Synthesis, characterization and application of monatomic catalysts

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Abstract. Supported metal nanocatalysts are the most commonly used catalysts in the research area of industrial heterogeneous catalysis. The size of metal particles is an important factor in determining its catalytic performance. Because coordinative unsaturated metals often show the relatively high catalytic activity, the specific activity of each metal atom commonly increases with decreasing the particle size. The limit of metal dispersion is the dispersion of single atom, that is the single-atom catalyst. The monatomic catalyst takes most advantage of the activity of the metal particles with maximum efficiency, which is particularly important for the novel metals. In addition, the single atom catalyst has high selectivity and high performance of catalysis. The preparation, characterization and study of catalytic properties of the monatomic catalysts supported on metal oxides, metals and graphene are mainly described here and their application in oxidation, water gas reaction and hydrogenation reaction is studied. The spatial distribution of the single atom and the interaction with the substrate are also discussed. This monatomic catalyst shows great potential for industrial application.

1. Introduction
Supported noble metal catalysts have been widely applied in fuel cell electrode catalysis, catalytic reforming in petrochemical industry, and the synthesis of various fine chemicals. However, the scarcity of novel metals determines its high price. Meanwhile, the unique physical and chemical properties of noble metals determine its irreplaceable role in various catalytic reactions. Therefore, how to improve the utilization ratio of noble metal atoms has been one of the key problems in the preparation of catalyst.

The reduction of metal particle size results in the low coordination number of the metal particles on the surface. Besides, the consequential quantum effect can change the HOMO-LUMO band gap. And the interaction between the metal and the substrate and charge transfer can also be affected. Therefore, the reduction of the size of nanoparticles can greatly change the catalytic performance. The recent theoretical calculation shows that the subnanometer catalyst has better catalytic activity and selectivity than the nanocatalyst. For example, the chemical inert gold from the body into nanoscale or even sub nanoscale scales show excellent catalytic performance in heterogeneous reaction. Nanoclusters, even with small sizes but still have many atoms, are not the best active sites for certain specific catalytic reactions. The metal is distributed on the surface of the carrier with the state of a single atom, and the single atom catalyst can make the most efficient use of the precious metal. A well-defined single atom active site is very important for improving the catalytic activity and studying the mechanism of the reaction. The Zhang Tao’s group in the Dalian Chemical Institute of China took the lead in reporting the Pt single atom catalyst, Pt1/FeOx, dispersed on the iron oxide substrate. Then scientists have developed a single atomic catalyst on various substrates, as shown in Figure 1.
2. Synthesis and catalytic properties of Single Atom Catalysis

2.1 Synthesis of monatomic catalysis

As shown in Figure 2, scientists have prepared the real monatomic catalysts\textsuperscript{9,13,19-24} by advanced means. The mass selection method is a very effective method for the preparation of supported metal nanoclusters and even single atomic catalysts. The use of molecular or atomic beams with selective mass can accurately regulate the size of metal particles and can also regulate the structure\textsuperscript{9,13,19} on the surface of the substrate. This technology provides a basic research model for atomic level catalysts, which can be used to study the interaction between substrate and metal and the size effect of particles. This method limits its application in the field of industrial heterogeneous catalysis because of its high price and low yield. Therefore, it is urgent to find other effective ways to prepare monatomic catalysts.

2.2 Characterization of single atom catalyst

The characterization of monatomic catalysts is another important factor limiting its development. Recently, atomic resolution chromatic aberration correction scanning transmission electron microscope (ACSTEM) is able to accurately determine the location of a single atom. It can provide structural information of single atom catalyst and location information of metal atoms on the base surface.
Combined with other advanced characterization technologies, such as X-ray absorption spectroscopy and theoretical calculation of chemical calculations, we can further characterize the structure of monatomic catalysts. In Zhang Tao group's reports of Pt1/FeOx monatomic catalyst reported, the details of Pt atoms on the base surface can be obtained through a series of spectral data and density functional theory\textsuperscript{15}. Similarly, in the research of Kwak et al, through Al-NMR, ACSTEM characterization and theoretical calculation, it is proved that Al\textsuperscript{3+} coordination unsaturated in γ-Al\textsubscript{2}O\textsubscript{3} makes it serve as a fixed site of platinum atom\textsuperscript{26}.

2.3 Catalytic performance of single atom catalyst
The monatomic catalyst is designed to improve the utilization efficiency of novel metals. The experimental results show that the single atom catalyst can improve the catalytic efficiency\textsuperscript{15,19,21,23,24} in a variety of heterogeneous catalytic systems. The effective means to evaluate the catalytic activity of single atom is to compare the specific activity of each atom respectively. When the catalytic active site is a single metal atom, the catalytic activity of the catalyst will increase with the decrease of the load particle size, until the single atom dispersion is achieved, and the catalytic activity will reach a constant. The application of several monatomic catalysts in the oxidation reaction is introduced here. The single atom catalyst can be applied to a series of oxidation reactions, which includes the oxidation of CO, the oxidation of alcohol, the oxidation of aldehydes and the oxidation of methane\textsuperscript{24}. In the oxidation reaction, the experimental results proved that the catalytic activity of Pt1/FeOx monatomic catalyst was 2-3 times higher than that of sub nanometer catalyst, and showed a long time stability\textsuperscript{15}. In the same case, Metiu and his collaborators reported that the more dispersed the Pt atoms can achieve on the substrate, the higher efficiency of the catalyst can reach in the reaction of methane oxidation. Lee et al observed that the size of metal particles increased and the catalytic activity of catalysts decreased, and it was found that the most effective catalyst in ethanol oxidation is Pd/meso-Al2O3 monatomic catalyst.

