

available at www.sciencedirect.comjournal homepage: www.sciencedirect.com/journal/chinese-journal-of-catalysis

Highlight

A macro library for monatomic catalysts



CrossMark

Jingyi Han, Jingqi Guan *

In recent years, the rational design and controllable synthesis of atom-scale catalysts have been booming [1]. Compared with traditional nanoscale catalysts composed of hundreds to thousands of atoms, single-atom catalysts (SACs) with isolated active metal centers can participate in catalytic reactions more freely [2]. The maximum atomic utilization, unique atomic structure and electronic properties, and outstanding catalytic performance make them become the leading edge of catalytic field. According to the types of metal element anchored onto the carrier, SACs can be divided into monometallic SACs (identical elements) and multimetallic SACs (different elements), in which the latter have synergistic catalytic effect. Therefore, the structure and properties of atomic active sites should be determined at the atomic level from the aspects of material synthesis and mechanism understanding. Writing in nature materials, Xin and colleagues [3] provided the largest SAC library to date, containing both high concentration monometallic and multimetallic SACs to reveal the unified principles of related catalyst design and pave the way for the targeted preparation of novel SACs.

The catalyst structure can be controlled in the case of high metal loading using a dissolution-and-carbonization method. This synthesis method is not only easy to operate but also can be used to prepare SACs on a large scale. Using this method, Xin and colleagues [3] successfully prepared SACs containing 37 elements with ultra-high metal loading, such as 25.39% for Zn SAC, which cover most of the transition metals widely used in the catalytic field. In addition, the sample with the largest metal precursor ratio of each prepared SAC was selected *via* a four-step screening process. This work reveals the structural properties including bond length and coordination number, the evolution rule of the composition like the loaded metal elements and the electronic properties like oxidation state, which not only provide a unified principle for understanding the structure and properties of different types of SAC, but also stimulate a deeper understanding of the formation mechanism of SAC. For example, the local environment of each SA element is the key to determine the catalytic performance, which includes the bond lengths of SA to its first shell neighbors, coordination number (CN) and coordination elements. Their study found that SA elements in groups 5B, 6B and 10B lost more

external electrons or had smaller CNs, resulting in shorter bond lengths, indicating a general principle that the oxidation state was negatively correlated with CN. It is to say that the longer the bond length, the lower the oxidation state and the larger the CN will be and vice versa. Furthermore, by analyzing the evolution process in the synthesis of Mo and Mn SACs, it is found that the central metal atom coordinates with O at low temperature firstly, and then the coordination O is replaced by N or C in turn at high temperature (Fig. 1). The final coordination environment of SACs depends not only on SA species, but also on the terminal temperature. Another general principle found in this work is that the SA loading is positively correlated with the maximum metal precursor ratio, indicating that the loading can be controlled by adjusting the metal precursor ratio. Additionally, they also found that the maximum metal precursor ratio and loading amount (SA wt%/m_a) both show an approximate parabolic relationship with electronegativity, even though the latter trend is not very obvious due to the varying degrees of evaporation of metal precursors. This rule can be used to quantitatively predict the upper limit of metal precursor ratio for the synthesis of corresponding SAC through metal electronegativity. Surprisingly, the loadings are positively correlated with O content while negatively correlated with N content in SACs, indicating that compared with N, O content plays a more crucial role in controlling SA loading.

The aggregation effect from the atoms themselves and any other metal elements makes the multimetallic SAC extremely difficult to synthesize [4,5]. The dissolution-and-carbonization method enables to solve this problem by combining different metal centers with the glucose chelate and separating them by the glucose skeleton. By controlling the types and concentrations of various metal precursors, they used this method to successfully synthesize 2-, 8- and even 12-element SACs with different metal elements anchored on the same carbon carrier. Impressively, the total metal loading of SAC containing 12 metals (Sc, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Pd, Hf and W) reaches 7.53 wt%, which is thought to be an ultra-high value for overcoming aggregation and thus maintaining SA active sites. Compared with monometallic SACs, less species of metal SACs such as 4-metal (Fe-Co-Ni-Mn) SAC and mechanically mixed 12 monometallic SACs, the OER catalytic activity and stability of

12-element multimetallic SAC have obvious advantages due to the uniformly atomic distribution of 12 different elements which firmly attach to the same carrier and the cumulative synergistic effect between a variety of metal elements. These studies have verified great application potential of multimetallic SACs and encouraged further exploration in this field.

