneling microscopy/spectroscopy study. *J. Phys. Chem. C* **2009**, *113*, 10198–10205.
- 48 Ghosh, T. K.; Nair, N. N. Rh₁/γ-Al₂O₃ single-atom catalysis of O₂ activation and CO oxidation: Mechanism, effects of hydration, oxidation state, and cluster size. *ChemCatChem* **2013**, *1002/cctc.201200799*.
- 49 Tang, Y.; Yang, Z.; Dai, X. A theoretical simulation on the catalytic oxidation of CO on Pt/graphene. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16566–16572.
- 50 Wang, H.; Feng, Q.; Cheng, Y.; Yao, Y.; Wang, Q.; Li, K.; Schwingenschlögl, U.; Zhang, X. X.; Yang, W. Atomic bonding between metal and graphene. *J. Phys. Chem. C* **2013**, *117*, 4632–4638.
- 51 Wei, X.; Yang, X.-F.; Wang, A.-Q.; Li, L.; Liu, X.-Y.; Zhang, T.; Mou, C.-Y.; Li, J. Bimetallic Au–Pd alloy catalysts for N₂O decomposition: Effects of surface structures on catalytic activity. *J. Phys. Chem. C* **2012**, *116*, 6222–6232.
- 52 García-Mota, M.; Cabello, N.; Maseras, F.; Echavarren, A. M.; Pérez-Ramírez, J.; Lopez, N. Selective homogeneous and heterogeneous gold catalysis with alkyne and alkenes: Similar behavior, different origin. *ChemPhysChem* **2008**, *9*, 1624–1629.
- 53 Hu, Z.; Metiu, H. Effect of dopants on the energy of oxygen-vacancy formation at the surface of ceria: Local or global? *J. Phys. Chem. C* **2011**, *115*, 17898–17909.
- 54 Shapovalov, V.; Metiu, H. Catalysis by doped oxides: CO oxidation by Au_xCe_{1-x}O₂. *J. Catal.* **2007**, *245*, 205–214.
- 55 Song, W.; Jansen, A. P. J.; Hensen, E. J. M. A computational study of the influence of the ceria surface termination on the mechanism of CO oxidation of isolated Rh atoms. *Faraday Discuss.* **2013**, *1039/C3FD20129E*.
- 56 Wang, C.-M.; Fan, K.-N.; Liu, Z.-P. Oxide-supported single gold catalyst for selective hydrogenation of acrolein predicted from first principles. *J. Catal.* **2009**, *266*, 343–350.