2.4 Monatomic catalysts on other supported substrates
In addition to attaching to the surface of metal oxides, single metal atoms can also be attached to metal, graphene and other materials to form novel monatomic catalysts, showing excellent performance. Toshima and others through the replacement reaction, Au atoms spontaneously dispersed to the Pd nanocluster surface, and thus synthesized the crown type Au/Pd nanocatalyst. This Au monatomic catalyst shows excellent catalytic performance\textsuperscript{16} in the oxidation of glucose. Kyriakou and others dispersed the single Pd atoms to the Cu surface, which effectively promoted the selective oxidation of styrene and acetylene. Sun and its collaborators immobilized the Pt atoms to the surface of graphene, which showed excellent catalytic performance in the oxidation of methanol.

3. Study on the catalytic mechanism of single atom catalyst
Metal materials can continuously reduce their size and become nanomaterials, subnanoclusters or even single atoms. As shown in Figure 3, the reduction of size leads to the increase of the coordination unsaturation of metal species and the increase of the surface free energy of metal particles, which makes the metal sites more active to chemical reactions. In monatomic catalysts, the free energy of metal surface reaches the maximum value due to the high activity of valence electrons, the electronic confinement and the discrete electron level of monatomic atoms, showing excellent catalytic activity.
3.1 The geometric effect of a single atom on the substrate
The fixed position of metal atoms is related to the structure of the substrate. For example, the Pt atom in Pt1/FeOx monatomic catalyst, which is reported by Zhang Tao, takes the place of Fe in the lattice. The density functional theory results show that the best position of Pt is to replace the position of Fe in FeOx and 3 oxygen coordination18. Metal is used as the substrate for the monatomic catalyst, and the position of the metal atom is dependent on the chemical potential of the base metal. For example, the chemical potential of Au is greater than that of Pd, and the Au atom tends to be fixed at the angle of the Pd nanocluster. If graphene is used as the base of the monatomic catalyst, the metal atom is located on the defect of the carbon atom of the graphene defect.

One of the most outstanding geometric effects of monatomic catalysts is to make full use of the activity of each metal atom, which is also the original intention of reducing the size of the metal until the single atom obtains the monatomic catalyst. Another prominent geometric effect is that every active site in the catalytic reaction is the same, making the study of the catalytic mechanism more simple.

3.2 Electronic effect
The metal atom’s position on the substrate and the interaction between the metal atom and the substrate make the properties of the metal atoms different from the nano catalysts. Because the single atom has very high coordination unsaturation, the electronic structure of single atom catalyst is more unstable, and the different unoccupied chemical potential between the substrate and metal sites will lead to charge separation. And this result that the attachment of atoms is possessing partial charge has been confirmed by a variety of spectral measurement and calculation model15,21,23. The X-ray absorption spectra of the Pt1/FeOx catalyst showed that the oxidation state of Pt atoms increased, which coincided with the blue phase of CO in the vibrational frequency of Pt atoms, as in Figure 4. The theoretical calculation also shows that a single Pt atom has a partial positive charge15 on the FeOx substrate. On the other hand, the combination of the mono metal atoms and the base surface groups will also lead to the coupling of the metal atoms with the quantum level of the substrate surface. Similarly, the electron transferring between metal monatomic and substrate will also lead to the change of electronic structure of metal atoms. For example, the electrical positivity of Pd on the surface of Au-Pd catalyst makes more D vacancies. Pt atoms have higher unsaturated 5D state density on graphene, which is similar to metal attachment on metal oxide surface.
3.3 Activation of the base

The strong interaction between the metal atoms and the substrate is bound to have an effect on the substrate, making the properties of the substrate change8,15. For example, the La atom scattering in γ-Al2O3 can improve the stability of substrate surface to prevent the deactivation of the catalyst, because there is a strong bond between the surface of the substrate La atoms with the substrate, which can prevent catalyst sintering and deformation24. In addition, it has been proved that precious metals can reduce the size of the reductive substrate, such as Pt/FeOx, Ir/CeO2 and so on8,15. This monatomic catalyst can efficiently activate the lattice oxygen on the substrate surface. The results of Zhang Tao's density functional theory prove that the promotion of Pt atoms makes Pt atoms more stable on the hematite than on the pure substrates.

4. Conclusion and Perspective

The size of metal particles has a great influence on the heterogeneous catalytic reaction of the supported metal catalyst. With the decrease of the size of metal nanostructures, from nanometer size to sub nanometer size to single atom, as well as the coordination environment, the quantum size effect and the interaction between metal and substrate will evidently change the activity of supported metal catalyst. Monatomic catalysts can maximize the efficiency of each atom activity, and monatomic catalysts have better catalytic activity and selectivity than nano catalysts in many heterogeneous catalysis. In addition, the monatomic catalyst can also be used as an ideal experimental model, which is convenient to compare with the theoretical calculation.

