

Advances in heterogeneous single-cluster catalysis

Xinzhe Li^{1,2,6}, Sharon Mitchell^{3,6}, Yiyun Fang², Jun Li^{4,5}✉, Javier Perez-Ramirez³✉ & Jiong Lu²✉

Abstract

Heterogeneous single-cluster catalysts (SCCs) comprising atomically precise and isolated metal clusters stabilized on appropriately chosen supports offer exciting prospects for enabling novel chemical reactions owing to their broad structural diversity with unparalleled opportunities for engineering their properties. Although the pioneering work revealed intriguing performance trends of size-selected metal clusters deposited on supports, synthetic and analytical challenges hindered a thorough understanding of surface chemistry under realistic conditions. This Review underscores the importance of considering the cluster environment in SCCs, encompassing the development of robust metal–support interactions, precise control over the ligand sphere, the influence of reaction media and dynamic behaviour, to uncover new reactivities. Through examples, we illustrate the criticality of tailoring the entire catalytic ensemble in SCCs to achieve stable and selective performance with practically relevant metal coverages. This expansion in application scope transcends from model reactions to complex and technically relevant reactions. Furthermore, we provide a perspective on the opportunities and future directions for SCC design within this rapidly evolving field.

Sections

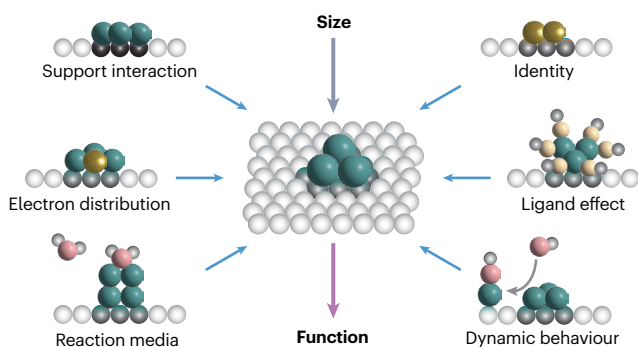
Introduction

SCC synthesis

Structure–property–reactivity relations of SCCs

Reactivity discovery

Opportunities and challenges ahead



A full list of affiliations appears at the end of the paper. ✉e-mail: junli@mail.tsinghua.edu.cn; jpr@chem.ethz.ch; chmluj@nus.edu.sg

Introduction

Heterogeneous catalysis often relies on metal-containing catalytic active centres to facilitate chemical reactions. Over the years, researchers have developed various strategies to understand the factors influencing catalytic performance in different chemical reactions^{1–5}. Efficient catalysts require optimized geometric and electronic structures of the active sites that enable easy adsorption or dissociation of reactants, optimized binding of intermediates and fast desorption of desired products^{6–9}. To engineer these properties, one key strategy is to design nanostructured materials containing active ensembles with well-defined atomic architectures and customized properties by controlling the composition and arrangement of metal atoms and the interaction with the support and other ligands or promoters^{10–12}.

The concept of catalysis with precise numbers of atoms emerged in the 1990s – driven by the desire to explore the unique properties and reactivity of metal clusters at the nanoscale^{13–20}. Early studies used mass selection techniques to precisely control cluster sizes in the gas phase. Soft landing approaches were subsequently used to deposit the gaseous ions onto surfaces with controlled kinetic energy in an effort to preserve their structures¹³. These studies, which have been comprehensively reviewed^{13,15,20}, had a crucial role in laying the foundation for scientific developments and advancing the field. However, despite considerable progress, limitations in both synthesis and analysis posed challenges to fully understanding these systems. Synthetically, the production of clusters was constrained to small quantities, and their poor stability on supports posed challenges for establishing their surface chemistry. Analytically, insufficient resolution and detection limits hindered the verification of cluster size, atomic geometries and uniformity on supports.

As the field has advanced, emerging strategies have brought fresh perspectives to the design of supported cluster catalysts, offering exciting opportunities for applications in sustainable chemistry. These materials, coined as single-cluster catalysts (SCCs)^{21,22}, consist of atomically precise and isolated metal clusters – typically ranging from 2 to 20 atoms in size (less than 1 nm in diameter) – supported on suitable matrices^{21–39} (Fig. 1). SCCs occupy a middle ground between heterogeneous single-atom catalysts (SACs) and traditional metal nanoparticle catalysts (MNCs) that often have a size range but without a precise number of atoms^{40–50}. At least, three subcategories of SCCs exist depending on the composition of their catalytic ensembles: homoatomic metal clusters containing a single type of metal and support; heteroatomic metal clusters with multiple metal types; and metal complex-like clusters with non-metal atoms as linkers or ligands (Fig. 1b). A key development in SCC design is the shift in focus from solely considering the size and composition of metal clusters to a more holistic embracement of their local environments. This encompasses the entire ensemble of the cluster, support, potential ligands and the reactive medium, which is recognized as key for unlocking novel reactivity pathways^{51–59}. Although earlier studies recognized the influence of support interactions on cluster properties and reactivity, the nature of the chemical interactions remained elusive. Consequently, there has been a growing emphasis on establishing strong bonds between the metal clusters and support materials, such as heteroatom-doped carbons, defective metal oxides and other metals (analogous to single-atom alloys, also named single-cluster alloys). Similarly, the impact of ligands on cluster catalysis – previously more or less overlooked – has gained recognition.

