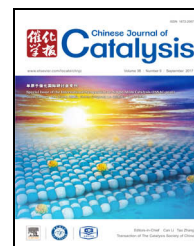


available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/chnjc](http://www.elsevier.com/locate/chnjc)

Review (Special Issue of the International Symposium on Single-Atom Catalysis (ISSAC-2016))

# Preparation, characterization and catalytic performance of single-atom catalysts

Liqiong Wang<sup>a</sup>, Liang Huang<sup>a,#</sup>, Feng Liang<sup>b</sup>, Simin Liu<sup>b</sup>, Yuhua Wang<sup>c</sup>, Haijun Zhang<sup>a,\*</sup><sup>a</sup> The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, Hubei, China<sup>b</sup> School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, Hubei, China<sup>c</sup> Hubei Province Key Laboratory of Science in Metallurgical Process, Wuhan University of Science and Technology, Wuhan 430081, Hubei, China

## ARTICLE INFO

## Article history:

Received 29 October 2016

Accepted 19 December 2016

Published 5 September 2017

## Keywords:

Single atom catalyst

Preparation method

Catalytic activity

Characterization

Electronic properties

## ABSTRACT

Supported and colloidal single-atom catalysts (SACs), which possess excellent catalytic properties, are particularly important in both fundamental studies and practical applications. The progress made in the preparation methods, characterization, catalytic performances and mechanisms of SACs anchored to metal oxides, two-dimensional materials and the surface of metal nanoclusters (NCs) are reviewed. The different techniques for SAC fabrication, including conventional solution methods based on co-precipitation, incipient wetness co-impregnation, and the chemical vapor deposition method, as well as the newer atom layer deposition (ALD) and galvanic replacement methods, are summarized. The main results from experimental and theoretical studies of various catalytic reactions over SACs, including oxidation reactions, hydrogenation, water gas shift, photocatalytic H<sub>2</sub> evolution and electrochemical reactions, are also discussed. Moreover, the electronic properties of the single atoms and their interactions with the supports are described to assist in understanding the origin of the high catalytic activity and selectivity of SACs. Finally, possible future research directions of SACs and their applications are proposed.

© 2017, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Supported and colloidal metal catalysts play important roles in a large number of chemical reactions owing to their high catalytic activity and/or selectivity [1–6]. The size of the metal particle is a major factor determining their catalytic performance, and the specific activity of these catalysts increases with decreasing the metal particle size. For example, the catalytic activity for aerobic glucose oxidation of poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected colloidal Au nanoclusters (NCs) increased with a decrease of their average diameter from ap-

proximately 100 to 2.6 nm [7], and similar results were observed for colloidal Au<sub>80</sub>Pt<sub>20</sub> bimetallic NCs [8] and Au<sub>170</sub>Pt<sub>20</sub>Ag<sub>10</sub> trimetallic NCs [9]. Additionally, as has been well documented in the literature, sub-nanometer clusters exhibit better catalytic activity and selectivity than their nanometer counterparts [10–12]. Upon decreasing the size of metal nanostructures from the nanometer to the sub-nanometer scale, and ultimately to single atoms, the catalytic performance could be substantially changed as a result of the low-coordination environment, quantum size effect, and improved strong metal-support interaction [13].

\* Corresponding author. Tel/Fax: +86-27-68862829; E-mail: zhanghaijun@wust.edu.cn

# Corresponding author. Tel: +86-27-68862258; E-mail: huangliang1986@wust.edu.cn

This work was supported by the National Natural Science Foundation of China (51472184 and 51472185), the Science and Technology Support Program of Hubei Province (2013BHE003), and the Program for Innovative Teams of Outstanding Young and Middle-Aged Researchers in the Higher Education Institutions of Hubei Province (T201602).

DOI: 10.1016/S1872-2067(17)62770-0 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 38, No. 9, September 2017

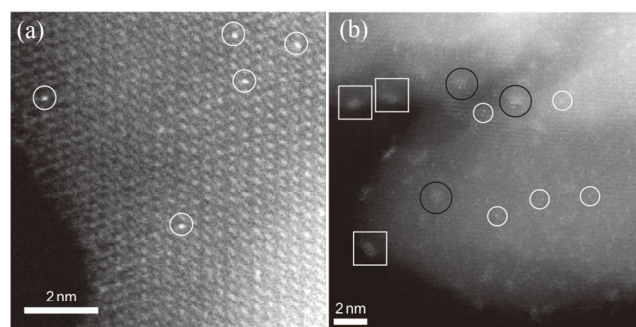
Single-atom catalysts (SACs) containing isolated metal atoms mono-dispersed on supports that possess excellent catalytic properties have attracted a great deal of research interest because they are ideal catalysts for minimizing the use of expensive noble metals [14]. SACs can be successfully synthesized by various approaches and their use has proven to be superior for many conventional chemical reactions including oxidation reactions [15–20], hydrogenation [21–24], water-gas shift [25,26], and photocatalytic H<sub>2</sub> evolution [27]. In addition, they have been found to be effective in several frontier areas, such as in sculpting graphene morphology [28], medical applications [29] and electrochemical reactions [30,31]. Recently, considerable efforts have been made worldwide in the preparation and catalytic performance evaluation of SACs. Great progress has been made and many promising results have been reported.

