SCIENCE CHINA Materials PERSPECTIVES

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Published online 10 July 2018 | https://doi.org/10.1007/s40843-018-9317-7
Sci China Mater 2019, 62(2): 149–153

New monatomic layer clusters for advanced catalysis materials

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Noble metals have been widely applied as catalysts in chemical production, energy conversion, and emission control [1–3], but their high cost and scarcity are major obstacles for any large-scale practical applications. It is therefore of great interest to explore new active material systems that require less mass loading of noble metal catalysts but with even better performance. Recently, intense research has been devoted towards downsizing the noble metals into single-atom catalysts (SACs) [4,5]. SACs, with single-atom active centers, were first reported by Qiao *et al.* [4]. They synthesized a single Pt atom catalyst supported on FeO_x (Pt_1/FeO_x), which offered extremely high efficiency on an atomic percent basis and showed excellent performance towards CO oxidation.

There is no doubt that SACs offer superior performance towards some catalytic reactions, because of the unsaturated coordination environment of their metal species and highly active valence electrons. In addition, the surface free energy of metal species reaches a maximum in SACs [6–10]. Nevertheless, it is worth noting that the catalytic selectivity plays an important part in catalytic reactions, and the SACs may limit application in some multi-electron catalytic processes [5]. In this case, we propose that if single atoms could assemble to monatomic layer clusters (*m*ALCs), they would exhibit higher catalytic activity and selectivity than SACs. Unlike SACs [11–13], the *m*ALCs materials are expected to be stable and to keep its structure under realistic catalytic conditions, which outperformes well-defined monatomic layer.

The coordination environment of *m*ALCs will be more saturated than that of single atoms, which indicates *m*ALCs materials could be more stable during catalytic reaction. In addition, under the realistic reaction condition, the atoms of *m*ALCs could work in synergy to catalyze the reaction. For example, neighboring Pt monomers showed better catalytic performance and lower activation energy than single Pt atoms towards CO_2 reduction; meanwhile, these neighboring Pt monomers did not aggregate during the catalytic reaction [8]. It is generally believed that the support materials could affect electronic configuration of noble metal atoms by rearranging the molecular orbitals. This phenomenon results in modification of local charge density in catalyst surface. Based on the combination ways between noble metal atoms and matrix atoms, there are two models to describe the interaction between noble metal atoms and matrix atoms corresponding to the simulating charge density maps, as shown in Fig. 1. For SACs, if the single noble atom is anchored by three or four matrix atoms, its charge density will be affected only by matrix atoms. Its low-coordination environment results in a high activity. In contrast, if the single atoms assemble to monatomic layer clusters (for example, two atoms or four atoms), their energy states and charge density will be determined by both matrix atoms and neighboring noble atoms through the hybridization. Moreover, the energy of the highest occupied molecular orbital (HOMO) could be close to that of adsorbed species (such as O_2 and CO_2), which will facilitate charge transfer and decrease the reaction energy. Compared with nanoparticles (shown at the right end of Fig. 1), the noble atoms in the *m*ALCs

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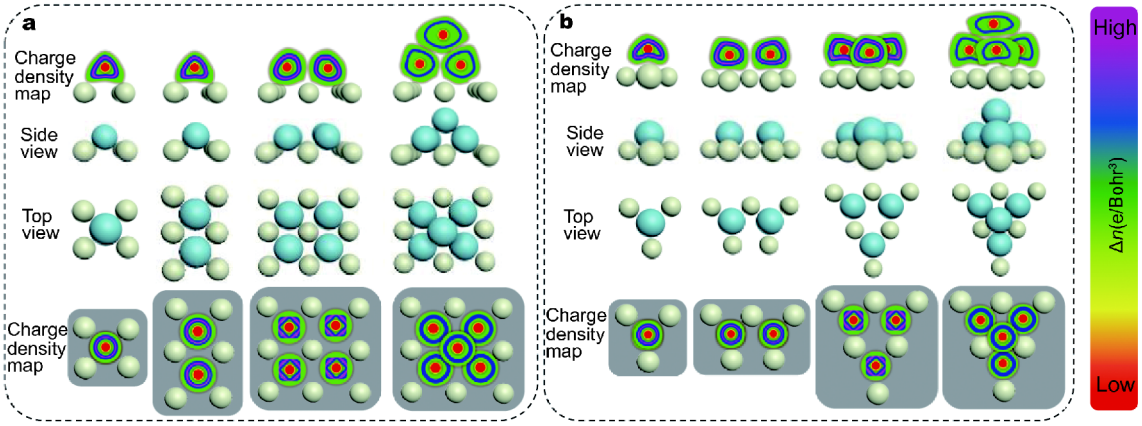

