Stablizing Catalyst Made of Single Atom

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Perspective

The most active new area in heterogeneous catalysis is single atom catalysts (SACs), which offer exceptional features for a wide range of chemical processes [1]. Every scattered single atom in SACs can operate as an active centre to take part in catalytic cycles thanks to the uniform coordination environment, exhibiting the highest atom usage efficiency. Additionally, these active centres' distinct electronic structures can offer a wealth of adsorption sites and a unidirectional electron transfer route, leading to SACs with enhanced catalytic activity, chemoselectivity, and stability. However, during the synthesis of SACs, the single metal atoms easily join to form nanoparticles due to the extraordinarily high atom surface energies, which consequently changes their chemical performances. Therefore, the strategies for single metal atoms stabilization are vital to the development of heterogeneous catalysis based on SACs.

During past decades, tremendous efforts on anchoring single atoms onto various supports have been devoted to obtaining SACs with distinctive and stable chemical performance, including mass-selected soft landing, atomic layer loading, wet-chemistry synthesis, etc. [2]. Owing to easy operation and feasibility of large-scale manufacturing, currently, the wet-chemistry synthetic method has attracted interest and has been developed rapidly. The strong interactions between the metal atoms and the supports play an indispensable role in SACs synthesis via wet-chemistry reaction, which is closely associated with the structure of supports. The support structures that are porous, functionalized, or defective have great potential for attaching single atoms and can produce four different types of stabilisation mechanisms, including ligand-combined SACs, electron-coordinated SACs, micropore-confined SACs, and defects-stabilized SACs.

The primary mechanism for synthesis of ligands-combined SACs is metal-oxygen interactions between the organometallic precursors and the surface -OH groups on the support [3]. It is common practise to graft organometallic precursors onto silica with a high concentration of -OH groups in order to produce catalysts with single-atom catalytic sites. Some transition-metal atoms, such as Zr, Ta, Mo, W, and Re, have so far been stabilised on silica surfaces and exhibit excellent activity in catalytic processes. The density of surface –OH groups plays an important role in anchoring metal precursors, which contributes to achieving ligands-combined SACs with high metal atom loading. Currently, mesoporous silica materials have attracted attention in synthesis of SACs due to their rich surface –OH groups, large surface areas and controllable pore diameters. However, reducing leaching and aggregation of these metal catalytic sites in its application is a big challenge, especially in liquid-phase reactions.

Supports with coordinating atoms that have lone pairs of electrons such as N, S, and O can stabilize isolated metal atoms via strong electronic coordination, thus obtaining electron-coordinated SACs [2]. For the manufacture of SACs, polymers containing N functional groups that can offer a wealth of coordination sites, a high specific surface, and functionalized ligands for metal atom anchoring are frequently utilised. After pyrolysis, solitary metal atoms can typically be equally anchored by neighbouring N atoms on supports. However, the abundance of catalytic sites severely limits the overall chemical activity of SACs. Exploiting other coordination properties of supports and adding foreign nitrogen or sulphur dopants are two effective methods utilised to improve the coordination sites for more metal atom capture in order to obtain high metal atom loading. Nitrogen-doped carbon materials, such as N-doped graphene and graphitic carbon nitrides, have been used as supports for SAC stabilisation because of their large surface areas and adaptable structure. These materials can control the electronic structure of single-atom catalytic sites and promote

electron migration, giving SACs unexpected catalytic performance. During this time, SACs are given a stable structure and a high metal loading by intensifying the contacts between coordination atoms and metal atoms. Electronic coordination may be impacted by the synthesis circumstances, including solvent type and solution pH. Metal atoms are typically constrained by physical or chemical methods, such as Zeolites, metal-organic frameworks (MOFs), or covalent organic frameworks (COFs), during the creation of micropore-confined SACs.