It is also important to emphasize that monatomic catalysts are not necessarily superior to traditional nanomaterials, such as the characteristics of single active sites, which limit their application in multi active site synergistic catalytic systems. However, new applications of atomic properties can be the catalyst to a series of single active site catalytic heterogeneous catalytic system. For example, Bao’s group creatively constructed single atoms of iron catalyst silicide lattice confinement and successfully realized the selective activation of methane under anaerobic conditions and effectively obtain lots of high value chemicals such as ethylene, hydrogen and aromatics 24. Now the study of monatomic catalysts is only a corner of the iceberg, and it is believed that it will lead to the revolution in some fields of the chemical synthesis industry.

Reference:
[1] Anderson J R, Boudart M. Catalysis Science and Technology[J]. Applied Catalysis, 1987, 5(1):134-134.
[2] Bell A T. The Impact of Nanoscience on Heterogeneous Catalysis[J]. Science, 2003, 299(5613):1688-91.
[3] Petit L, Svane A, Szotek Z, et al. First-principles calculations of PuO(2+/x)[J]. Cheminform, 2003, 301(5632):498-501.
[4] Haruta M. Size- and support-dependency in the catalysis of gold[J]. Catalysis Today, 1997, 36(1):153-166.
[5] Sidorov A N, Gaskill K, Buongiorno Nardelli M, et al. Charge transfer equilibria in ambient-exposed epitaxial graphene on (0001 xAF) 6 H-SiC[J]. Journal of Applied Physics, 2012, 111(11):112107-177.
[6] Hammer B, Norskov J K. Why gold is the noblest of all the metals[J]. Nature, 1995, 376(6537):238-240.
[7] Hodgson A, Moryl J, Traversaro P, et al. Energy transfer and vibrational effects in the dissociation and scattering of D 2, from Cu (111)[J]. Nature, 1992, 356(6369):501-504.
[8] Haruta M. Novel catalysis of gold deposited on metal oxides[J]. Catalysis Surveys from Asia, 1997, 1(1):61-73.
[9] Haruta M. When gold is not noble: catalysis by nanoparticles[J]. Chemical Record, 2003, 3(2):75–87.
[10] Sachtl W M H. Catalysis by Metal and Oxide Nanoparticles, Single Metal Atoms and Di-Nuclear Oxo-Ions in Zeolites[M]// Nanotechnology in Catalysis. Springer New York, 2007:139-151.
[11] Thomas, J. M.; Raja, R.; Lewis, D. W. Single-site heterogeneous catalysts. Angew. Chem., Int. Ed. 2005, 44, 6456–6482.
[12] Shylesh S, Schünemann V, Thiel W R. Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis[J]. Angewandte Chemie International Edition, 2010, 49(20):3428-3459.
[13] 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.
[14] Lu Y H, Zhou M, Zhang C, et al. Metal-Embedded Graphene: A Possible Catalyst with High Activity[J]. Journal of Physical Chemistry C, 2009, 113(47):20156-20160.
[15] 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/FeOx. Nat. Chem. 2011, 3, 634–641.
[16] Oksengendler B L, Askarov B, Nurgaliyev I N, et al. Nanocatalysis: hypothesis on the action mechanism of gold[J]. 2015:249-261.
[17] Li F, Li Y, Zeng X C, et al. Exploration of High-Performance Single-Atom Catalysts on Support M1/FeOx for CO Oxidation via Computational Study[J]. Acs Catalysis, 2015, 5(2):544-552.
[18] Ranocchiarı, M.; Lothsch€utz, C.; Grolimund, D.; van Bokhoven, J. A. Single-atom active sites on metal-organic frameworks. Proc. R. Soc. A 2012, 468, 1985–1999.
[19] Fang H, Wen M, Chen H, et al. Graphene stabilized ultra-small CuNi nanocomposite with high activity and recyclability towards catalysing the reduction of aromatic nitro-compounds[J]. Nanoscale, 2015, 8(1):536.
[20] Miller J T, Kropf A J, Zha Y, et al. The effect of gold particle size on Au, Au bond length and reactivity toward oxygen in supported catalysts[J]. Journal of Catalysis, 2006, 240(2):222-234.
[21] 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/A12O3 catalysts for selective aerobic oxidation of allylic alcohols. Angew. Chem., Int. Ed. 2007, 46, 8593–8596.
[22] Kappers M J, Maas J H V D. Correlation between CO frequency and Pt coordination number. A DRIFT study on supported Pt catalysts[J]. Catalysis Letters, 1991, 10(5-6):365-373.
[23] Flytzani-Stephanopoulos, M.; Gates, B. C. Atomically dispersed supported metal catalysts. Annu. Rev. Chem. Biomol. Eng. 2012, 3, 545–574.
[24] Guo, X., Fang, G., Li, G., Ma, H., Fan, H., Yu, L., Bao, X. (2014). Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen. Science, 344(6184), 616-619.