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Deciphering the issue of single-atom catalyst stability

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In the pursuit to synthesize high-loading and effective single-atom catalysts (SACs), the strong likelihood of aggregation due to high surface free energy cannot be ignored. Catalyst stability encompasses several factors, such as resistance to deactivation (e.g. sintering or poisoning) and recyclability. Of particular importance for SACs is the ability to maintain single-atom configuration, either during synthesis or reaction conditions. Evaluating SAC stability is equally as important as catalyst performance but has not received the same level of scrutiny. In this review, we discuss key factors affecting SAC stability, such as reducing environments and high temperatures. We highlight the relationship between environment and aggregation, emphasizing the complexities involving metal, support, and reaction conditions and their influence on catalytic performance.

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Introduction

The advances in nanotechnology made over the past few decades have dramatically improved a variety of catalyst-driven chemical syntheses and reaction processes across scientific disciplines. Significant efforts have been made to enhance the atomic efficiency of the nanocatalysts, as only a fraction of metals on the surface participate in surface catalysis, while the rest are buried within the cluster and remain unused. This inherent design limitation can be of major concern for reactions that require scarce and expensive metals, such as the platinum group metals. The development of single-atom catalysts (SACs), also known as atomically dispersed catalysts or single-site catalysts, aims to alleviate such issues by maximizing atom utilization. By dispersing individual metal atoms anchored to a support material, SACs can achieve 100% atomic efficiency in theory. Additionally, they lack metal–metal bonding that is characteristic of nanoparticles, which enables unique reaction pathways and product selectivity.

As materials are downsized to smaller dimensions, from the bulk to nanoparticles to the theoretical minimum limit of single atoms, the proportion of surface to bulk atoms exponentially increases. Surface atoms are less coordinated than bulk atoms; whereas bulk atoms are fully coordinated and surrounded by other like atoms, as is the case in nanomaterials, surface atoms are unsaturated and contain many dangling bonds. This not only endows SACs with distinctively beneficial catalytic properties, but also makes surface atoms less stable than bulk atoms due to the excess energy of atoms at the surface compared with the bulk (i.e. surface free energy) [1].

The term 'stability' encompasses a variety of concepts that we aim to discuss in this review. From the viewpoint of SACs, stability most often refers to resistance against aggregation (i.e. structural stability). This occurs in two aspects: (1) creating synthesis conditions that do not result in the formation of clusters containing metallic bonding, and (2) preventing aggregation during reactions (i.e. catalyst sintering). More broadly, catalyst stability, which includes structural stability, can be defined by sustained performance over time (e.g. recyclability) and resistance to deactivation/poisoning. For aqueous-phase reactions, minimal metal leaching (i.e. metal dissolution from the support) is another important parameter. In this review, we overview recent literatures studying SAC stability, particularly highlighting single-atom mobility and aggregation through material characterization and offer a perspective on critical factors to consider for comprehensive SAC research.

Single-atom catalyst stability under reaction conditions

Recent literatures that observed SAC instability are summarized in Table 1, where we categorized these reports based on whether stability was studied in an oxidative and/or reductive environment. Although the sample size is too small to draw a generalized conclusion, we found that a larger fraction of studies reporting instability involved reductive conditions rather than oxidative conditions (Figure 1a). It is noteworthy that, of the works that studied SAC stability in both oxidative

Table 1

Literature examples of SAC stability/instability.