When using microporous Zeolites as the supports, the metal precursors are often physically contained within the micropores of the Zeolites and then converted to SACs. To ensure that metal precursors diffuse and adhere effectively, their diameter must be less than the size of the pore. When MOFs or COFs with well-defined porous structures and a wealth of organic ligands are used as the supports, they can not only provide suitable cages or pores for metal precursor confinement but also provide chemical combination sites for SACs stabilisation, particularly when the organic ligands contain coordinating atoms with lone pairs of electrons. For improving SAC stability, N-doped carbon, g-C_3N_4, and metal oxides can be added to the pore space of MOFs or COFs. In order to isolate guest species such SACs, metal clumps, and nanoparticles, the well-defined pore structure contributes to this. It also integrates the benefits of both the guest species and the microporous supports to synergistically boost the catalytic activity. MOFs have emerged as one of the most promising microporous materials for the manufacture of SACs due to their enormous surface areas, well-defined structure, good designability, and tailorability [4,5]. There are three ways that the impacts of MOFs on stabilising metal atoms have been documented. The first method involves using post-treatments to graft metal atoms onto the organic ligands of MOFs. The second method involves adding metal atoms to the MOFs' inorganic nodes. The third method involves attaching metal atoms to a visitor species that is contained inside a MOF pore. The variety of framework architectures and the mixtures of both organic ligands and inorganic nodes seen in MOFs can facilitate the development of dual-atom catalysts as well as the stability of various metal atoms [6]. Besides, in order to overcome the problem of metal atoms leaching, 2D structural MOFs have been recently developed for SACs synthesis. It has been shown that surface flaws in nanomaterials with distinctive electronic structures and unsaturated coordination environments serve as "trap" sites for the stability of single metal atoms [7-9]. High adsorption energies and diffusion barriers at defect locations prevent the migration and aggregation of single metal atoms, according to experimental and theoretical data. In addition to having a stabilising impact on individual metal atoms, surface flaws can make it simpler for molecules to adsorb and transfer electrons, which greatly simplifies catalytic reactions. Currently, many different types of defects are employed to create SACs with distinctive chemical activity and stable structures, including carbon defects, doped defects, anion defects (O, S, N), and cation defects (Ni^{2+}, Al^{3+}, Ce^{4+}) . Evidently, a crucial factor in the chemistry of the defects-stabilized SACs is the defect density. A large density of surface defects has been successfully obtained through reaction condition control and the construction of 2D structural supports, which can give more anchoring sites for single-atom stabilisation. Furthermore, several experimental findings have shown that the homologous metallic oxide can create various surface flaws, each of which has a unique electrical structure and is crucial for the production of SACs. For instance, the step edge defect sites and Ce vacancies of the CeO_2 surface can be used to selectively stabilise single Au and Pt atoms. The adsorption behaviour of Pt and Au atoms on oxygen defects at faulty TiO_2 surfaces, however, clearly differs, with Au atoms preferring to be anchored on the bridging oxygen defective sites and Pt atoms more frequently stabilising on the basal oxygen defective side. The same metal atoms dispersed on different supports show different catalytic performance. Therefore, the relationship between the electronic structure of defects and the metal atoms should be considered in the synthesis of defects-stabilized SACs.

In addition to the traditional strategies for SACs stabilization discussed above, some new methods are developed for making SACs with high atoms loading and high production yield under mild reaction condition. Wei et al. [10] proposed an iced-photochemical reduction method via ultraviolet irradiation of frozen Pt metal precursor solution for anchoring Pt SACs on various substrates (e.g., mesoporous carbon, graphene, carbon nanotubes, TiO_2 nanoparticles, and ZnO nanowires) By creating H-Pt-OH intermediate when Pt precursor is frozen, water molecules can stabilise Pt precursor, preventing breakdown and assuring the production of Pt SACs after reduction by UV irradiation. Fan et al. [11] described an electrochemical corrosion method for synthesising isolated Ni atoms, in which small Ni NPs were removed using a direct constant potential together with the creation of Ni SACs. Ni SACs formed following CV treatment, which was attributed to the significant oxidation ability of A-Ni-C in the anodic-going scan, and Ni nanoparticles gradually reduced. SACs can also be created using ionic liquids [12] created ionic liquid-stabilized SACs, where the electrical double-layer of the ionic liquid provided electrostatic stabilisation against the aggregation of the metal atoms in the vicinity. Practically speaking, the methods to produce SACs on a big scale are urgently needed. Keg-scale CeO_2-supported Au SACs were created by Gan et al. [13] by the ball milling and calcination processes. To improve the mean distance between Au atoms and prevent the aggregation of Au species, in the typical preparation, 1:1000 (wt) $Au(Ac)_3$ and $Ce(Ac)_3$ precursors were thoroughly mixed by ball milling. Au SACs could be anchored to the surface of CeO_2 after calcination. They proved that there is no

discernible difference between Au_1/CeO_2 SACs in terms of their structure and catalytic performance. High activity, selectivity, and stability for CO oxidation were seen at both plant-scale (1000 g) and lab-scale (10 g), demonstrating their importance in real-world applications.

In conclusion, supports with distinct electronic structures and surface groups can offer a wealth of "traps" for limiting the migration and aggregation of solitary metal atoms, opening up access to more active sites. The key factor in the strong dependence of SACs stabilisation on the nature of supports and reaction circumstances is the strong interactions between metal atoms and supports. Low metal loading and production yield still restrict the practical use of SACs, despite significant advancements. For the production of stable and heavily metal-loaded SACs, more efficient methods are required.

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