Advances in synthetic approaches and a heightened emphasis on carrier engineering have facilitated the preparation of stable SCCs with high coverages through practical methods such as wet chemical routes

and pyrolysis²⁵. In this context, dual-atom catalysts – an extension of SACs, in which two adjacent metal atoms in sub-nanometre proximity cooperate – have emerged as a subject of intensive study and can be considered as the simplest form of SCCs^{31–34}. The improved stability and higher metal contents of SCCs have broadened their scope of applications beyond simple model reactions (such as CO oxidation, water–gas shift, CH₄ oxidation and propylene epoxidation) to tackle more complex chemistries, demonstrating promising performance in thermochemical^{60–67} and electrochemical reactions^{68–75}. The utilization of advanced analytical tools has had a crucial role in deepening our understanding of SCCs, particularly in terms of their structures and dynamic behaviour. Furthermore, rapid advances in the field of SACs have changed the focus in SCC design towards bridging the gap between SACs and MNCs.

With the aim of driving further advances in SCC design, this Review examines the current understanding of their structures and reactivity patterns. It delves into strategies for manipulating the geometry and electronic properties of active ensembles, including aspects such as adsorption site arrangement and accessibility, frontier orbital energy levels, spin states, ligand field splitting and electrochemical properties. This Review illustrates the promising reactivity of SCCs in thermocatalytic, electrocatalytic and photocatalytic applications highlighting the relationship between cluster environments and their performance. Additionally, we explore innovative approaches such as bio-inspired design, artificial intelligence techniques and structural dynamics to uncover new reactivity in SCCs and propel the development of advanced catalytic technologies. The future prospects of SCCs are discussed, including opportunities and challenges in the synthesis, characterization and applications.

SCC synthesis

In the sub-nanometre regime, in which metal clusters typically consist of less than 20 atoms, the chemical identity and position of each atom can substantially impact the electronic and catalytic properties^{2,65,76}. The pronounced influence of surface effects, coupled with the confinement of electrons into discrete energy levels with varying band-gaps, amplifies their sensitivity. Precise atomic control over the size, arrangement and composition of sub-nanometre clusters is therefore crucial for tuning the activity, selectivity and stability of the clusters in different catalytic applications. Although considerable efforts have been devoted to developing strategies for synthesizing SCCs with well-defined atomic composition and structures^{77–81}, achieving such control has proven challenging, particularly with physical methods, such as gas-phase condensation or vapour deposition, ion implantation or laser ablation used in early works^{15,82–84}. These techniques faced limitations in controlling the size and shape distribution of the supported clusters, as well as restrictions in obtaining high coverages, and scalability. There has been an increasing recognition regarding the importance of engineering robust interactions among metal precursors, clusters and support materials. This newfound understanding has enabled the development of more stable SCCs with higher metal cluster coverages through practical routes, for example, via wet chemical syntheses or pyrolysis. The improved stability and higher metal contents coupled with advances in analytical approaches have facilitated direct confirmation of the resulting metal speciation.

A commonly used strategy for the synthesis of SCCs involves the wet deposition of pre-synthesized multinuclear metal precursors in a two-step procedure^{45–48} (Fig. 2a). In the first step, precursor molecules adsorb onto the coordination sites of the support material.

