SPECIAL TOPIC: Single-atom Catalysts

Recent progresses in the research of single-atom catalysts

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In modern industry, nearly 80% industrial processes involve catalysts and consequently catalysis plays a critical role in world economy as it is estimated to account for some 30%–40% GDP of the globe. Nowadays, catalysis can be simply classified into homogenous catalysis, biocatalysis, and heterogeneous catalysis in terms of the reaction media, characteristics of catalytic reactions, and catalyst material involved.

Catalytic reactions are widely believed to occur at an active center, as proposed by Taylor in 1925 [1]. While it is somewhat less difficult to identify the active center for homogenous and biological catalysts, the structure and constitution of the active center of a heterogeneous catalyst are often unknown due to the complicated nature of the nanoparticles or dynamically changing, and defected bulk surface involved. Nanoparticles are usually an assemble of nanostructures with a range of constituents, sizes and morphologies. They have many different surface sites, yet they likely have many energetically accessible isomers or nearly degenerate electronic states during the catalytic reactions. Therefore, it remains challenging to determine the active center for a heterogeneous catalytic reaction, which becomes the key obstacle for understanding of the reaction mechanisms and for rational design of heterogeneous catalysts. Preparation of heterogeneous catalysts remains largely a practice of trial and error.

On the other hand, heterogeneous catalysis usually involves noble metals, which are rare and have been becoming more and more expensive for industrial applications. In heterogeneous catalysis, the atom utilization efficiency of nanoparticles is notoriously low because only a small portion of the surface atoms are actively involved in catalytic processes. For example, for

metal nanoparticles with sizes of 4 to 100 nm, there are roughly 2000 to 30×10^6 atoms in total, while the surface active-site atoms available for possible reaction are usually extremely limited. Therefore, to increase the atom utilization efficiency and enhance the stability, selectivity, and activity of the catalyst for a given reaction becomes a holy grail in heterogeneous catalysis.

Smaller nanoparticles are usually more reactive in catalysis due to the large surface/volume ratio that is inversely proportional to the size of the nanoparticles, but they tend to become more and more unstable because of decreased formation enthalpy with reduced size. It is thus a dream to design a precisely constructed single-atom active center in heterogeneous catalysis. Involvement of “invisible” single atoms in heterogeneous catalysis probably has a very long history, but the existence of single atoms in heterogeneous catalysis was largely overlooked over a long history of catalysis. Even with the rapid progress of modern catalysis science and technology, the role of surface-supported single atoms had been underappreciated due to lack of practical chemical approach for the preparation of catalysts with only single atoms on surface, lack of clear-cut characterization of the heterogeneously supported single atoms, and lack of theoretical understanding of the atypical stability and reaction mechanisms of such extremely small “surface species”.

The negligence of surface-supported single atoms in heterogeneous catalysis remains both norm and orthodox in catalysis science until 2011 when Zhang, Li, and Liu [2] provided unequivocal evidence of the role and mechanism of single atoms in CO oxidation and proposed a new concept of “Single-Atom Catalysis” based on the first practically fabricated Pt_1/FeO_x heterogeneous catalyst. They proposed to use $\text{M}_1/\text{support}$ as a notation to re-

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present heterogeneous single-atom catalysts (SACs) with single-atom M anchored on a support. SACs are also viewed as a bridge for homogenous (including biological) catalysis and heterogeneous catalysis [3]. The field of research on SACs grows significantly since the proposal of this new concept, as shown by the citation of this paper in the past decade (Fig. 1) [4]. Systematic theoretical and computational studies are also carried out to elucidate the mechanism and stability of SACs [5,6].

In this kind of catalysts, the single atoms typically, if not always, serve as the active centers because the distinctive difference with the interfacial atoms on the support. The surprising stability and activity of the heterogeneous Pt_1/FeO_x catalyst for CO and preferential CO oxidation (PROX) reaction immediately aroused interest in the catalysis community. This work prompted the preparation and characterization of a huge number of SACs as well as computational studies on elucidation of their stabilities and reaction mechanisms. Because of the well-defined active center, research on SACs becomes a well-recognized frontier area in heterogeneous catalysis. Significant efforts have been made in exploring SACs as an efficient way to develop in the heterogeneous domain non-noble metal catalysts, high-temperature/pressure catalysts, and catalysts durable under alkali/acidic conditions, among others. SACs are also an ideal platform for the heterogenization of homogeneous catalysts that can combine the advantages of well-defined active center with heterogeneous interface.

Currently, nearly all the metal (sometimes non-metal) atoms can be used as the active center single atoms. The SACs are prepared for most catalytic reactions, including CO oxidation, water-gas-shift reaction, hydrogenation reaction, Fischer-Tropsch reaction, CO_2 reduction, CH_4 conversion, as well as N_2 fixation, and conversion to NH_3 . SACs are not only extensively studied for thermal catalysis, but are widely explored for electrocatalysis and photocatalysis as well. SACs are ideal not only for fundamental understanding of heterogeneous active centers and reaction mechanism, but also for practical utilization of SACs that seem to be promising for industrial applications.

In this special topic of *Science China Materials* for the theme of single-atom catalysis, we invited a selected group of leading scientists in the field of research on SACs. After standard peer reviews, we have accepted totally 10 papers, with three review papers and 7 original research articles. Yu Q *et al.* [7] summarize the recent studies of graphene-supported SACs. He *et al.* [8] review the recent research progress of gas phase atomic clusters

Figure 1 Citation of the 2011 *Nature Chemistry* paper by Qiao *et al.* [2] (as of May 20, 2020; data source: Web of Science).

for catalytic CO oxidation. Chen *et al.* [9] make a thorough inquiry on electrocatalyst engineering and structure–activity relationship of nanostructures and single atoms for hydrogen evolution reaction. The exciting research results reported in this gallery include Pd_1/TiO_2 for selective hydrogenation of phenylacetylene (Yan *et al.* [10]), Pd_1/CeO_2 for alkoxycarbonylation of aryl iodides (Qiao *et al.* [11]), single-atomic Pt catalyst for anti-Markovnikov hydroboration of alkenes (Wang *et al.* [12]), Au–Pd single atom alloy (SAA) for CO oxidation (Xu *et al.* [13]), high-loading and thermally stable $\text{Pt}_1/\text{MgAl}_{1.2}\text{Fe}_{0.8}\text{O}_4$ SACs for high-temperature applications (Li W *et al.* [14]), Fe-N_x moieties with enhanced activity in Fe–N–C electrocatalysts *via* phosphorus doping (Lin *et al.* [15]), and non-noble metal SACs with phosphotungstic acid (PTA) support (Yu X *et al.* [16]).

These research works represent the diversity and richness of the efforts in the field of SACs. There are two *International Symposium on Single-Atom Catalysts* (ISSAC) that were held in 2016 in Dalian and 2018 in Beijing. This special topic has been initiated from the talks given at the second ISSAC. Two previous special issues were published on the topic of SACs [17,18]. We hope this new collection of original and review papers from the active researchers in the field will present a brief view of the dynamics of the field and inspire more researchers to explore the science and application of SACs in various reactions essential for industrial applications.

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