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Highlight

Controllable synthesis of dual-atom catalysts by a confinement-pyrolysis strategy

Jingyi Han, Jingqi Guan *

Dual-atom catalysts (DACs), an upgraded version of single-atom catalysts (SACs), can achieve stronger interactions with the supporting substrate as well as a more flexible and adjustable geometric/electronic structure of the active centers. Therefore, they possess unique advantageous long-range interactions between atomic pairs while retaining the advantages of SACs, such as 100% atomic utilization efficiency. Thus, the kinetic and energy barriers of the related reactions can be considerably accelerated and weakened, respectively, to achieve a catalytic performance beyond the theoretical limit [1]. Consequently, DACs have emerged as ideal catalyst candidates in recent studies. However, the controllable synthesis of DACs reported to date is still based on basic SAC methods, including atomic layer deposition (ALD), wet chemical methods, and high-temperature pyrolysis, all of which have significant disadvantages (Table 1). ALD is costly and the applicable composite objects are not universally available. In addition, owing to the wet chemical method based on physical/chemical adsorption, the obtained DACs struggle to cope with unsatisfactory thermal and chemical stabilities. As metal atoms are bound to aggregates during synthesis, conventional thermochemical treatments cannot prevent the generation of unwanted cluster impurities [2]. Therefore, more efficient and ingenious methods of preparing DACs must be urgently developed [3].

Recently, in the Journal of the American Chemical Society, Niu *et al.* [4] reported a universally applicable synthesis method based on confinement pyrolysis, which led to the successful establishment of a DACs library covering homonuclear and heteronuclear metal sites. In particular, the synthesis pathway can be divided into two steps: encapsulation and pyrolysis. Its

Table 1
Comparison of synthesis methods for DACs.

Method	Principle	Advantage	Disadvantage	Ref.
Confinement-pyrolysis strategy	metal atoms are prevented from aggregating through the confined effect of the template	high metal loading and stability; high ratio of diatomic pair; even distribution of active sites; regulable diatomic coordination structure; universal applicability of metal elements	precursor requires careful design; size effect limitation	[4]
Typical high-temperature pyrolysis	high temperature energized breaking/forming chemical bonds to anchor atomic sites	mature technique; universal applicability of metal elements	low metal loading; low ratio of diatomic pair; high aggregation probability; poor dispersion of active sites; severe high temperature synthesis condition	[5]
Double solvent wet chemical method	substrates can trap metal atoms via the hydrophilic/hydrophobic properties of different solvents	simple synthesis procedure; mild experimental condition;	low metal loading; low ratio of diatomic pair; high aggregation probability; poor dispersion of active sites	[6]
ALD technique	the vapor precursors alternately pulse to form the deposition film, which is then chemically adsorbed on the substrate and via self-limiting reactions to form the atomic layer	adjustable parameters; even distribution of active sites; remarkable reproducibility	high cost; special requirements for metal precursors and substrates; limited applicability of metal elements; time-consuming	[2]
Mechanical ball-milling method	sever and reconstruct the chemical bonds of precursors by applying physical stress	potential for large-scale production; low cost; universal applicability of metal elements	low metal loading; low ratio of diatomic pair; high aggregation probability; poor dispersion of active sites	[7]
Electrochemical deposition method	metal atoms can be electrodeposited on electrodes via external current	adjustable applied electrochemical parameters	low metal loading; low ratio of diatomic pair; high aggregation probability; poor dispersion of active sites	[8]
Ultrashort thermal shock route	thermal shock wave with rapid energy input to obtain atomic sites	high metal loading; high ratio of diatomic pair; universal applicability of metal elements	harsh experimental conditions; high cost; not applicable on a large scale	[9]

core lies in mediating the DAC structure by encapsulating the macrocyclic metal complex (M^1M^2L) into the cavity of a porous material (ZIF-8) (Fig. 1). The elaborately designed multifunctional Robson-type macrocyclic ligands provide a versatile coordination platform that is compatible with the embedding of various combinations of homo/heterobimetallic sites. The limited internal capacity of the porous carbon framework as an encapsulation shell has a spatial restriction effect on the macrocyclic complex, which fundamentally suppresses adverse thermal migration and agglomeration trends during subsequent high-temperature treatment, thus maintaining the bimetallic structure to a large extent. The unprecedented design ideas presented in their work motivated researchers to broaden the innovation directions and inspire the following aspects of inspiration for future vigorous development of DACs.