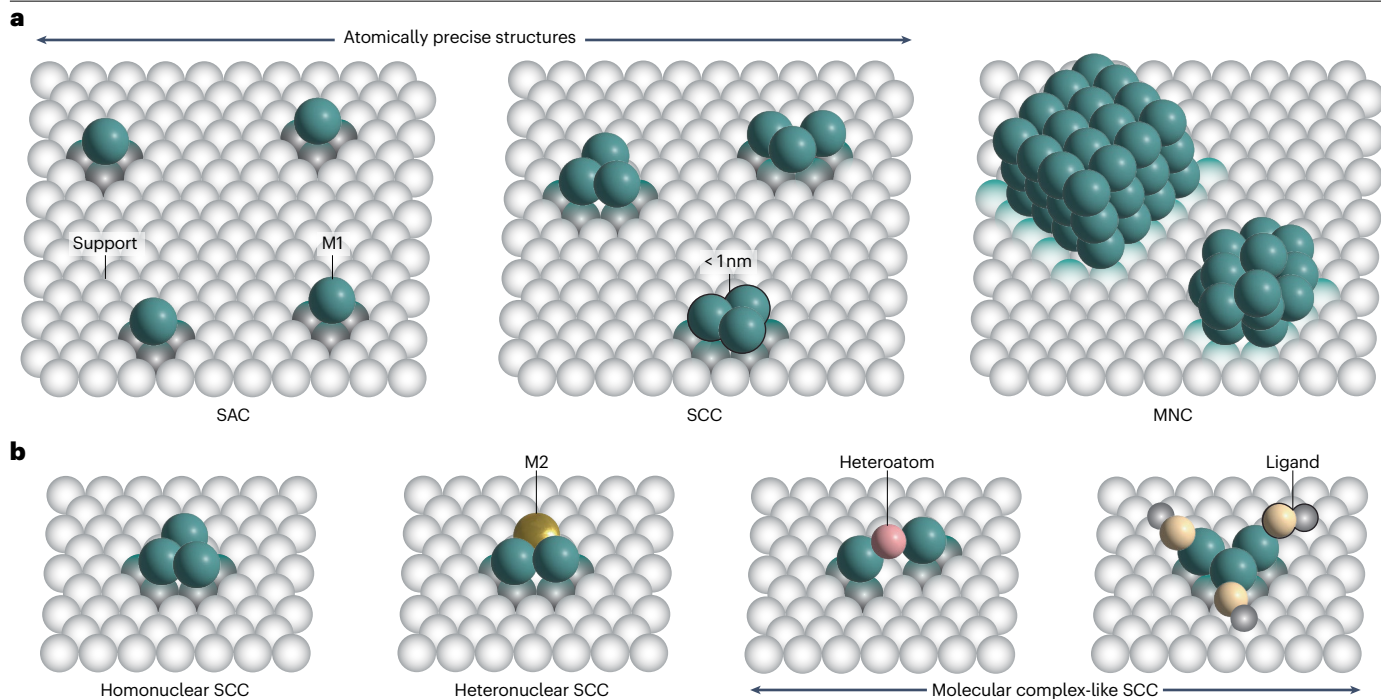


Fig. 1 | Defining features of single-cluster catalysts. **a**, Single-cluster catalysts (SCCs) bridge the gap between single-atom catalysts (SACs), consisting of isolated single-metal atoms stabilized by a support or alloyed with another metal, and metal nanoparticle catalysts (MNCs), composed of metal nanoparticles (diameters ranging from 1 nm to 100 nm). They are characterized by atomically precise metal nanoclusters anchored on suitable supports through

specifically tailored interactions, with sizes typically in the sub-nanometre regime (<20 atoms). **b**, The catalytic centres of SCCs can be divided into three distinct subcategories: homoatomic metal clusters, heteroatomic metal clusters (in which M1 and M2 represent chemically distinct metals) and metal complex-like clusters with non-metal atoms as linkers or ligands.

Subsequently, the ligands of the metal precursors are removed by calcination or photolysis. These methods rely on kinetic or thermodynamic trapping of metal clusters of a desired size, composition and shape, which can be directed by tailoring the ligand structure of the metal-containing precursor, establishing specific cluster–support interactions and optimizing the synthesis conditions. An early example of this approach involved the fabrication of atomically dispersed Fe₂ dimers supported on a mesoporous form of graphitic carbon nitride using a specific precursor, bis(dicarbonylcyclopentadienyliron), the structures of which were supported by extended X-ray absorption fine structure fitting and theoretical predictions⁴⁶. Similar approaches have also been extended to other metals, such as Pd₂ and Ir₂ dimers⁴⁶, Fe₃ trimer³³ and Ru₃ trimers^{45,48}, highlighting the general applicability of this method in synthesizing multiatomic clusters. Graphitic carbon nitride has been extensively studied as a support material for SCCs as it provides abundant coordination sites decorated with nitrogen atoms, which can coordinate metal clusters of varying sizes⁸⁵. Successful preparation of SCCs using molecular precursor-based approaches requires the availability of appropriate precursors with well-defined metal:ligand ratios and suitable ligands to prevent metal aggregation or dissociation during synthesis, while maintaining atomic precision in the final clusters. The choice of support material and its surface properties are also crucial, as it affects the adsorption and dispersion of precursor molecules and the stability of the resulting clusters. Moreover, synthesis conditions such as reaction temperature, duration and post-treatment procedures markedly impact the stabilization of

the desired cluster size and shape. Similar to this two-step wet deposition procedure, the synthesis of SCCs through thermal treatment of a mixture containing single-metal atom precursors adsorbed onto support material or support precursors has been reported to produce several SCCs with excellent electrocatalytic performance (Fig. 2b), such as f-FeCoNC900 (ref. 86), CoNi-SAs/NC (ref. 87), Fe-NiNC-50 (ref. 88) and Zn/CoN-C (ref. 52).

In general, challenges still exist in achieving complete control over the synthesis of SCCs, particularly in terms of obtaining a uniform distribution of SCCs and preventing the formation of larger nanoparticles during hydrothermal and high-temperature treatments. A widely used method for SCC synthesis is atomic layer deposition (ALD)^{32,44}. The ALD process involves the chemical deposition of metal-containing precursors on the support through sublimation, followed by a second thermal oxidation step for ligand removal^{44,89}. Precise control over the adsorption site of metal precursors through chemically specific interactions with the support or predeposited metal species enables the stepwise atom-by-atom fabrication of SCCs (Fig. 2c). For example, heteronuclear Pt-Ru dimer structures on nitrogen-doped carbon nanotubes and Pt-O₂-Pt dimers on graphene have been prepared using ALD^{32,44}. The knowledge obtained from the optimization of ALD approaches also has inspired chemists to fabricate SCCs via traditional chemical methods such as impregnation and pyrolysis methods. For example, a ‘single-atom to single-atom’ modulation strategy was reported to graft Pt atoms onto Fe-N₄ structures through a bridging oxygen molecule, generating Pt₁-O₂-Fe₁-N₄-C structures⁷⁵. Similarly, the

