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REVIEW

Carbon-supported metal single atom catalysts

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Abstract: Metal single atom catalysts (SACs) have been attracting increasing attention in recent years owing to their incredible performance in several key catalytic reactions such as the oxygen reduction reaction and CO oxidation. The construction of well dispersed stable SACs can not only make it possible to understand the catalytic reactions on the atomic scale, but is also important for developing novel industrial catalysts. Recent efforts have been focused on dispersing metal SACs on carbon substrates rather than on metals or metal oxides for improved catalytic behavior. Especially, graphene-based materials have proven to be excellent candidates for supporting SACs due to their unique structural and electronic properties. Nevertheless, the anchoring mechanism between metal SACs and carbon substrates is not well understood. Here we review the many roles of carbon materials as the support of SACs and highlight the anchoring mechanism. We also propose some suggestions to improve the experimental and theoretical research methods to expand the number of applications and realize industrial applications.

Key Words: Metal single atom catalysts; Carbon substrate; Graphene; Electron microscopy

1 Introduction

In heterogeneous catalysis system, supported metal catalysts are widely used in many important industrial catalytic reactions. It has long been recognized that downsizing the metal particles is a key process to improve the performance of the supported metal catalysts (shown in Fig. 1)[1]. Extensive investigations have revealed that sub-nanometer clusters have a better catalytic activity or selectivity than larger particles[2-4] and, in particular, Qiao et al. [5] first prepared a well dispersed Pt single atom catalysts (SACs) supported on iron oxide with an improved catalytic activity and stability in the CO selective oxidation reaction. Isolating metal atoms greatly improved the utilization efficiency of the metal catalyst, and the adsorption / desorption selectivity of the active species on the different molecules can be changed, which affected the reaction kinetics[6]. Accordingly, metal SACs have recently attracted much attention owing to their incredible catalytic behaviors and the potential to explore new catalytic mechanism[7].

Nevertheless, reducing the size of metal particles to single atom level can result in extremely the high surface free energy[1]. Their high reactivity would lead to serious aggregation and catalyst deactivation in the preparation and catalysis process, which is an enormous challenge in the industrial applications of SACs. Adopting a high-surface-area support material that strongly interacts with the metal atoms could prevent their aggregation, creating finely dispersed stable metal SACs. Till now, in most single atom catalyst systems, the isolated metal atoms are uniformly anchored to supports such as metal surfaces, metal oxides and carbon materials. Recently graphene-based carbon materials have been adopted to disperse nanoparticles or single atoms for novel catalyst[8] owing to their large specific surface area (high catalyst loading), high electrical conductivity (facilitated electron transfer), and potential low manufacturing cost.

Herein, we introduce recent advances in the selection of carbon substrate, preparation methods, and the anchoring mechanism of metal SACs. Based on the understanding of single atom catalytic activity, we discuss the development trend and application prospect of this research field.

2 Selection of substrates

The improvement of catalyst substrate cannot be avoided in designing the catalyst system because the catalytic behavior

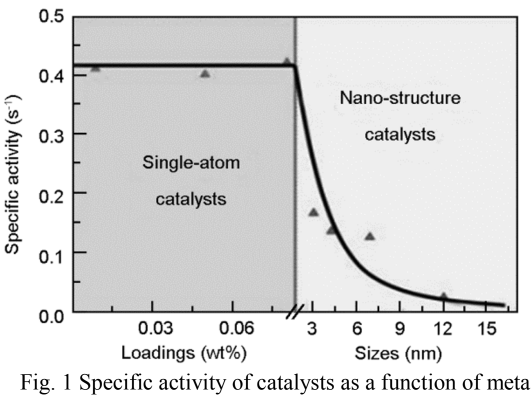

Fig. 1 Specific activity of catalysts as a function of metal loadings and sizes[1].

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of the catalyst can be greatly influenced by the properties of the support material.

The effects of the substrate on catalysis include decorative effect, electronic effect, new alloy phase formation and generation of new interface sites[6]. When SACs are mentioned, their high mobility would result in serious aggregation and coarsening, interfering with the density of active sites and limiting the catalytic durability and efficiency[9, 10]. Accordingly, it is necessary to screen out suitable carriers to anchor metal single atoms to avoid the catalyst deactivation due to agglomeration.

Some metals, like Cu, Au and Pd, have been used as substrates of SACs and exhibit improved catalytic performances[11-15], in which the single atoms interact with the host metal substrate to form monatomic alloys[16]. Various metal oxide, such as iron oxides, hydroxides[17], and oxide of anionic clusters[18], hollandite-type manganese oxide (HMO)[19], aluminum and cluster anions[20], cerium, titanium and zinc oxides, have also been proven to be good substrate candidates for SACs. It is found that surface defects of metal oxide could serve as anchoring sites for metal clusters or even single atoms[21-23]. In addition, molecular sieves[24, 25] have the advantage superior to metal oxides, providing highly homogeneous sites for the attachment of metal active components. Covalent triazine frameworks (CTFs)[26] and CTFs hybridized with carbon nanoparticles[27], silicon oxide[28] and silicate[29] have been used to load SACs. Recently, metal–organic frameworks (MOFs)[30] have also been widely considered as the substrates for SACs, which have great application prospects. However, the above mentioned SAC supports are of disadvantages including low loading density, instability, or poor tolerance, which could be overcome by using carbon materials instead.

Graphene, a unique structure of two-dimensional (2D) carbon sheet with one-atomic layer thick[47], is considered to be the building block of many carbon materials such as carbon nanotubes, carbon nanoonions[48] and nanoporous carbon[49]. It is expected that graphene-based materials with unique electric and microstructural characteristics will offer a new type of carbon-metal nanocomposite for the next generation of catalysts[50-53].

Sun et al. [54] observed the Pt single atoms and sub-nanometer clusters on graphene nanosheet (GNS) by high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) (Fig. 2).

Table 1 Loadings of different metal single atoms on different carriers.

Substrate	Metal	Loading	Reaction
Cu	Pd[31]	1%	Hydrogenation of styrene and acetylene
	Pt[12]	1.4±0.2%	Selective hydrogenation of 1,3-butadiene
Pd	Au[14]	4.2%	Glucose oxidation
	Ru[15]	5.9wt%	Chemoselective hydrogenation of alkene
Au	Pd[13]	0.16wt%	Ullmann reactions of aryl chlorides
FeO_x	Pt	2.5wt%[5]	CO oxidation
		0.08wt%	Hydrogenation of 3-nitrostyrene[32]
			Reduction of triiodide[33]
	Ir	0.22wt%[24] 0.01wt%[34]	CO oxidation
			Water gas shift reaction
	Au[35]	5wt%	CO oxidation
Al_xO_y	Pt[36], Rh[37], Au[38]		CO oxidation
CeO_2	Au[39-41]		CO oxidation
	Au^{3+}[42]	≤0.08%	1,3-dicarbonyls with alcohols
	Pt[43]	1wt%	CO oxidation
Co_3O_4	Rh[44]	0.51wt%	NO reduction
TiO_2	Au[45]		CO oxidation
	Pd[7]	1.50%	Hydrogenation of C=C bonds
ZnO	Rh[46]	0.03%,0.006%	Hydroformylation of olefins