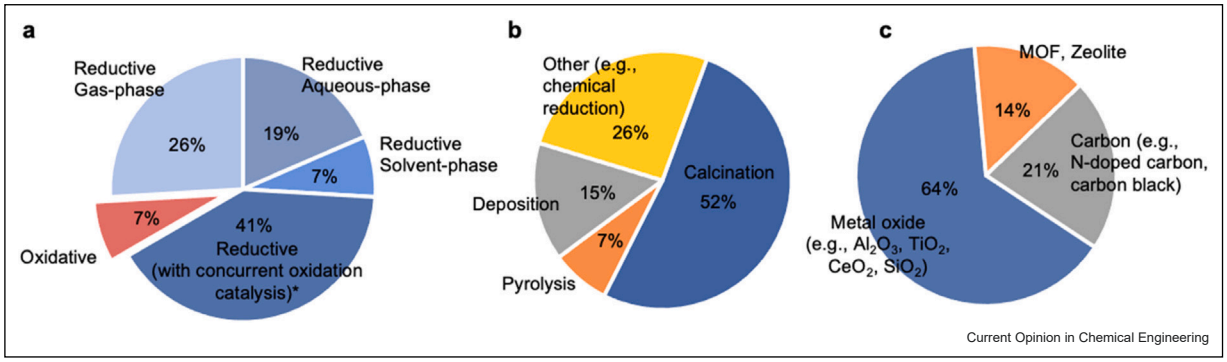
	SAC	Loading (wt%)	Synthesis method	Environment	Temperature (°C)	Stability results	Ref.
Reductive	Pt/CeO_2	0.94	IWI + calcination	Gas phase (CO oxidation: CO/O_2/He)	RT — 500	Pt–O–Ce bonds break to form small Pt clusters for T > 150 °C	[12]
	Ru/Al_2O_3	0.1	IWI + calcination + reduction	Gas phase (CO_2 reduction: CO_2/H_2/He)	350	Formation of Ru clusters promotes CH_4 selectivity	[23]
	Rh/Al_2O_3 Rh/TiO_2	0.05 0.1	SEA + calcination	Gas phase (H_2/He or CO/He)	100–500	Modification of support with MPA reduced the degree of sintering	[22]
	Ir/SiO_2 $Ir/\gamma\text{-}Al_2O_3$ Ir/MgO	1.0	Reaction of Ir precursor and support in n-pentane	Gas phase (H_2)	RT — 120	Degree of aggregation varied by support	[20]
	Rh/TiO_2	0.05	SEA + calcination	Gas phase (H_2/He)	100 or 300	Formation of Rh clusters at 300 °C	[24]
	$Pt/CeO_x/SiO_2$	0.4	SEA + calcination IWI + calcination	Gas phase (H_2/He)	400–600	CeO_x islands on SiO_2 promoted stability over bare CeO_2 and SiO_2 supports	[25••]
	Pt/CeO_2	1.0	IWI + calcination	Gas phase (CO/He)	275	SAC activated by CO to form Pt NP	[26]
	Cu/UiO-66	1.9	Metal ion deposition	Aqueous phase (electrochemical nitrate reduction)	RT	Formed 4 nm nanoclusters	[16]
	Cu/N–C	1.0	IWI + pyrolysis	Aqueous phase (electrochemical nitrate reduction)	RT	Reversible formation of 5 nm NP	[17]
	Cu/N–C	1.4	Ball milling + pyrolysis	Aqueous phase (electrocatalytic CO_2 reduction)	RT	Reversible formation of NP	[27]
	Cu/carbon black	0.4	Amalgamated Cu–Li method	Aqueous phase (electrocatalytic CO_2 reduction)	RT	Reversible formation of clusters	[18]
	Pt/TiO_2	————	Dark deposition/ impregnation	Aqueous phase (photocatalytic H_2 evolution)	RT	Photoinduced aggregation of Pt SA	[28]
	Pt/N–C	0.34 – 1.30	Atomic layer deposition	Liquid phase (para-chloronitrobenzene hydrogenation: H_2)	65		[29•]

Table 1 (*continued*)

