New monatomic layer clusters for advanced catalysis materials

Binwei Zhang
University of Wollongong, bz370@uowmail.edu.au

Long Ren
University of Wollongong, lr289@uowmail.edu.au

Yunxiaow Wang
University of Wollongong, yunxiao@uow.edu.au

Yi Du
University of Wollongong, ydu@uow.edu.au

Lei Jiang
Beihang University

See next page for additional authors

Follow this and additional works at: https://ro.uow.edu.au/aiimpapers

Part of the Engineering Commons, and the Physical Sciences and Mathematics Commons
New monatomic layer clusters for advanced catalysis materials

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

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

Authors
Binwei Zhang, Long Ren, Yunxiao Wang, Yi Du, Lei Jiang, and Shi Xue Dou

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/3369
Novel monatomic layer clusters for advanced catalysis materials

Bin-Wei Zhang\textsuperscript{1}, Long Ren\textsuperscript{1}, Yun-Xiao Wang\textsuperscript{1*}, Yi Du\textsuperscript{1,2*}, Lei Jiang\textsuperscript{2,3,4} and Shi-Xue Dou\textsuperscript{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 control \textsuperscript{1-3}. 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) \textsuperscript{4,5}. SACs, with single-atom active centers, were first reported by Qiao et al. \textsuperscript{4}. They synthesized a single Pt atom catalyst supported on FeO\textsubscript{x} (Pt/FeO\textsubscript{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 \textsuperscript{6-10}. 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 processes \textsuperscript{5}. In this case, we propose that if single atoms could assemble to monatomic layer clusters (mALCs), they would exhibit higher catalytic activity and selectivity than SACs. Unlike SACs \textsuperscript{11-13}, the mALCs 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.
The coordination environment of mALCs will be more saturated than that of single atoms, which results in mALCs materials could be more stable during catalytic reaction. In addition, under the realistic reaction condition, the atoms of mALCs 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 \( \text{CO}_2 \) reduction; meanwhile, these neighboring Pt monomers don’t 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 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 \( \text{O}_2 \) and \( \text{CO}_2 \)), which will facilitate 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 mALCs also have a lower coordination number and higher surface free energy. These two features of mALCs lead their higher activity and selectivity, as compared with SACs and conventional nanomaterials.

![Figure 2](image_url)

**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 \( \text{HClO}_4 \) (0.1 M) at 333 K and 1600 revolutions per minute on \( \text{Pt}_3\text{Ni(hkl)} \) 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 \( \text{HClO}_4 \) solution \(^{16} \). 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 Pt\(_3\)Ni (111) surface is more active towards the ORR than the Pt\(_3\)Ni (100) surface or the Pt\(_3\)Ni (110) surface \(^{17} \), as shown in Fig. 2.

![Figure 3](image_url)

**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 surfaces \(^{10} \). 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 CO$_2$. 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/SiO$_2$ (C). Signals of H$_2$ (mass to charge ratio, $m/z = 2$), H$_2$O ($m/z = 18$), 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.

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 performances. For example, Kaden et al. studied Pd$_n$ clusters ($n \leq 25$) on rutile TiO$_2$(110) for their performance 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 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 CO$_2$ is equal to that of rutile TiO$_2$(110). A study has been conducted to investigate the oxidation of CO using Au$_n$ cluster catalysts, which demonstrates that Au$_{25}$ on MgO(001) is the smallest Au cluster active towards CO oxidation at 140 K. This study also reveals that the support will influence the electronic properties of Au$_{25}$, 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. 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 Au, 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 mAlCs would exhibit higher activity and selectivity than nanomaterials, even SACs. To the best of our knowledge, mAlCs 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.

Received xxx 2015; accepted xxx 2015;
Published online xxx 2015

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 the Baosteel-Australia Joint Research and Development Center (Baosteel Grant no. 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 that they have no conflict of interest.
Lei Jiang is currently a Professor at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS), and Dean of the School of Chemistry and Environment, Beihang University. He received his BSc degree (1987), MSc degree (1990), and PhD degree (1994) from Jilin University of China (Jintie Li’s group). He then worked as a postdoctoral fellow in Professor Akira Fujishima’s group in Tokyo University. In 1996, he worked as a senior researcher in Kanagawa Academy of Sciences and Technology under Professor Kazuhiro Hashimoto. He joined ICCAS as part of the Hundred Talents Program in 1999. He was elected academician of Chinese Academy of Sciences in 2009 and the Academy of Sciences for the Developing World in 2012. His scientific interests are focused on bioinspired, smart, multiscale interfacial (BSMI) materials.

Shi-Xue Dou is the director of Institute for Superconducting and Electronic Materials and a Distinguished Professor at University of Wollongong. He received his Ph.D. in chemistry in 1984 at Dalhousie University, Canada and D.Sc. at the University of New South Wales in 1994. He was elected as a Fellow of the Australian Academy of Technological Science and Engineering in 1994. He is a program leader for Automotive Corporative Research Center-2020.

新型的单原子层团簇催化剂
张斌伟1, 任龙1, 王云晓1*, 杜轶1,2*, 江雷2,3,4, 窦士学1,2

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。