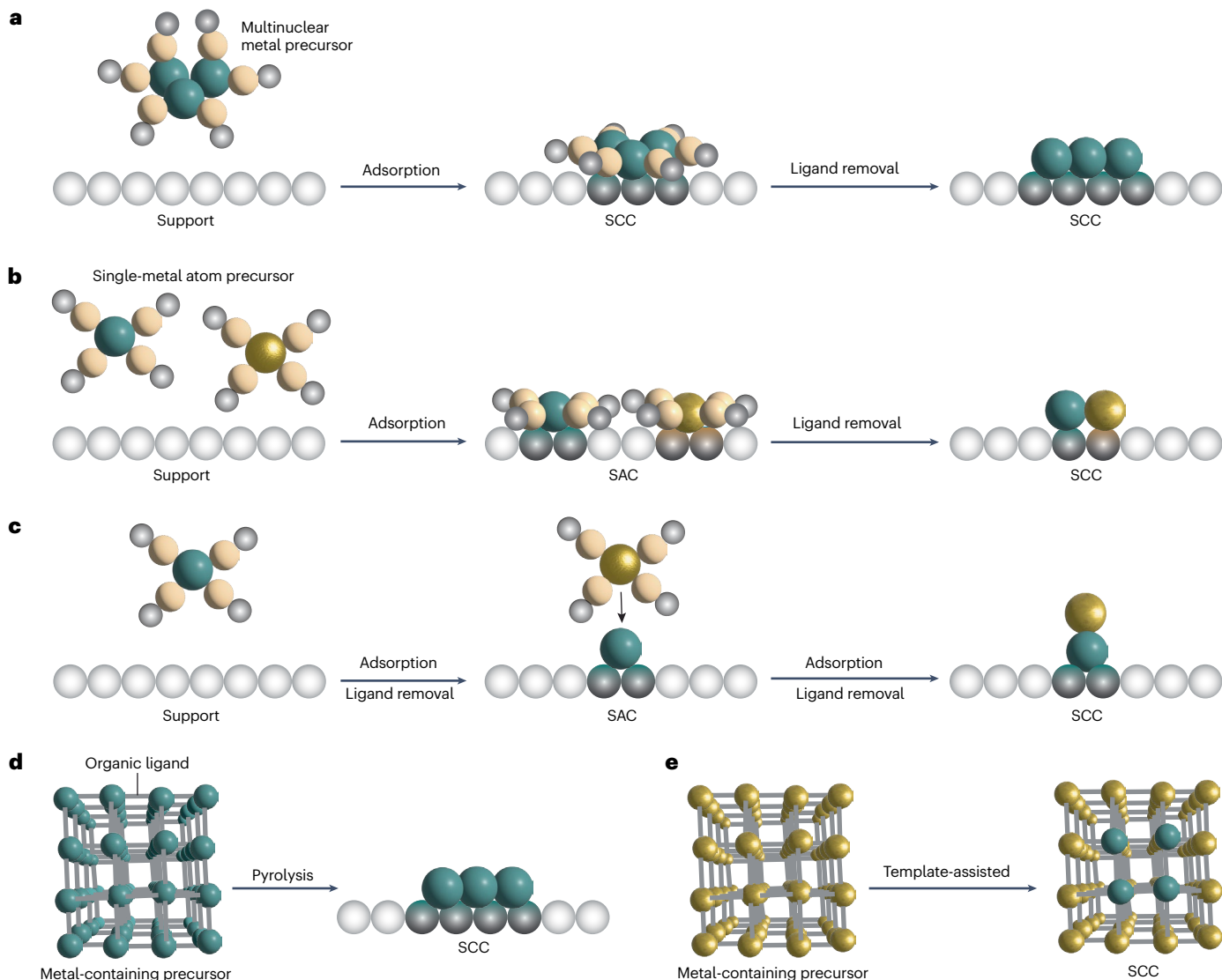


Fig. 2 | Synthetic strategies for producing single-cluster catalysts.

a, Deposition of a pre-synthesized metal cluster complex onto a support, followed by partial or complete removal of the ligands to expose the active site. **b**, Co-adsorption and ligand removal process using suitable metal precursors. The adsorption and ligand removal steps in parts **a** and **b** can be photochemically or electrochemically driven. **c**, Atomic layer deposition method, in which a single-metal atom site formed in a single-atom catalyst (SAC) serves as a new

adsorption site for the deposition of a second atom of the same or a different metal to form a single-cluster catalyst (SCC). Ligand removal processes in part **c** follow the principles described for parts **a** and **b**. **d**, Metal-organic frameworks (MOFs) can be used to fabricate SCCs, by incorporating multinuclear metal complexes into the channels of porous MOFs followed by pyrolysis. **e**, MOFs and other open framework materials can also serve as templates to fabricate clusters, for example, through ion exchange.

possibility of coupling cobalt atoms dispersed on nitrogen-doped carbon (Co-N-C) with iron species by electrochemical activation was also demonstrated, leading to the formation of a Co-Fe diatomic catalyst (Co-Fe-N-C)³⁶.

In addition to the aforementioned methods, several other approaches (including template-assisted synthesis, ion-exchange and electrochemical reduction) have been explored to fabricate SCCs^{51,55}. Aside from this, porous materials with molecular-scale cages can be used to confine precursors and prevent metal atom agglomeration after removing the organic ligands¹¹. Specifically, metal-organic frameworks (MOFs) show promise in the direct fabrication of SCCs (Fig. 2d)

and can also serve as templates for SCC synthesis⁵¹ (Fig. 2e). Each of these approaches has unique advantages and limitations, but they all offer valuable tools for synthesizing new SACs and SCCs.