	SAC	Loading (wt%)	Synthesis method	Environment	Temperature (°C)	Stability results	Ref.
						Higher CN and less pyridinic N more resistant to aggregation and leaching	
	Ir/zeolite Y	1.0	Reaction of Ir precursor and support in n-pentane	Liquid phase (cyclohexene hydrogenation: H_2)	72	Bimolecular and autocatalytic aggregation of SA	[30]
Oxidative	Au/MWCNT	0.1	Mild chemical reduction	Liquid phase (thiophenol oxidation: O_2)	RT	Aggregation of SA into clusters and then NP	[14]
	Pt/Co_3O_4 Pt/CeO_2 Pt/ZrO_2 Pt/graphene	0.5 1.1 0.2 0.4	Atomic layer deposition	Aqueous phase (dehydrogenation of ammonia borane)	RT	Aggregation of SA on CeO_2, ZrO_2, and graphene, and 30–50% metal leaching	[19]
Reductive and oxidative	$Pt/\gamma\text{-}Al_2O_3$	0.30	IWI + calcination	Gas phase (air or H_2)	RT — 300	Pt valency reduced more in H_2 than air	[2]
	Pt/Fe_2O_3	1.66	IWI + calcination	Gas phase (O_2/He, CO/He, or H_2/He)	250	SAs stable in O_2 and aggregate in CO and H_2	[3]
	Pt/TiO_2	0.025	SEA + calcination	Gas phase (H_2/He or O_2/He or rWGS; H_2/CO_2/He)	400 (H_2) or 250 (O_2 and rWGS)	Pt SA aggregates in H_2 and redisperses in O_2	[7]
	$Pt/\gamma\text{-}Al_2O_3$	0.31 0.96	IWI + calcination	Gas phase (air or H_2 or CO oxidation; CO/O_2/He)	RT — 300	Formation of clusters from SA improves catalytic activity	[4]
	Pd/CeO_2	1.0 5.0	IWI + calcination or FSP	Gas phase (O_2/He and CO oxidation; CO/O_2/He)	50–300	Synthesis method impacted the degree of sintering during CO oxidation	[5•]
	Pd/Al_2O_3 $Pd/La\text{–}Al_2O_3$	0.5	Dry impregnation + calcination	Gas phase (O_2/He or CO oxidation; CO/O_2/He)	700 (O_2) RT — 300 (CO oxidation)	La^{3+} stabilized Pd SA; SA regenerated in O_2	[8]
	Pt/CeO_2	0.05– 1.0	SEA + calcination IWI + calcination	Gas phase (O_2/He or H_2/He)	300 (O_2) or 250–600 (H_2)	Low SA loading more resistant to sintering	[15]
	$Cu/\gamma\text{-}Al_2O_3$	————	IWI + calcination	Gas phase (H_2/Ar or O_2/N_2)	500 (H_2) 300 (O_2)	H_2O promotes redispersion into SA	[9]
	Pt/CHA	0.21	Hydrothermal crystallization	Gas phase (H_2/He or O_2/He)	RT — 400 (H_2) RT — 500 (O_2)	Reversible conversion of SA and NP	[10]
	Pt/MCM-22	0.17	Swelling + calcination	Gas phase (H_2 or O_2 or NO or CO/O_2 or CO/H_2O or CO/NO or H_2/NO)	200–800 (H_2) 500–700 (O_2) RT (NO) RT — 400 (CO/O_2 or CO/H_2O) 200–1200 (CO/NO) RT — 1200 (H_2/NO)	SA aggregates and redisperses in response to gas and temperature	[11]
	Ru/CeO_2 Rh/CeO_2 Pd/CeO_2 Ir/CeO_2 Pt/CeO_2	0.6– 0.9	Precipitation + calcination IWI + calcination	Gas phase (CO/Ar or CO/O_2/Ar or H_2/Ar)	RT — 250	Resistance to aggregation followed Rh > Ru > Ir > Pt > Pd	[6••]

Works are categorized by whether SAC stability was studied under reductive, oxidative, or both conditions. SA: single atom; NP: nanoparticle; SEA: strong electrostatic adsorption; rWGS: reverse water gas shift reaction.

Figure 1



Relative proportions of SAC **(a)** stability condition environment, **(b)** synthesis method, and **(c)** support material of literature listed in Table 1. Total number of papers = 27. *Note that for literature that evaluated both oxidative and reductive conditions, all observed aggregation in reductive environments. In most cases, the applied oxidative conditions stabilized single-atom configuration.

and reductive conditions, most SACs that aggregated under reductive conditions remained stable [2–6••] or redispersed into single atoms from clusters [7–11] under oxidative conditions. Liquid-phase reactions typically involved electrochemical applications operated at negative, reducing potentials or hydrogenation reactions.

