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New monatomic layer clusters for advanced catalysis materials

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Abstract

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 (Pt₁/FeO_x), which offered extremely high efficiency on an atomic percent basis and showed excellent performance towards CO oxidation.

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Novel monatomic layer clusters for advanced catalysis materials

Bin-Wei Zhang¹, Long Ren¹, Yun-Xiao Wang^{1*}, Yi Du^{1,2*}, Lei Jiang^{2,3,4} and Shi-Xue Dou^{1,2}

ABSTRACT Monatomic layer clusters with well-defined active centers are presented as novel materials for the design of advanced catalysis materials. On the basis of recent achievements in single-atom catalysts and catalysis by different crystal planes and clusters we believe that monatomic layer clusters could be higher activity and offer better selectivity than nanomaterials, even single-atom catalysts.

Keywords: monatomic layer cluster catalysis, well-defined active centers, high selectivity

Noble metals have been widely applied as catalysts in chemical production, energy conversion, and emission control¹⁻³. Their high cost and scarcity are major obstacles for any large-scale practical applications. It is therefore of great interest to explore novel active material systems that require less mass loading of noble metal catalysts but with even better performance. Recently, intense researches have 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 (Pt₁/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 SACs⁶⁻¹⁰. Nevertheless, it is worth noting that the catalytic selectivity plays an important part in catalytic reactions, and the SACs may have limited application in some multi-electron catalytic processes⁵. 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 SACs¹¹⁻¹³, the *m*ALCs materials are expected to be stable and to keep its structure under realistic catalytic conditions, which is given rise to well-defined monatomic layer.

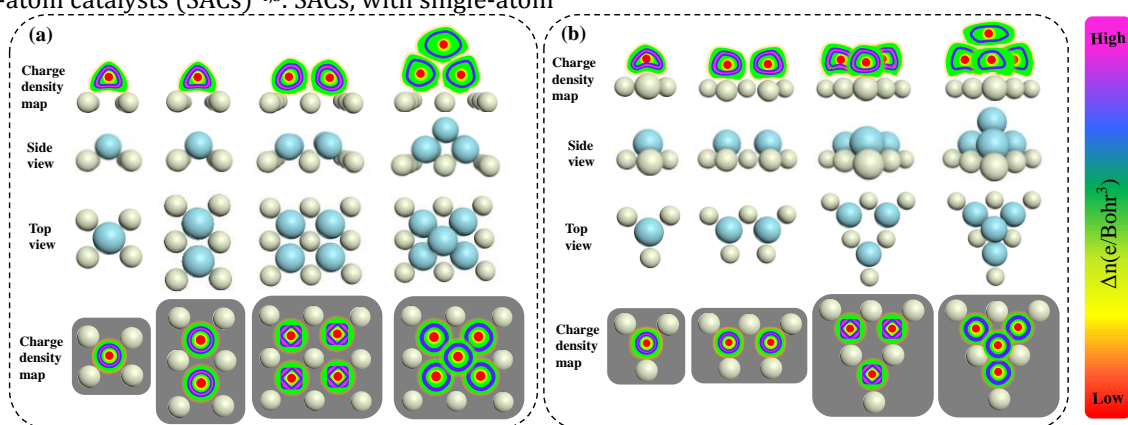


Figure 1 Two different types of noble metal atoms (blue) anchored on matrix atoms (white), and corresponding simulated charge density map.

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The coordination environment of *m*ALCs will be more saturated than that of single atoms, which results in *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 CO₂ reduction; meanwhile, these neighboring Pt monomers don't aggregate during the catalytic reaction⁸. It is generally believed that the support materials could affect electronic configuration of noble metal atoms by rearranging the molecular orbital. This phenomenon results in modification of local charge density in catalyst surface. Based on the combination ways between noble metals atoms with matrix atoms, there are two models to describe the interaction between noble metal atoms and matrix atoms (in the support materials) corresponding to the simulating charge density maps, as shown in Fig. 1a and 1b. For SACs, no matter the single noble atom is arched 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 absorbed species (such as O₂ and CO₂), which will facilitates charge transfer and decrease the reaction energy. When compared with nanoparticles (shown at the right end of Fig. 1a and 1b) the noble atoms in the *m*ALCs also have a lower coordination number and higher surface free energy. These two features of *m*ALCs lead their higher activity and selectivity, as compared with SACs and conventional nanomaterials.

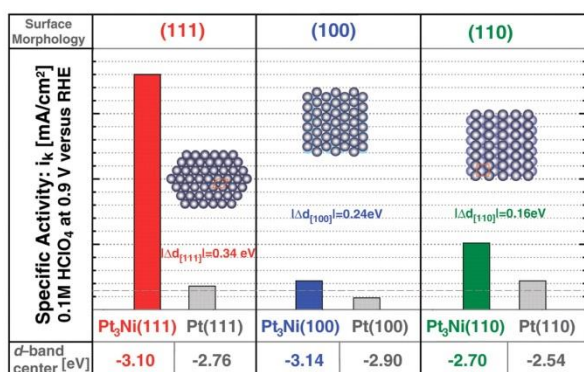


Figure 2 Influence of the surface morphology and electronic surface properties on the kinetics of the ORR. Rotating ring-disk

electrode measurements of the ORR in HClO₄ (0.1 M) at 333 K and 1600 revolutions per minute on Pt₃Ni(*hkl*) surfaces are shown as compared to the corresponding Pt(*hkl*) surfaces. Reprinted with permission from Ref. [17], Copyright 2007, AAAS.