Although the largest library containing 37 metal elements reveals many rules of SAC structures and properties, and it combined with relevant theoretical calculations for oxygen evolution reaction application, there are still points needed to be further improved. In fact, it is reported that under operating conditions, the active sites of SA will undergo atomic configuration reconstruction, accompanied by valence changes [6,7]. This means that the interactions between SAs and the carrier will be self-regulated, thereby facilitating the catalytic reactions. In order to simulate the catalytic process more realistically, the particular structural response behavior, the physical adsorption and desorption process between reactants and SA catalytic sites as well as the poisoning and deactivation of SACs should be considered. Moreover, the mutual synergistic effects of different metal atoms are still worthy of further study to explore the law such as the distance between various SAs and their coordination environment.

Owing to the outstanding catalytic activity and stability, the SACs have become the most promising material for future practical application. The library created by their work reveals many evolution principles and provides guidance for further development of novel SACs with higher loading and multiple metal elements. The regular and instructive large databases in this work might provide guidance for researchers to establish other categories of catalysts, such as MOFs [8] and graphene-based catalysts [9], for electrocatalytic carbon dioxide reduction and nitrogen reduction.

*Corresponding author

Jingqi Guan

Institute of Physical Chemistry, College of Chemistry,
Jilin University, Changchun 130021, Jilin, China

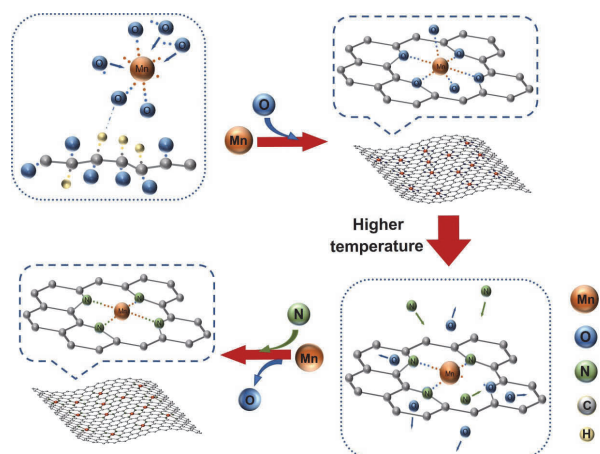


Fig. 1. Schematic diagram of the atomic structure evolution during the formation of monometallic SACs using Mn SAC as an example. Metal ions primarily coordinate with O atoms that reflects the electronegativity of metal ions. When the temperature continues to rise to a higher level, O atoms are replaced by N/C atoms, and thus the metal elements are firmly embedded onto the carrier.

E-mail: guanjq@jlu.edu.cn

Received 26 May 2022

Accepted 15 July 2022

Published 10 December 2022

[https://doi.org/10.1016/S1872-2067\(22\)64153-6](https://doi.org/10.1016/S1872-2067(22)64153-6)

© 2023, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

References

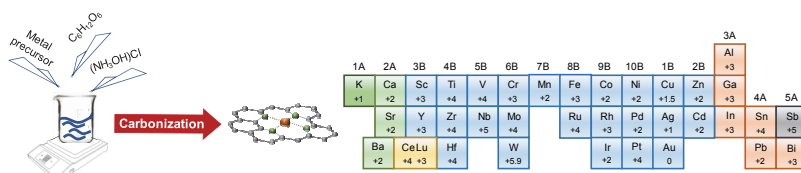
- [1] J. Guan, Z. Duan, F. Zhang, S. D. Kelly, R. Si, M. Dupuis, Q. Huang, J. Q. Chen, C. Tang, C. Li, *Nat. Catal.*, **2018**, 1, 870–877.
- [2] X. Cui, W. Li, P. Ryabchuk, K. Junge, M. Beller, *Nat. Catal.*, **2018**, 1, 385–397.
- [3] L. Han, H. Cheng, W. Liu, H. Li, P. Ou, R. Lin, H. T. Wang, C. W. Pao, A. R. Head, C. H. Wang, X. Tong, C. J. Sun, W. F. Pong, J. Luo, J. C. Zheng, H. L. Xin, *Nat. Mater.*, **2022**, 21, 681–688.

Graphical Abstract

Chin. J. Catal., 2023, 44: 1–3 doi: 10.1016/S1872-2067(22)64153-6

A macro library for monatomic catalysts

Jingyi Han, Jingqi Guan *
Jilin University



Atomically dispersed catalysts have become a research frontier due to their excellent catalytic activity and selectivity, but the controllable synthesis is still challenging. A library containing 37 elements was created to guide the fabrication of monoatomic catalysts.

