

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/190041/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Wang, Aiqin, Qiao, Botao, Yang, Xiaofeng, Huang, Yanqiang, Hutchings, Graham J. and Zhang, Tao 2026. Distinguishing single-site from single-atom catalysts. *Nature Reviews Chemistry* 10.1038/s41570-026-00882-z

Publishers page: <https://doi.org/10.1038/s41570-026-00882-z>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



Distinguishing single-site from single-atom catalysts

Aiqin Wang,¹ Botao Qiao,¹ Xiaofeng Yang,¹ Yanqiang Huang,¹ Graham J. Hutchings,^{2*} Tao Zhang^{1,3*}

¹State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China.

²Cardiff Catalysis Institute, Department of Chemistry, School of Physics Chemistry and Environmental Sciences, Cardiff University, Translational Research Hub, Cardiff, UK.

³University of Chinese Academy of Sciences, Beijing, China.

*e-mail: G.H.; hutch@cf.ac.uk, T.Z.; taozhang@dicp.ac.cn

Single-atom catalysis has triggered an enormous research-boom. Nevertheless, inconsistent terminology is widely encountered in the literature, particularly for single-atom versus single-site catalysts. Clarification is thus highly desirable. This Comment returns to their origins, distinguishes their criteria and structural boundaries, before proposing standardized characterization benchmarks and writing norms to unify terminology.

Definition of SAC versus SSC

The concept of active sites was first introduced by Taylor in 1925,¹ and it has remained one of the most fundamental theories in heterogeneous catalysis over the past century. For most supported metal catalysts, however, the structural inhomogeneity in particle size, morphology, and surface microstructure, together with the diverse and dynamic reaction pathways under working conditions, severely hinders the fundamental understanding of surface active sites and catalytic mechanisms. The development of heterogeneous catalysts with well-defined, structurally uniform active sites has become a persistent research goal in the field.

In this context, Thomas et al.² proposed the concept of ‘single-site heterogeneous catalysts (SSHC, hereafter briefed as single-site catalysts, SSC)’ in their landmark review in 2005.² Based on the elaboration therein, they say that the active sites in SSC may consist of one or more atoms, but they are spatially isolated from one another, and there is no spectroscopic or other cross-talk between such sites. Each site has the same energy of interaction between it and a reactant as every other single site, and each such site is structurally well-characterized, just as the single sites in homogeneous molecular catalysts are. This concept is derived from molecular homogeneous catalysts, with an original intention of constructing solid catalysts with structurally uniform, discrete active sites that resemble the well-defined coordination centers

of molecular homogeneous catalysts and enzymes, so as to achieve comparable high chemo-, regio-, and stereoselectivity on heterogeneous counterparts.³

In total contrast, the concept of single-atom catalysts (SACs) is rooted in the evolutionary trajectory of nanocatalysts in an attempt to maximize precious metal atom utilization and understand catalytic chemistry on an atomic scale when the metal entity is ultimately reduced to isolated single atoms; the extreme limit of downsizing nanocatalysts. SAC was first proposed and coined by Zhang et al. in their seminal research work on single-atom catalysis of CO oxidation using Pt_1/FeO_x in which SAC is defined as a catalyst that consists of only isolated single metal atoms anchored to the surface of a support.⁴ SAC is denoted as $\text{M}_1/\text{support}$ and represents a class of supported metal catalysts with isolated single-metal-atom sites. The core metal atoms in the active sites are not connected to each other and lack Metal-Metal bonds; instead, they interact with and are stabilized by the support. The divergent propositions result in the conceptual distinction between SAC and SSC.