Reducing gases such as H_2 and CO have been shown to induce SAC aggregation, particularly at elevated temperatures. For example, gaseous CO induced Pt_1/CeO_2 to change in SAC structure when temperature was raised above 150 °C; the breakage of Pt–O–Ce bonds subsequently led to the formation of small Pt clusters [12]. This was supported by density functional theory (DFT) calculations that demonstrated distortion of Pt_1 out of the fourfold hollow site of CeO_2 due to the chemisorption of CO to Pt_1. The degree of CO-induced distortion was found to depend on metal atom identity and charge transfer to the support [13]. As another example, in an H_2 atmosphere, the oxidation state of Pt_1/γ-Al_2O_3 was found to become progressively reduced as a function of increased temperature, based on X-ray absorption spectroscopy (XAS) and scanning transmission electron microscopy (STEM) analyses [2]. Comparatively, calcination (i.e. heating in air) at the same elevated temperatures resulted in a much lower degree of Pt reduction. DFT calculations supported these observations, revealing sintering to be more thermodynamically favorable under H_2 than air. We also note that several studies reported the aggregation of single atoms during CO oxidation under a CO/O_2/He atmosphere [4,5•,8,11,12]. While this reaction occurs in the presence of both O_2 (oxidizing) and CO (reducing) gases, we here classify CO oxidation as a reducing environment since CO was the main cause of SAC instability. For example, a Pd_1/CeO_2 SAC exposed to O_2 at 300 °C retained single-atom configuration, but when exposed to a 1:1 mixture of CO and O_2, resulted in the formation of Pd aggregates [5•].

In contrast to reducing environments, there were fewer studies reporting SAC aggregation under oxidizing environments. One example involved Au_1 on multiwalled carbon nanotubes (MWCNT) during thiophenol oxidation [14]. This reaction observed an induction period of 6 min before the production of disulfide, which coincided with the aggregation of Au_1 into more active Au clusters. Further overaggregation into nanoparticles then resulted in catalyst deactivation. Some studies investigated both oxidative and reductive conditions to compare how various gases influenced single-atom aggregation behavior. Only a small number of cases found oxidative conditions leading to aggregation [6••,15]; even so, compared with the accompanying reductive condition, oxidative treatment always led to a lower degree of sintering (i.e. smaller and fewer clusters or nanoparticles formed). Furthermore, for several SACs, oxidative treatment following reductive aggregation redispersed the metal atoms into single-atom configuration [7–11]. Dessal et al. experimentally demonstrated the stabilizing and destabilizing effects of O_2 and H_2 atmospheres, respectively, on Pt_1/Al_2O_3 and computationally supported these findings using DFT calculations [2]. Pt_1 under an O_2 environment (in the form of Pt_1O_4) improved sinter resistance due to the O atoms bonding to both Pt_1 and the Al_2O_3 support *via* Al–O bonds. Compared with O atoms, H atoms more weakly interacted with the support and more strongly interacted with Pt. Under an H_2 atmosphere, sintering to form Pt clusters allowed for increased interaction with H atoms and was enthalpically favorable.

Single-atom mobility has also been detected in aqueous-phase reactions, primarily in electrochemical applications. For example, Cu single atoms deposited into a metal–organic framework (MOF) underwent clustering to small, uniform nanoclusters (ca. 4 nm) due to the confinement of the MOF structure during the electrocatalytic reduction of

nitrate to ammonia [16]. In another work for the same application, a Cu SAC on a N-doped carbon support restructured into 5 nm nanoparticles under applied negative potential [17]. Subsequent air exposure redispersed the Cu nanoparticles into the original $Cu–N_4$ single-atom structure by the proposed pathway of (i) oxidation of the Cu nanoparticles by oxygen and/or water in air, (ii) dissolution into $[Cu(OH)_4]^{2-}$, and (iii) entrapment of $[Cu(OH)_4]^{2-}$ by pyridinic nitrogen. Similarly, a Cu SAC for CO_2 reduction under an applied – 0.7 V potential transitioned from Cu single atoms with primarily Cu–O single-atom binding to Cu–Cu binding with 3- or 4- atom Cu clusters [18]. This transformation was also reversible, where once the potential was switched off to – 0.4 V, Cu–O binding returned as the Cu clusters were re-oxidized to single atoms.