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 hence catalytic activity. For example, the Pt (111) surface shows more activity than the Pt (100) and Pt (110) towards the oxygen reduction reaction (ORR) in HClO₄ solution¹⁶. This indicates that the multi-electron transfer process involved in the ORR that takes place on different Pt crystal planes will result in different reaction barriers. This is not only the case for monometallic catalysts, bimetallic catalysts also have the same properties. For instance, Stamenkovic et al. demonstrated that the Pt₃Ni (111) surface is more active towards the ORR than the Pt₃Ni (100) surface or the Pt₃Ni (110) surface¹⁷, as shown in Fig. 2.

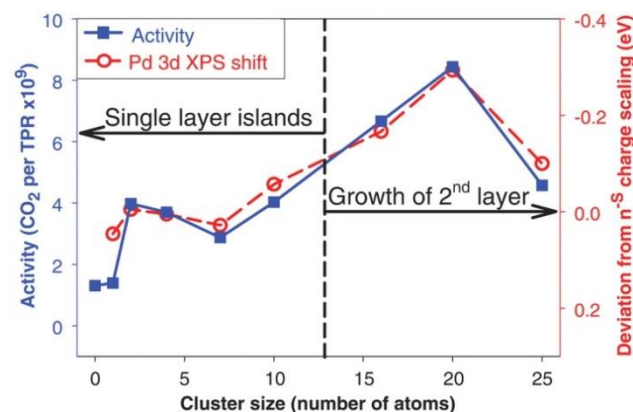


Figure 3 CO oxidation activity observed during temperature-programmed reduction (TPR) (left axis, solid squares) compared with shifts in the Pd 3d binding energy, relative to expectations from smooth bulk scaling (right axis, open circles), as a function of cluster size. Reprinted with permission from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

It suggests 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 equivalent low-index Pt surfaces¹⁸. Although the high-index facet nanomaterials have high specific activity, it remains a challenge to decrease their size (usually ~ 100 nm) to meet application requirements (commercial Pt/C catalyst particles are normally ~ 3 nm in size). Significant efforts have been devoted in synthesis of small nanomaterials with controllable high-index facets. For example, Liu et al.

developed a noble electrochemically seed-mediated method to synthesis sub-10 nm tetrahedral Pt nanomaterials with high-index facets, possessing higher mass activity than commercial Pt/C towards ethanol electrooxidation to CO₂¹⁹. From exploration of the structure–catalytic functionality relationship, 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.

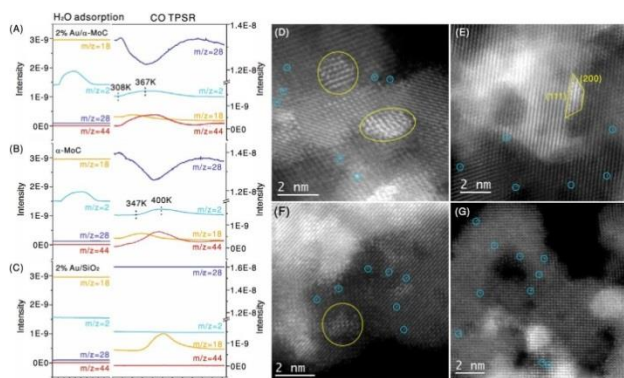


Figure 4 Mechanism study and electron microscopy characterization. Water adsorption (at 303 K) followed by CO – temperature programmed surface reaction (TPSR) on 2% Au/ α -MoC (A), α -MoC (B), and 2% Au/SiO₂ (C). Signals of H₂ (mass to charge ratio, $m/z = 2$), H₂O ($m/z = 18$), CO ($m/z = 28$), and CO₂ ($m/z = 44$) 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.

Clusters containing only a few atoms can 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 significant change in catalytic performances²⁰. For example, Kaden et al. studied Pd_{*n*} clusters ($n \leq 25$) on rutile TiO₂(110) for their performance towards CO oxidation²¹. They found that Pd₂ and Pd₂₀ clusters exhibited higher relative activity because of their unstable

valence shell, which strongly depends on the size and electron count 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 CO₂ is equal to that of rutile TiO₂(110). A study has been conducted to investigate the oxidation of CO using Au_{*n*} cluster catalysts, which demonstrates that Au₈ on MgO(001) is the smallest Au cluster active towards CO oxidation at 140 K²². This study also reveals that the support will influence the electronic properties of Au₈, which can enhance the catalytic performance towards CO oxidation. In order to reach a better understand 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 limitations on the preparation of well-defined clusters of industrial-scale quantities so far, which are ideal for identifying the catalytic characteristics. In 2017, atomic Au layered clusters (~2 nm) supported on α -MoC were proved to exhibit higher water-gas shift reaction activity than single atom Au²⁵, as shown in Fig. 4. Meanwhile, the atomic-layered Au clusters keep their morphology up to 473 K water-gas shift reaction. On the basis of the above knowledge, we believe that *m*ALCs would exhibit higher activity and selectivity than nanomaterials, even SACs. To the best of our knowledge, *m*ALCs are currently in their research infancy but are likely to lead to great opportunities and challenges in the fields of chemistry, materials science, and nanotechnology.

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

Conflict of interest The authors declare that they have 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, 不同与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的单原子层催化剂. 单原子层团簇催化剂的活性中心明确, 而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.