Although much progress has been achieved in SCC synthesis, many challenges remain to control the number and arrangement of atoms in metal clusters upon stabilization on support materials, especially with high metal content. Currently, the number of demonstrated SCC systems remains relatively small, with most systems limited to two to three metal centres in size, such as two-atom and three-atom SCCs. Expanding the chemical space of SCCs and exploring larger cluster sizes are important areas for future research. Preventing the aggregation of

metal atoms into nanoparticles after the removal of organic ligands and during catalytic reactions remains a key challenge in SCC synthesis. Agglomeration can occur owing to the high mobility of metal atoms, leading to a loss of site uniformity. Designing support materials that enable highly stable and selective interactions with metal species is another critical aspect in preventing agglomeration. The choice of support material and its surface properties have a crucial role in adsorbing and dispersing precursor molecules, as well as stabilizing the resulting clusters. Furthermore, there is still a need to develop efficient methods to provide detailed information about the arrangement, coordination and electronic structure of metal atoms in SCCs that will enable the next level of precision in their design.

Structure–property–reactivity relations of SCCs

Sub-nanometre metal clusters exhibit unique physical and chemical properties owing to quantum size effects, electronic confinement effects and their orbital hybridization of clustered atoms^{90–92}. Conceptually, atomically precise metal clusters have discrete molecular-orbital-like energy levels that can be modified in various different ways between the continuous band structures of metal particles and the discrete atomic orbitals determined by specific interactions with the support materials in SACs, resulting in highly tailorable properties such as energy positions, and electron affinities^{2,66,93}. The properties of SCCs, such as the electronic structure, morphology and active site density, are known to be influenced by various factors such as the type of metal and support, the specific metal–support interaction and the presence

of ligands (Fig. 3a). However, gaining insights into the structure–performance relationship of SCCs remains very challenging owing to the vast number of possible architectures and the complexity of assessing their properties⁹⁴ (Fig. 3b,c). Because of the difficulty in experimentally controlling the synthesis and discriminating between the structures of SCCs, theoretical modelling and computational simulations often have a central role in understanding the structure–property–performance relations. Here, we highlight some of the promising features that have been identified for SCCs related to enhancing their activity, selectivity and stability in different applications.

Activity and selectivity

The strength of interactions between catalytically active sites and reactive intermediates is crucial in determining their performance, as described by the Sabatier principle^{95–101}; catalysts that interact too weakly cannot bind reactant molecules, whereas those that interact too strongly cannot desorb products from their surface. For SACs, SCCs and MNCs, the adsorption strength and geometry of reactive intermediates can influence both catalytic activity and selectivity (Fig. 4a). In some cases, the adsorption strength of reactants over SACs and MNCs can be too weak or too strong. For instance, the interaction between O₂ and Fe nanoparticles is too strong to participate actively in the epoxidation reaction of aerobic *trans*-stilbene, whereas the interaction between iron porphyrin and O₂ on Fe single atoms is too weak to trigger the catalytic reaction⁴⁶. However, Fe dimers on carbon nitride exhibited high conversion and stereo-selectivity (91% and 93%, respectively)