In this review, we provide an overview of the recent studies on the preparation, characterization, catalytic activity and mechanism of the following three representative types of SACs: SACs anchored to metal oxides (Fig. 1(a)), two-dimensional materials (Fig. 1(b)) and the surface of metal NCs (Fig. 1(c)). In the last section, we will briefly discuss the current development, expected improvements and future outlook in this research area.

## 2. SACs anchored to metal oxides

Noble metal catalysts downsized to clusters or single-metal atoms are structurally unstable owing to their natural tendency for high activity and a large specific surface area. Thus, supports, which can efficiently stabilize single atoms, are crucial for the performance of SACs. So far, various metal oxides have been attempted to anchor single atoms, such as FeO<sub>x</sub> [20], SiO<sub>2</sub> [23] and TiO<sub>2</sub> [32]. Generally, SACs anchored to metal oxides usually exhibit several advantages, including easy fabrication by using feasible preparation methods, such as co-precipitation, photochemical strategy and co-impregnation, and are relatively cheaper than other supports, such as graphene and noble metal NCs.

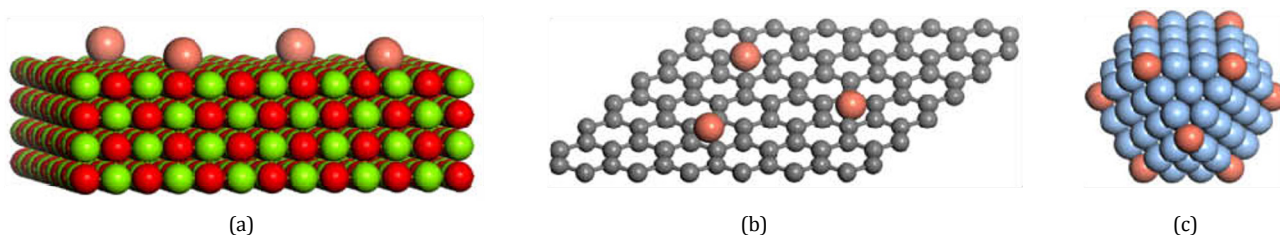
Zhang's group were the first to propose the concept of SACs and synthesized a series of Pt- [20], Ir- [25] and Au- [33,34] based SACs. The SACs were anchored onto the metal oxides by carefully tuning the co-precipitation conditions in addition to controlling the concentration of the metal precursors. The anchored SACs exhibited excellent catalytic performance in CO oxidation, the preferential oxidation of CO in H<sub>2</sub> and water-gas shift reactions, and the results indicated that the SACs were



**Fig. 2.** HAADF-STEM images of Pt/FeO<sub>x</sub>SACs sample (a) and nanocluster sample (b). Reprinted with permission from Ref. [20]. Copyright 2011 Nature Publishing Group.

more active, selective and stable than their conventional nanoparticle counterparts in all cases.

By using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in combination with X-ray absorption fine structure spectroscopy and density functional theory (DFT) calculations, Zhang's group [20] determined the exact structures of Pt/FeO<sub>x</sub> SACs. As shown in Fig. 2 (a), single atoms of Pt were uniformly dispersed on the FeO<sub>x</sub> support and located exactly at the positions of the Fe atoms. When the Pt loading was higher, two-dimensional Pt rafts and three-dimensional Pt clusters appeared, in addition to the individual Pt atoms (Fig. 2(b)). The extended X-ray absorption fine structure (EXAFS) spectra revealed that the Pt–O bonding distance was close to that in PtO<sub>2</sub>, indicating the oxidation state of Pt and the strong metal-support interaction. The white line intensity in the X-ray absorption near-edge structure (XANES) spectra, which reflects the oxidation state of Pt in the SACs sample, was intermediate between the intensities of Pt foil and PtO<sub>2</sub>, while the other samples clearly showed lower white line intensities, further indicating that the Pt single atoms carried positive charges. To investigate the catalytic performance of the Pt/FeO<sub>x</sub> SACs, CO oxidation and the preferential oxidation of CO in H<sub>2</sub> were chosen as the probe reactions. The results showed that Pt/FeO<sub>x</sub> SACs were the most active for both reactions among a number of supported Pt catalysts. Since the support itself was essentially inactive for the preferential oxidation of CO in the H<sub>2</sub> reaction at 80 °C, the high activity of Pt/FeO<sub>x</sub> SACs should originate from the intrinsic nature of single Pt atoms dispersed onto the FeO<sub>x</sub> surfaces. DFT calculations were also conducted to elucidate the nature of the binding of Pt single atoms to the FeO<sub>x</sub> support and the exceptionally high catalytic activity of single Pt atoms (Fig. 3). After pre-treatment by H<sub>2</sub>,



**Fig. 1.** Schematic diagrams illustrating SACs on different supports: single metal atoms anchored to (a) metal oxides, (b) two-dimensional materials, and (c) the surface of metal NCs.

Download English Version:

<https://daneshyari.com/en/article/6505837>

Download Persian Version:

<https://daneshyari.com/article/6505837>

[Daneshyari.com](https://daneshyari.com)