Figure 1 Two different types of noble metal atoms (blue) anchored on matrix atoms (white), and the corresponding simulated charge density map.

also have a lower coordination number and higher surface free energy. These two features of *m*ALCs lead to their higher activity and selectivity than those of SACs and conventional nanomaterials.

It is well-known that catalytic reactions take place on the surface of catalysts [14,15]. Even with the same element, different crystal planes could possess a very different work function and catalytic activity. For example, the Pt (111) surface shows higher activity than the Pt (100) and Pt (110) towards the oxygen reduction reaction (ORR) in $HClO_4$ solution [16]. This indicates that the multi-electron transfer process involved in the ORR on different Pt crystal planes will result in different reaction barriers. This is not only the case for monometallic catalysts, but also for bimetallic catalysts. For instance, Stamenkovic *et al.* [17] demonstrated that the Pt_3Ni (111) surface is more active than the Pt_3Ni (100) surface or the Pt_3Ni (110) surface towards the ORR, as shown in Fig. 2.

It is suggested that the surface structure of nanomaterials directly determines their performance in catalytic reactions. The high-index facet nanomaterials, with a large density of atomic steps and dangling bonds have demonstrated much enhanced specific activity compared to low-index Pt surfaces [18]. Although the high-index facet nanomaterials have high specific activity, it remains a challenge to decrease their size (usually ~100 nm) to meet commerical demands (commercial Pt/C catalyst particles are normally ~3 nm in size). Significant efforts have been devoted to the synthesis of small nanomaterials with controllable high-index facets. For example, Liu *et al.* [19] developed a novel electrochemically seed-mediated method to synthesize sub −10 nm tetrahexahedral Pt nanomaterials with high-index facets, possessing higher mass activity than commercial Pt/C towards ethanol

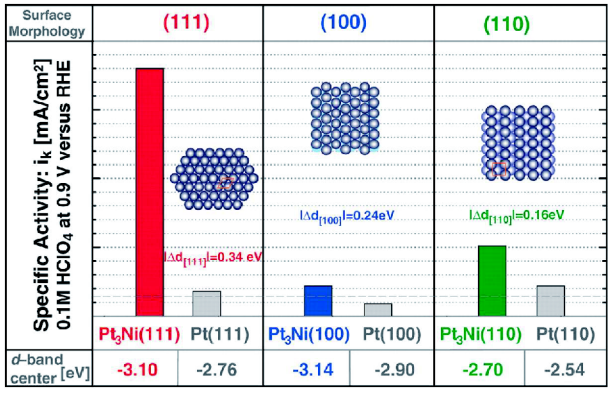

Figure 2 Influence of the surface morphology and electronic surface properties on the kinetics of the ORR. Rotating ring-disk electrode measurements of the ORR in $HClO_4$ (0.1 mol L^{-1}) at 333 K and 1,600 revolutions per minute on Pt_3Ni(*hkl*) surfaces are shown as compared to the corresponding Pt(*hkl*) surfaces. Reprinted with permission from Ref. [17], Copyright 2007, the American Association for the Advancement of Science (AAAS).

electrooxidation to CO_2. From the dependence of the structure-catalytic performances, we believe that synthesis of abundant active step sites is an effective approach to enhancing catalytic performance and avoiding the occurrence of side effects. Based on this consideration, SACs may not meet this requirement.