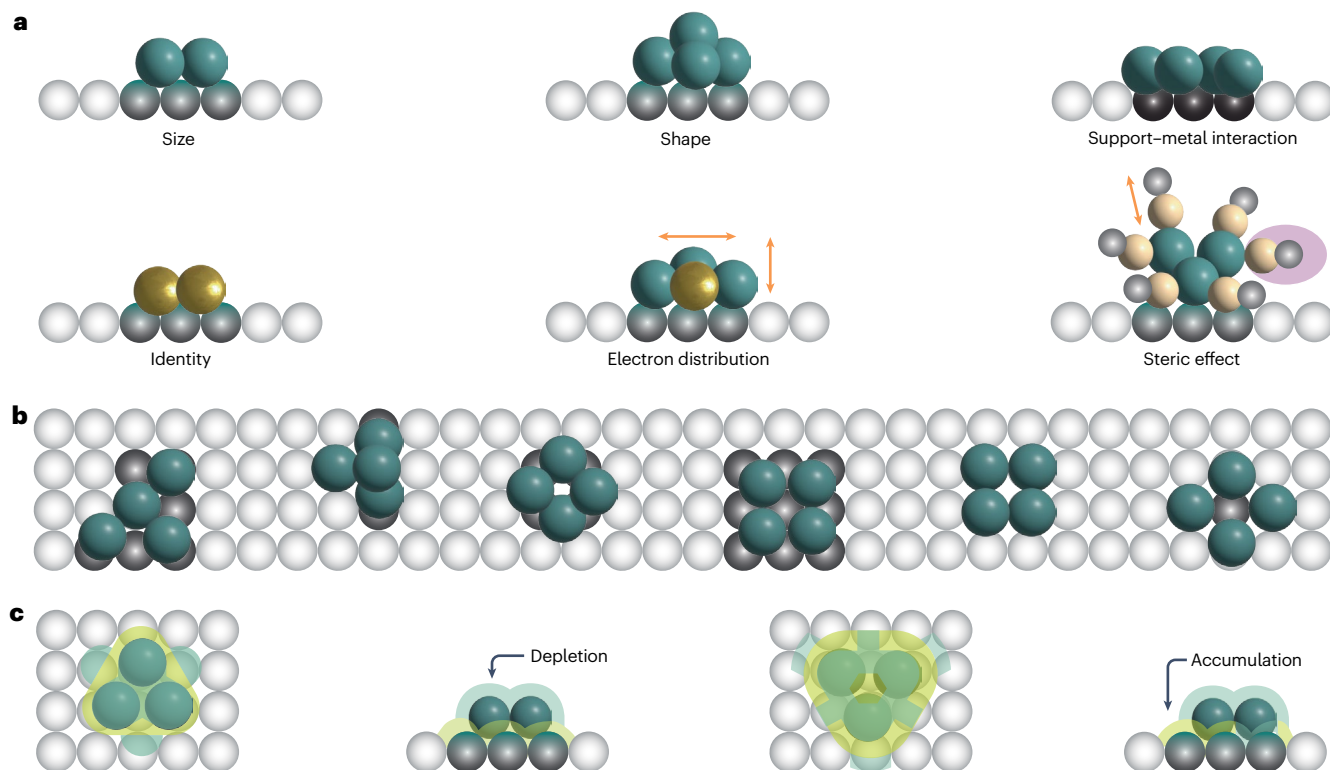


Fig. 3 | Properties of single-cluster catalysts. **a**, Factors influencing the geometric and electronic properties of single-cluster catalysts include size, shape, metal identity, presence of heteroatoms or ligands, metal–support interaction and electronic and steric effects. **b**, Distinct possible configurations of metal tetramer clusters on a cubic surface of a transition metal carbide

support. **c**, Charge density difference plots of Co and Pt trimers stabilized on the hexagonal surface of molybdenum carbide illustrate the potential variation in electronic properties as a function of cluster composition. The ability to tune these properties is key to achieving the desired activity and selectivity in single-cluster catalysts.