Similarities and differences

Based on the above definitions, SAC is fundamentally distinct from SSC. SSC is defined exclusively by full structural and energetic equivalence of all active sites: every catalytic center share identical geometric configuration, electronic distribution and substrate adsorption enthalpy, with no inter-site spectroscopic cross-talk. This definition imposes no restriction on the nuclearity of metal active units; active sites can be isolated metal ions, single atoms, monodisperse metal clusters or ordered intermetallic ensembles bearing fixed Metal-Metal bonds. In sharp contrast, SAC only enforces geometric isolation of individual metal atoms, requiring the complete absence of Metal-Metal bonds, while imposing no mandatory constraint on coordination uniformity of anchoring microenvironments. Disordered oxide and carbon supports inherently generate multiple inequivalent Metal-X (where X refers to N, O, S, and others) coordination moieties, rendering most reported SACs multi-site mixtures that do not conform to the definition of SSCs. Their conceptual intersection corresponds to ideal mononuclear SSCs anchored on defect-free crystalline supports, where every isolated metal atom shares an identical inner and outer coordination shell, satisfying the criteria of both SAC and SSC in these specific circumstances. The relationship between SAC and SSC is schematically illustrated in Fig. 1a.

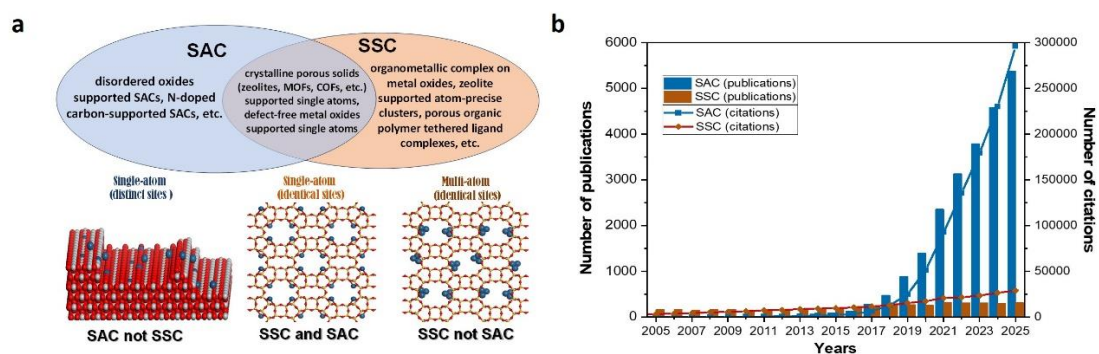


Fig.1 | Comparing Single-Atom Catalysts (SACs) and Single-Site Catalysts (SSCs). (a) Illustration of the relationship between SACs and SSCs, and (b) number of publications and citations of SAC and SSC by topic keywords (single-atom catal* and single-site catal* respectively) in web of science.

Discriminating criteria

The long-standing community confusion mainly arises from the misuse of the concept of SSC, ignoring the clear and rigorous definition of SSC. SSC is a perfect but overly idealized concept, such catalysts are very difficult to obtain and realise in practice and therefore the concept lacks experimental criteria. Here we propose that a set of complementary experimental criteria must be fulfilled to verify whether a catalyst can be termed as an SSC. First, turnover frequency (TOF) should remain constant across a series of catalysts with varying metal loadings. If TOF rises or falls as metal content changes, multiple inequivalent active sites coexist within the material, whereas loading-independent intrinsic activity strongly indicates uniform active centers.⁵ Second, selective poisoning titration with probe molecules serves as another critical test: a perfectly linear correlation between catalytic activity loss and the amount of added poison confirms a single type of active sites.⁶ Third, Fourier-transform infrared (FTIR) spectroscopy (using CO or other probe adsorbates) provides spectroscopic evidence: a narrow full width at half-maximum (FWHM, typically $<10\text{ cm}^{-1}$) of the characteristic adsorption peak signifies homogeneous coordination environments around metal atoms; broad, overlapping peaks correspond to a mixture of distinct single-atom species with various surrounding ligands.⁷ Additional supporting characterizations including operando X-ray absorption spectra and temperature-programmed desorption can further validate site uniformity. Crucially, the mere observation of atomically dispersed metal species via high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is insufficient to claim a single-site nature. Without the above comprehensive experimental evidence, it is inappropriate to label a catalyst as an SSC.