The ability of dexterous Robson-type ligands to achieve strong coordination with most metal ions endows the synthesis method with the versatility to cover almost all the transition metals widely used in catalysis, thereby implying a desirable ability to synthesize DACs with different elements. Thus, they successfully fabricated a DACs library of six homonuclear (Fe_2, Ni_2, Mn_2, Co_2, Cu_2, and Pd_2) and four heteronuclear (Fe–Ni, Fe–Cu, Cu–Co, and Cu–Mn) M^1M^2L. For example, in FeCu-DAC, the abundant bright spots in the high-angle annular dark-field scanning transmission electron microscopy image represent metallic sites, and the fraction of Fe-Cu metal pairs identified by electron energy loss spectroscopy was up to 70%. Additionally, they coimpregnated Fe/Cu nitrates into ZIF-8 and pyrolyzed them to prepare Fe/Cu-SAC control samples. Analysis of the time-of-flight secondary ion mass spectra revealed that the former had an $[FeCuN_4O_2]$ ensemble structure similar to that of the $FeCuLCl_2$ precursor, which was further confirmed by the similar characteristics in their extended X-ray absorption fine structure spectra, whereas the latter was composed primarily of $[FeN_4]$ and $[CuN_4]$ moieties. Furthermore, the K-edge X-ray absorption near-edge structure spectrum revealed electronic interactions between the Fe and Cu atoms. These results strongly indicate that FeCu-DAC has M–N/O and M–O–M structures. Notably, because single/paired atomic sites are thermodynamically unstable, the proportion of diatomic groups in DACs synthesized using common methods presents uncontrollable ambiguity and is generally unsatisfactory. By contrast, metal pairs accounted for more than 70% of all the DACs they worked on owing to the confinement effect of the ZIF-8 encapsulation of M^1M^2L. Furthermore, the metal coordination environment in each DAC was nearly identical to that of the corresponding precursor, further confirming the successful formation of diatomic pairs. Most metal elements fit into the $M^1M^2N_4O_2$ configuration, thus demonstrating the wide applicability of this synthetic approach.

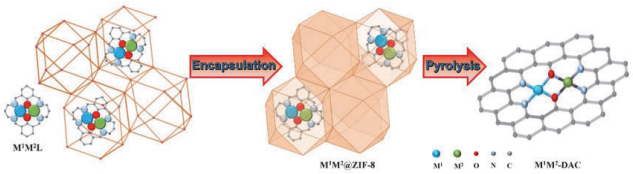

Fig. 1. Schematic of the confinement-pyrolysis strategy for the synthesis of DACs by using porous ZIF-8 to encapsulate macrocyclic M^1M^2L precursors with mediated effect.

Most importantly, theoretical studies have demonstrated that DACs with two adjacent active metal centers can realize reaction pathways that are inaccessible to SACs. The successful synthesis of the M^1M^2-DAC library allowed researchers to explore this possibility through experiments [10]. For example, in terms of the oxygen reduction reaction (ORR), the O–O bond can be weakened by side bridge adsorption at the diatomic sites of both Fe_2-DAC and FeCu-DAC, thereby resulting in a low yield of H_2O_2. However, they exhibited different activity losses after the accelerated stress test (AST); essentially, FeCu-DAC exhibited higher stability, thus suggesting that they should follow different ORR mechanisms. For Fe_2-DAC, previous studies have reported that demetallization and carbon corrosion are the two main processes that lead to durability, which can be further aggravated by reactive oxygen species (ROS) produced by Fe-based catalysts through Fenton-like reactions [11]. Intriguingly, they found that the ORR-catalyzed cycle of the Fe–Cu DAC is not based on the general Fenton-like pathway but rather on an accidentally unlocked two-electron reduction process, through which the by-product H_2O_2 can be reduced to H_2O with high activity rather than harmful ROS, thus allowing the basic reaction steps to be controlled. They further combined theoretical calculations to explore the mechanisms and found that the •OH ROS in the Fe_2 DAC is more inclined to desorption, followed by another *OH adsorbed at the Fe–Fe bridge. For the Fe–Cu DAC, because only few positively charged metal centers exist on the heterogeneous Cu sites, their synergistic interaction with Fe atoms causes the Fe *d*-band center to shift to the Fermi level, thereby resulting in a strengthened Fe–O bond that significantly curbs the desorption/adsorption tendency of •OH and *OH. In addition, the Gibbs free energy of hydrogen peroxide reduction ($*OH + H^+ + e^- = *H_2O$) on Fe–Cu DAC was significantly lower than that on Fe–Fe DAC, thus corroborating the existence of the above favorable pathway. Therefore, the ORR catalytic performance of Fe–Cu DAC stands out among all the studied atomic materials as it exhibits remarkable stability with a $\Delta E_{1/2}$ of merely 5 mV after 10000 potential cycles. These findings indicate that the synthesis method reported in their work releases the catalytic potential of DACs in numerous other electrochemical reactions, such as oxygen evolution, CO_2 reduction, and N_2 reduction.