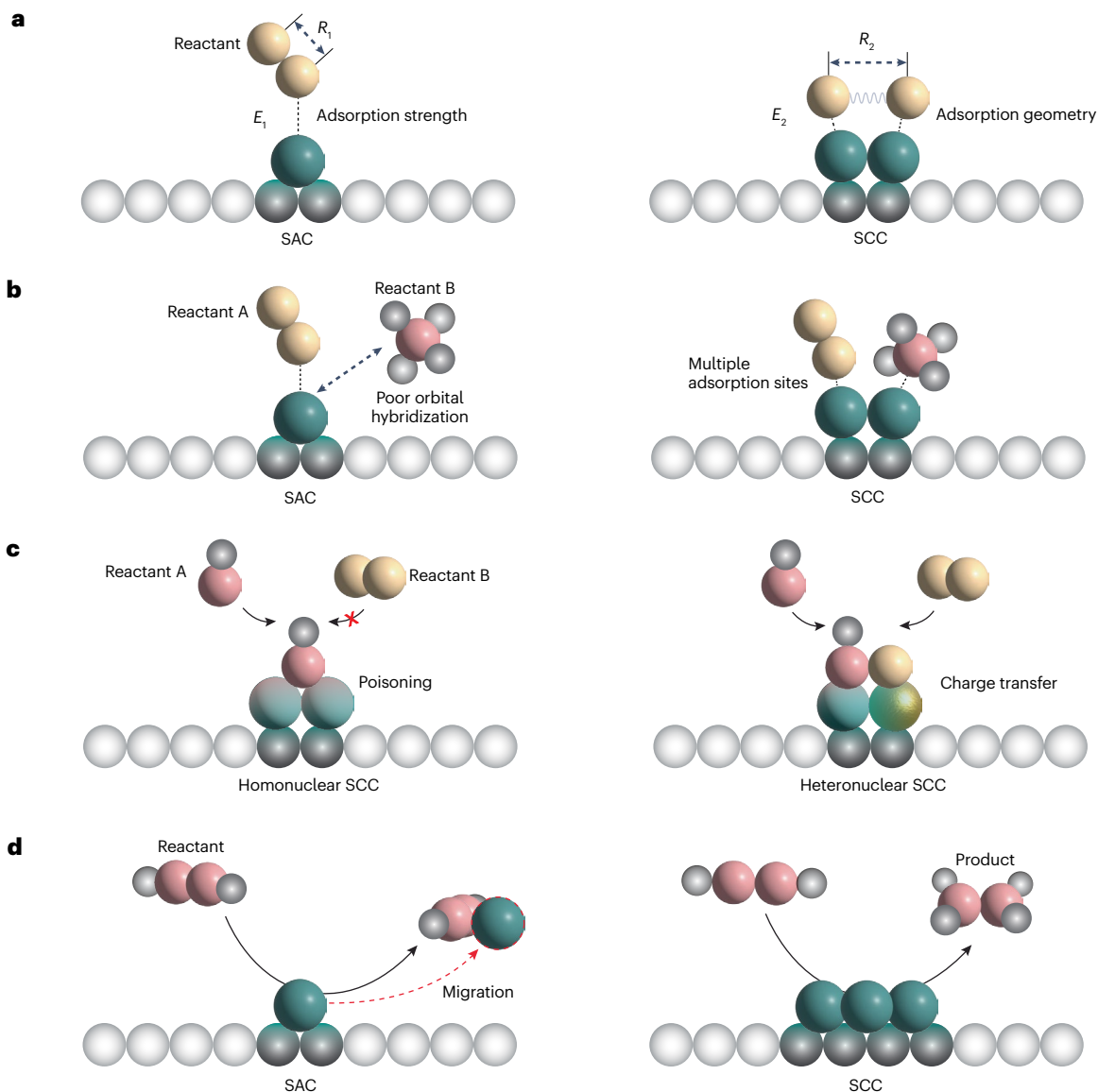


Fig. 4 | Enhancing reactivity of single-cluster catalysts. **a**, Single-atom catalysts (SACs) and single-cluster catalysts (SCCs) can interact differently with reactive intermediates influencing the adsorption strength and configuration. **b**, The multiple adsorption sites and tailored electronic structure of SCCs permit a broader variety of more demanding reaction paths compared with SACs. **c**, The incorporation of heteroatoms in SCCs can provide adsorption sites with varied

properties, improving the catalytic efficiency in reactions requiring activation of different reactive intermediates. **d**, SCCs may exhibit enhanced stability compared with SACs owing to differences in the metal–support interaction, electronic confinement, ensemble dynamics and associated coordination of reactive intermediates.

of *trans*-stilbene oxide production, which was linked to the possibility of adsorbing a singly bonded oxygen atom on the active site, that favours the formation of active oxygen species. An increase in the number of metal atoms in SCCs results in different spatial arrangements of metal atoms in the cluster, providing opportunities for tuning the adsorption geometry of reactive intermediates. For example, Ru₃ on carbon–nitrogen species exhibits superior performance for the oxidation of 2-aminobenzyl alcohol into 2-aminobenzaldehyde, with 100% conversion and selectivity, and unprecedented turnover frequency⁴⁵ (Fig. 5a). Density functional theory (DFT) calculations indicated that

the specific adsorption energy between one Ru atom in the cluster and both the -NH₂ and -OH groups in 2-aminobenzyl alcohol facilitates the oxidation of the -OH group. By contrast, the interaction between Ru nanoparticles and 2-aminobenzyl alcohol is too strong, blocking the active site on the surface for the subsequent reaction steps. Comparatively, a more favourable adsorption of the amino group on single Ru atoms results in poor activity⁴⁵.

SACs display exceptional activity and selectivity in various catalytic processes. However, their ability to accelerate reactions involving multiple reactant molecules and intermediates as well as multistep

redox processes is limited owing to the geometric constraints of isolated metal centres^{60,67}. SCCs with tailored electronic structures and multiple adsorption sites offer improved potential for catalysing complex reactions compared with SACs (Fig. 4b). For example, the direct conversion of methane to methanol by Pd-based SACs remains challenging owing to the weak interaction between Pd single atoms and CH₄, evidenced by the absence of hybridization between Pd 4d^{z²} orbitals and C 2p_z orbitals of CH₄ at the Fermi level⁶⁰. However, unlike Pd SACs, Pd dimers can provide multiple adsorption sites for the simultaneous activation of CH₄ and O₂. Similarly, a stable Cu₁⁰-Cu₁^{x+} atom-pair structure yielded a Faradaic efficiency greater than 92% for CO in the electrocatalytic reduction of CO₂, owing to the specific structure of the active site³⁵. The precise synthesis of Ru-based nanoclusters on reduced graphene oxide via an interface confinement strategy also led to enhanced activity compared with Ru or RuO₂ nanoparticles and homogeneous Ru catalysts for the oxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline and other complex oxidative reactions involving three reactants⁶² (Fig. 5b). Each metal centre of the SCC could be specifically linked to the elementary steps contributing to the overall transformation, akin to the advantages of dual-atom alloy

catalysts consisting of well-defined dual-atom sites embedded in the surface layer of a metal host^{102,103}.

The incorporation of heteroatoms in SCCs introduces adsorption sites with varied properties, providing a valuable strategy to tune reactivity patterns. Heteroatom dopants can donate or withdraw electrons to or from metal clusters to regulate their electronic properties^{104–106}. A large variety of heteronuclear SCCs consisting of different metal atoms have been synthesized for electrocatalytic applications, including hydrogen evolution reaction, oxygen evolution reaction, oxygen reduction reaction, CO₂ reduction reaction and N₂ reduction reaction. Several studies have demonstrated possible synergies between heteroatom-paired metal centres linked to the electronic structure^{88,104–113} (Figs. 4c and 5c). The catalytic performance of nanoclusters can be modulated by controlling ligand spheres and spin states as evidenced by the alkynyl-protected Au₃₈ for the semi-hydrogenation of alkynes and [4Fe–3S] clusters with a low-spin electronic configuration owing to the planar geometry and short Fe–S bonds, respectively^{114,115}.

The size-dependent electronic properties of SCCs can effectively trigger a noticeable change in the oxidation state of metal atoms.