Clusters containing only a few atoms exhibit unique and unexpected properties, which could serve as individual active sites in the catalytic process. On the basis of this behavior, clusters have attracted much attention because every atom could have a substantial effect on the catalytic selectivity and activity. Even a subtle change in cluster size may lead to a significant change in catalytic performances [20]. For example, Kaden *et al.* [21] studied Pd_n clusters ($n \leq 25$) on rutile TiO_2(110) for their perfor-

mance towards CO oxidation. They found that Pd_2 and Pd_{20} clusters exhibited higher relative activity because of their unstable valence shell, which strongly depends on the size and electron number of the cluster, as shown in Fig. 3. The results also demonstrated that single Pd atoms are not active towards CO oxidation, and their production of CO_2 is equal to that of rutile TiO_2(110). A study on the oxidation of CO using Au_n cluster catalysts demonstrates that Au_8 on MgO(001) is the smallest Au cluster active towards CO oxidation at 140 K [22]. This study also reveals that the support will influence the electronic properties of Au_8, which can enhance the catalytic performance towards CO oxidation. In order to reach a better understanding of the fundamental properties of catalytic active sites on the atomic scale, combined experimental and computational investigations have been undertaken [23,24]. Clusters, which are relatively small in size, are suitable for computational modelling because of such systems being quite unambiguous.

Nevertheless, there are some limitations on the preparation of well-defined clusters in industrial-scale quantities. In 2017, atomic Au layered clusters (~2 nm) supported on α-MoC exhibited higher water-gas shift reaction activity than single atom Au [25], as shown in Fig. 4. Meanwhile, the atomic-layered Au clusters keep

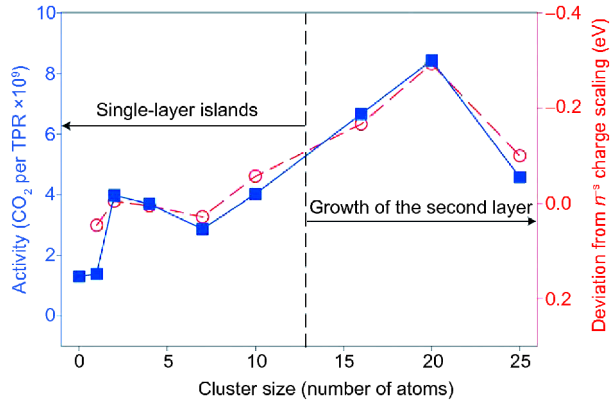

Figure 3 CO oxidation activity observed during temperature-programmed reduction (TPR) (left axis, solid squares) compared with shifts in the Pd 3d binding energy, relative to expectations from smooth bulk scaling (right axis, open circles), as a function of cluster size. Reprinted with permission from Ref. [21], Copyright 2009, AAAS.