The literature suggests that the extent of SAC aggregation can depend on the synthesis method. For example, Pd_1/CeO_2 synthesized by impregnation was more prone to reduction under CO oxidation compared with the same material synthesized by flame spray pyrolysis (FSP) [5•]. The improved stability of FSP Pd_1 was attributed to enhanced electronic metal-support interactions (EMSI) in this catalyst, as Pd was doped into the CeO_2 lattice, modifying the redox properties of this catalyst. The literature also suggests that the identity of metal and support factors heavily into the aggregation propensity. For example, the stability of Pt single atoms during the dehydrogenation of ammonia borane was greatly influenced by the type of support (Co_3O_4, CeO_2, ZrO_2, or graphene) [19]. Pt_1/Co_3O_4, which had the strongest EMSI of the studied SACs, was the only catalyst to retain single-atom configuration. Each of the other catalysts deactivated, either *via* aggregation or leaching. In another work, Ir single atoms on SiO_2, γ-Al_2O_3, and MgO differed in resistance to aggregation under H_2; $Ir_1/\gamma\text{-}Al_2O_3$ formed clusters, Ir_1/SiO_2 formed nanoparticles, and Ir_1/MgO remained single atoms [20]. DFT calculations revealed that the degree of electron-donor character from the support ($MgO > \gamma\text{-}Al_2O_3 > SiO_2$) influenced the bond strength between Ir_1 and the support. Finally, the inclusion of organic ligands can be a determining factor in SAC stability [21]. For example, anchoring methylphosphonic acid (MPA) to Rh_1/Al_2O_3 and Rh_1/TiO_2 SACs mitigated sintering in reductive environments (CO and H_2) [22], due to either MPA weakening the metal–gas interaction or serving as a physical diffusional barrier to single-atom aggregation. Among the studies we examined, calcination was most frequently used as the final synthesis step (i.e. preceded by incipient wetness impregnation (IWI) or electrostatic anchoring) (Figure 1b) and metal oxides were the most commonly utilized substrates (Figure 1c), leaving a large room for further studies employing a wider range of synthesis methods and substrate types.

Characterization tools for stability evaluation

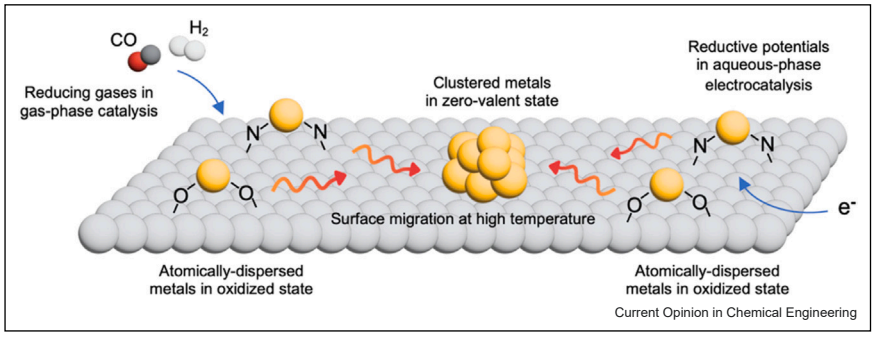
The dynamic nature of SACs exemplifies the importance of proper characterization of metal sites, without which there is the possibility of the misattribution of the true active species. Many studies utilize XAS and high-angle annular dark-field-STEM that provide chemical and visual confirmation, respectively, of single-atom dispersion. The addition of other supplementary techniques such as conventional TEM, X-ray photoelectron spectroscopy, or X-ray diffraction, can be helpful to determine whether large nanoparticles formed (i.e. as a negative control to exclude large nanoparticles), but they cannot be used alone to confirm single-atom state.