In contrast to SSC whose identification remains elusive and challenging, SAC is far easier to

authenticate. Typically, aberration-corrected scanning transmission electron microscopy (AC-STEM) coupled with X-ray absorption spectroscopy and IR spectroscopy can provide solid evidence to verify whether a catalyst is indeed an SAC. Since each active site in SACs consists of the central metal atom together with surrounding atoms from the support forming an ensemble, the homogeneity of such surrounding microenvironments ultimately determines whether the catalyst belongs to the SSC family.^{8,9} Owing to this feature, SACs have attracted substantially greater research attention than SSCs (Fig. 1b). The carbon-supported gold catalyst used for industrial acetylene hydrochlorination represents a typical and commercially successful SAC.¹⁰ In situ X-ray absorption fine structure (XAFS) and AC-STEM characterizations confirm that Au species are atomically dispersed on carbon without Au-Au bonding, which meets the basic definition of SACs. However, this catalyst cannot be classified as a SSC because the coexistence of Au(I) and Au(III) species during the reaction does not meet the rigorous SSC criterion requiring structurally and electronically uniform active sites.

Outlook

Looking ahead, distinct development trajectories are anticipated for SACs and SSCs. Benefiting from straightforward definition criteria and mature characterization methodologies, SACs will continue to attract extensive research interest from both academia and industry. Future efforts should focus on regulating the local coordination environment of isolated metal atoms, improving metal loading and operational stability, and promoting scalable synthesis towards practical industrial applications.

In contrast, SSCs overlap with aspects of the fundamental research on SACs that demands identical active centers, which represents an ultimate pursuit for catalytic science. Well-defined SSCs serve as ideal platforms to unravel intrinsic catalytic mechanisms of various reactions, bridging homogeneous and heterogeneous catalysis. However, stringent synthetic requirements and formidable characterization barriers remain major bottlenecks. A long-term goal is to transform heterogeneous SACs into genuine SSCs via precise atomic engineering. Beyond the independent advancement of these two categories, the catalysis community should further standardize relevant terminology to eliminate conceptual confusion, avoiding indiscriminate interchange of the two definitions in publications.

References

1. Taylor, H. S. A theory of the catalytic surface. *Proc. R. Soc. Lond. A* **108**, 105–111 (1925).
2. Thomas, J. M., *et al.* Single-site heterogeneous catalysts. *Angew. Chem. Int. Ed.* **44**, 6456–6482 (2005).
3. Copéret, C., *et al.* Homogeneous and heterogeneous catalysis: bridging the gap through surface organometallic chemistry. *Angew. Chem. Int. Ed.* **42**, 156–181(2003).

4. Qiao, B., et al. Single-atom catalysis for CO oxidation using Pt₁/FeO_x. *Nat. Chem.* **3**, 634-641 (2011).
5. Yang, X. F., et al. Single-atom catalysts: a new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **46**, 1740-1748 (2013).
6. Liu, W. et al. Discriminating catalytically active FeN_x species of atomically dispersed Fe-N-C catalyst. *J. Am. Chem. Soc.* **139**, 10790-10798 (2017).
7. DeRita, L. et al. Structural evolution of atomically dispersed Pt catalysts dictates reactivity. *Nat. Mater.* **18**, 746-751 (2019).
8. Zhang, L. et al. On the coordination environment of single-atom catalysts. *Acc. Chem. Res.* **58**, 1878-1892 (2025).
9. Wang, A. et al. Heterogeneous single-atom catalysis. *Nat. Rev. Chem.* **2**, 65-81 (2018).
10. Malta, G., et al. Identification of single-site gold catalysis in acetylene hydrochlorination. *Science* 2017, 355, 1399-1403.

Conflicts of interest

The authors declare they have no conflicts of interest.

Acknowledgements

Funding is acknowledged from by the NSFC Center for Single-Atom Catalysis (Grant No. 22388102), the DICP.CAS-Cardiff Joint Research Units (121421ZYLH20230008), and the NSFC International (Regional) Cooperation and Exchange Program (Grant No. 22690210011). We also that the EPSRC for financial support (Grant No. EP/Z531285/1).