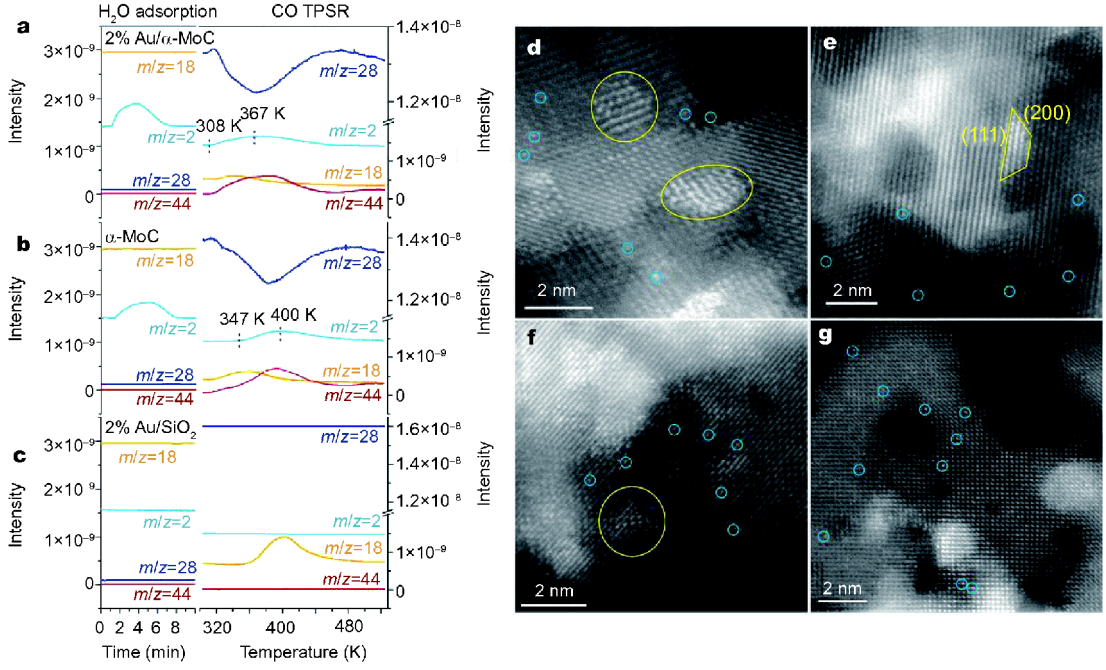

Figure 4 Mechanism study and electron microscopy characterization. Water adsorption (at 303 K) followed by CO-temperature programmed surface reaction (TPSR) on 2% Au/α-MoC (a), α-MoC (b), and 2% Au/SiO_2 (c). Signals of H_2 (mass to charge ratio, m/z=2), H_2O (m/z=18), CO (m/z=28), and CO_2 (m/z=44) were detected. (d and e) High-resolution high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images of 2% Au/α-MoC fresh catalyst, with single atoms of Au marked in blue circles and Au layered-structures highlighted in yellow. (f) HAADF-STEM image of 2% Au/α-MoC catalyst after reaction, in which the sample still contains both single-atom Au and Au layered-clusters. (g) HAADF-STEM image of the NaCN leached 2% Au/α-MoC catalyst, showing predominantly single atom Au, most of which overlaps with Mo sites in the support lattice. Reprinted with permission from Ref. [25], Copyright 2017, AAAS.

their morphology up to 473 K during water-gas shift reaction. On the basis of the above knowledge, we believe that *m*ALCs would exhibit higher activity and selectivity than other nanomaterials, even SACs. To the best of our knowledge, currently, *m*ALCs are still in their research infancy but are likely to lead to great opportunities and challenges in the fields of chemistry, materials science, and nanotechnology.

Received 24 April 2018; accepted 26 June 2018; published online 10 July 2018

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Acknowledgements This research was supported by the Australian Research Council (ARC) (DE170100928 and DP170101467), the Commonwealth of Australia through the Automotive Australia 2020 Cooperative Research Centre (AutoCRC), and Baosteel-Australia Joint Research and Development Center (BA14006). The authors acknowledge the use of the facilities at the UOW Electron Microscopy Centre funded by ARC Grants (LE0882813 and LE0237478) and Dr. Tania Silver for her critical reading.

Author contributions Jiang L proposed the concept of monatomic layer clusters. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

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新型的单原子层团簇催化剂

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摘要 “单原子层团簇”催化剂这一新概念, 不同于单原子催化剂和传统的纳米颗粒催化, 是由单原子建造新型的二维单原子层催化剂. 单原子层团簇催化剂的活性中心明确, 且原子间的相互作用会极大提高催化反应的选择性. 因此该催化剂材料不仅具有优异的催化性能, 还具有良好的选择性. 基于此, 作者同时分析和指出了未来的单原子层团簇催化剂的可能重点研究方向以及挑战.