More informative than *ex situ* post-reaction characterization, though, is the use of *in situ* or *operando* characterization, which continuously probes the catalyst directly under realistic conditions. In particular, *in situ*/*operando* XAS has enabled such characterization under simulated environments or reaction conditions, especially for gas-phase and electrochemical applications, allowing the monitoring of structural changes as a function of time, temperature, or environment (e.g. atmosphere or applied potential). Only using these techniques could the reversible aggregation [17,18,27] or change in coordination to support be detected. For example, *operando* XAS during the electrochemical oxygen reduction reaction revealed structural changes to a $Cu–N_4$ SAC, as it tracked the evolution of $Cu–N_4$ to $Cu–N_3$ to $Cu–N_2$ [31]. Similar findings have been noted in other works [32–35], as well as corroborated by DFT calculations [36•].

Advancements in microscopy capabilities have improved the ability to visualize single-atom dynamics in real time; specialized environmental S/TEM cells allow for the *in situ* characterization of catalysts under elevated temperature and/or gaseous/liquid environments. For example, *in situ* environmental TEM has displayed aggregation of Ir single atoms into nanoparticles at elevated temperatures [37], as well as the conversion of Pd, Pt, and Au nanoparticles into single atoms [38]. *In situ* STEM has been used to observe the disappearance of Pt nanoparticles as calcination caused their conversion into single atoms [39], as well as the response of Pt_1/TiO_2 [40] and Pt_1/CHA [10] to O_2 and H_2 environments at elevated temperatures.

Loss in coordination to the support could also potentially lead to metal leaching, in which metal atoms detach from the support and dissolve into the solution matrix. The metal ions that leach could function as homogeneous catalytic sites, potentially acting as the catalytic centers of the reaction and consequently leading to the overestimation of SAC catalytic efficiency. The extent of

Figure 2



Illustrative schematic of major mechanisms responsible for SAC instability.

metal leaching is quantified using methods such as inductively coupled plasma-mass spectrometry, which can detect amounts on the order of parts per trillion. Last, recyclability should only be used as a supplementary metric of catalyst stability, not standalone, as it does not provide concrete information about the catalyst structure. Unfortunately, it is too common a practice to equate strong repeat performance to the stability. If performance declines over many cycles, catalyst poisoning could also be a reason for deactivation, in addition to SAC aggregation and leaching [5•,41]. Common catalyst poisons include carbon monoxide, sulfur, and halides, with noble metals being particularly susceptible to poisoning. Even though literature suggests that SACs can be poisoned to a lesser extent than nanoparticles [42–44], the possibility of poisoning should not be discounted.

Concluding remarks and forward perspective

While it is simpler to synthesize SACs with low metal loading as a strategy to retain atomically dispersed single atoms, a challenge (and goal) of many in the SAC field is to synthesize high-loading SACs to maximize the spatial density of single atoms and boost the number of available active sites [45,46]. However, increased metal loading increases the likelihood of the formation of larger metallic clusters; thus, synthetic strategies aimed to mitigate this through improved metal-support interactions have been developed. Common strategies include spatial confinement (e.g. MOFs or zeolites with defined pores), ligand anchoring [21,47,48], nonmetal dopants [49,50], and defect/vacancies [51–53]. Such stabilization is especially important for reactions in which single atoms are the active species; for example, Au_1/C was active for acetylene hydrochlorination, but once aggregation occurred, the catalyst deactivated [54]. Alternatively, if single atoms are not the most active catalyst form, as was the case for Au_1/MWCNT for thiophenol oxidation [14], instability can actually be beneficial. This outlines the interplay between stability and performance, where the line between them is not always clear.

We suggest that studies on SACs should, at the minimum, perform post-reaction characterization to evaluate single-atom stability, even if the study is not focused on stability itself. We further suggest *in situ* or *operando* characterization techniques should be expanded for various catalyst scenarios and widely adopted for SAC studies. Without such careful characterization of SAC alteration during the course of reaction, there is the possibility of mistaking the true active species. Especially in the cases shown to promote single-atom aggregation (depicted in Figure 2), the importance of characterizing the metal species cannot be discounted. Only proper characterization before, during, and after catalysis can reveal which configuration is responsible for catalytic performance. Utilizing a suite of the above-mentioned techniques will yield a comprehensive representation of active site structure and any potential changes. SAC stability can either be a benefit or detriment to catalytic performance, and only materials' characterization can make this determination.

Data Availability

No data were used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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