- [4] H. Zhang, K. Kawashima, M. Okumura, N. Toshima, *J. Mater. Chem. A*, **2014**, 2, 13498–13508.
- [5] S. K. Kaiser, Z. Chen, D. Faust Akl, S. Mitchell, J. Perez-Ramirez, *Chem. Rev.*, **2020**, 120, 11703–11809.
- [6] S. Fang, X. Zhu, X. Liu, J. Gu, W. Liu, D. Wang, W. Zhang, Y. Lin, J. Lu, S. Wei, Y. Li, T. Yao, *Nat. Commun.*, **2020**, 11, 1029.
- [7] M. T. Greiner, T. E. Jones, S. Beeg, L. Zwiener, M. Scherzer, F. Girgsdies, S. Piccinin, M. Armbruster, A. Knop-Gericke, R. Schlogl, *Nat. Chem.*, **2018**, 10, 1008–1015.
- [8] Y. S. Wei, M. Zhang, R. Zou, Q. Xu, *Chem. Rev.*, **2020**, 120, 12089–12174.
- [9] H. Y. Zhuo, X. Zhang, J. X. Liang, Q. Yu, H. Xiao, J. Li, *Chem. Rev.*, **2020**, 120, 12315–12341.

单原子催化剂大数据库

韩璟怡, 管景奇*

吉林大学化学学院, 物理化学研究所, 吉林长春130021

摘要: 单原子催化剂(SAC)是在基底材料上锚定孤立的金属原子, 具有金属位点结构稳定以及活性中心高度均匀、配位环境可调和原子利用效率高等优点。因此, SAC有着桥接非均相和均相催化的巨大潜力。此外, SAC还为探索催化结构-性能关系以及研究原子尺度的催化机制提供了一个基本平台。近年来, SAC的合理设计和可控合成得到较大发展, 它们表现出在金属表面上无法实现的显著的催化活性和选择性。尽管近期SAC研究十分热门, 但仍然存在着一些巨大的挑战。首先, 缺乏一套统一标准为新型SAC的设计提供指导。不同的金属中心具有不同的化学和电子特性, 因此合成一种SAC的指导原则不能简单地外推到另一种。其次, 由于缺乏对SAC形成机制的全面了解, SAC材料中的键长、氧化态、配位数和配位阴离子种类等局部结构仍然难以调控。此外, 金属单原子(SA)的负载量也难以有效控制, 这主要是由于吉布斯-汤姆逊效应经常导致锚定的单原子发生团聚。虽然, 氮掺杂可以缓解原子聚集, 但是简单地增加氮含量并不能总是提高SA的负载量。目前, 如何将不同的金属元素位点合成于一个SAC材料中还存在很多知识盲区。

本文评述了Xin等(*Nat. Mater.*, **2022**, 21, 681–688)通过一种高温碳化法在氮掺杂的碳基底上合成基于37种单金属元素的单原子催化剂, 作者结合原位技术对催化剂进行表征和分析, 建立了一个从单金属到复杂多金属材料的单原子催化剂库。该催化剂库一方面可以为单原子催化剂的合理设计提供指导, 另一方面为SAC材料中关于氧化态、配位数、键长、配位元素和单原子的金属负载量等方面的分析提供借鉴。众所周知, 每个单原子元素的局部环境是决定催化性能的关键, 包括单原子与距离其最外壳层最近原子间的键长、配位数等。研究发现, 第5副族、第6副族和第10副族的单原子金属元素通常会失去更多的外部电子或具有更小的配位数, 从而导致它们的键长更短, 这说明氧化态与配位数呈负相关性。也就是说, 键长越长, 氧化态越低, 配位数越大, 反之亦然。此外, 金属单原子的负载量与最大金属前驱体的比例(金属Mo元素和葡萄糖的摩尔比)呈现出正相关的关系, 这表明可以通过调节金属前驱体比来有效控制负载量, 并且最大金属前驱体比例和负载量与电负性均呈现出近似抛物线的关系, 尽管由于金属前驱体在制备过程中挥发损失的程度不同, 电负性的抛物线趋势不是很明显。该规律可用于通过金属电负性定量预测合成相应SAC的金属前驱体比上限。另外, 金属单原子的负载与O含量呈正相关, 而与N含量呈负相关, 指明N、O含量对金属单原子负载量的调控极为关键。同时还提出SACs的最终协调环境不仅与单原子金属的种类有关, 还与制备过程的反应温度有关。最后, 该研究为多金属单原子催化剂的可控制备打开一扇大门, 并证明使用该方法可以成功构建一种包含多达12种不同金属元素的复杂的单原子催化剂材料。

关键词: 单原子催化剂; 析氧反应; 金属负载量; 氧化态; 多金属位点

收稿日期: 2022-05-26. 接受日期: 2022-07-15. 上网时间: 2022-12-10.

*通讯联系人. 电子信箱: guanjq@jlu.edu.cn (管景奇).