Although their work is epochal and inspiring, it presents room for further improvement. The sample size of this DACs library must be further increased to explore unified principles with guiding significance and thus create more conditions for the orientational preparation of advanced DACs. Reportedly, the active groups of DACs undergo evolutionary remodeling accompanied by valence changes during the catalytic process for autonomous optimization, and sometimes partially toxic inactivation occurs [12]. These mysterious structural responses should be given sufficient attention to further reveal the laws of long-distance synergies and the coordination environment of the DACs atom pairs, thus paving the way for unlocking more ideal catalytic pathways for diverse reactions.

Graphical Abstract

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Controllable synthesis of dual-atom catalysts by a confinement-pyrolysis strategy

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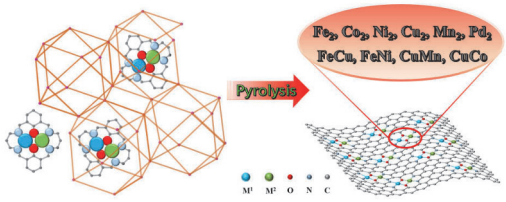

Dual-atom catalysts are at the forefront of the latest research because they exhibit outstanding catalytic properties owing to their unique synergistic effects; however, their controllable synthesis methods remain limited. In this study, a confinement pyrolysis strategy was used to efficiently prepare various dual-atom catalysts.

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通过限域-热解策略可控合成双原子催化剂

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摘要: 双原子催化剂(DACs)是单原子催化剂(SACs)的升级版, 在保留SACs 100%原子利用效率等优点的同时, 其与支撑衬底间的相互作用更强, 活性中心的几何/电子结构更灵活可调, 双原子对之间具有独特的协同作用优势. 因此, DACs可以超越单原子位点反应性能理论极限, 成为更加理想的催化剂. 尽管DACs跻身最新的研究前沿, 但目前报道的可控合成DACs途径仍是基于制备SACs的方法, 包括成本高昂、适用性有限的原子层沉积法, 产物稳定性差的湿化学法和易发生不利团聚的高温热解法等, 这些方法都存在不可忽视的缺点. 因此, 迫切需要探索更高效巧妙且具有普适性的制备DACs方法.

本文对Niu等(*J. Am. Chem. Soc.*, **2023**, 145, 4819–4827)的工作进行了评述. 作者报道了一种普适性的基于封装-热解策略的合成方法, 并由此成功建立了一个涵盖同核和异核双金属位点的DACs库. 报道的合成途径可分为封装和热解两步,

其核心是将大环金属配合物(M^1M^2L)包封到多孔金属-有机骨架材料(ZIF-8)的腔体中实现对最终DACs结构的介导. 精心设计的多功能Robson型大环配体提供了一个能够与大多数金属离子实现强配位的多功能配位平台, 使得该合成方法可以普遍适用于几乎所有广泛用于催化领域的过渡金属元素, 可兼容对多种同核/异核双金属位点组合的包封. 作为封装外壳的多孔ZIF-8框架内部容量有限, 对Robson型大环配合物前体具有空间限制作用, 从根本上抑制了后续高温热解处理过程中不利的热迁移和团聚趋势, 从而在很大程度上保持了同Robson型前体高度近似的双金属配位结构. 该工作所呈现出的可控合成的设计理念, 激励着研究者们拓宽创新方向来助力DACs未来的蓬勃发展. 相关研究表明, 脱金属化和碳腐蚀是降低耐久性的两个主要过程, 而铁基催化剂通过类芬顿反应产生的活性氧(ROS)可以进一步削弱稳定性. 然而, 研究发现Fe-Cu DAC在催化氧还原反应(ORR)时不是基于一般的类芬顿途径, 而是基于一种双电子还原过程, 经过该过程, 副产物H_2O_2可以高活性地被还原为H_2O而不是有害的ROS, 使得基本反应步骤可控. 此外, 作者结合理论计算研究进一步证实了上述有利途径的存在. 因此, Fe-Cu DAC表现突出的ORR催化性能和较好的稳定性, 在10000个电位循环后, $\Delta E_{1/2}$仅为5 mV. 综上, 该文章报道的合成方法将启发人们解锁DACs在许多其他电化学反应中的未知反应途径, 从而极大释放DACs的催化潜力, 如析氧反应、CO_2还原反应、N_2还原反应等.

关键词: 双原子催化剂; 多金属; 金属负载量; 异核; 反应途径

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