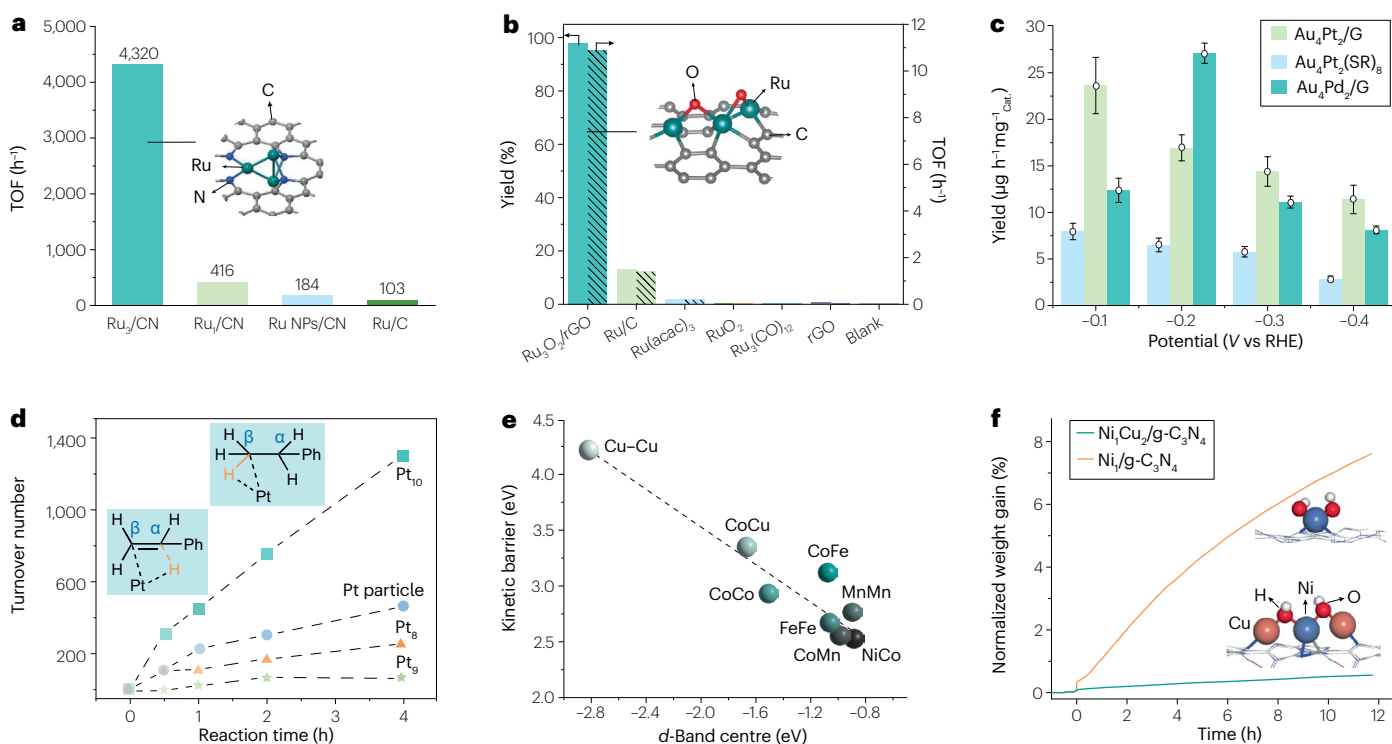


Fig. 5 | Reported property–performance relationships on single-cluster catalysts. **a**, Turnover frequencies (TOFs) of Ru catalysts of different nuclearities supported on nitrogen-doped carbon (CN) or activated carbon (C) in the oxidation of 2-aminobenzyl alcohol to 2-aminobenzaldehyde. The higher TOF of Ru₃ catalyst on CN (inset) was linked to the optimized geometry of 2-aminobenzyl alcohol on the cluster compared with the other catalysts. **b**, Yield and TOF comparison of Ru₃O₂ supported on reduced graphene oxides (rGOs, inset) and reference catalysts for the direct oxidative coupling of alcohols. **c**, Electrochemical N₂ reduction yield using Au₄Pt₂(SR)₈ (SR represents an organic ligand), Au₄Pt₂ on graphene (G) and Au₄Pd₂ on graphene catalysts, illustrating the effect of distinct heteroatoms. **d**, Turnover numbers of styrene conversion by Pt₈, Pt₉, Pt₁₀ and Pt nanoparticles (NPs) on carbon. The Pt₁₀ catalyst lowered

the reaction barrier of the α-insertion owing to rigid pyramidal structure and electron-rich property (insets). **e**, Linear correlation between the d-band centre and kinetic energy barrier reveals that metal identities influence the electronic properties of single-cluster catalysts. **f**, Thermal measurements of coke deposition on Ni₁Cu₂ and Ni₁ on graphitic carbon nitride (g-C₃N₄) catalysts (insets). The enhanced coke tolerance of Ni₁Cu₂ clusters was linked to a spatial confinement effect. Part **a** adapted with permission of ref. 45, ACS. Part **b** adapted with permission of ref. 62, Wiley. Part **c** adapted with permission of ref. 24 under a Creative Commons licence CC BY 4.0. Part **d** adapted with permission of ref. 37 under a Creative Commons licence CC BY 4.0. Part **e** adapted with permission of ref. 122 under a Creative Commons licence CC BY 4.0. Part **f** adapted with permission of ref. 30, Springer Nature Ltd.

Therefore, regulating the number of atoms in a cluster can greatly impact the electronic and catalytic properties of the metal atoms. For example, a comparison of Pd₁, Pd₂ and Pd₃ species supported on exfoliated carbon nitride (ECN) revealed that the degree of oxidation decreased with increasing Pd nuclearity, as evidenced by the increasing ratio of Pd²⁺:Pd⁴⁺ species identified by X-ray photoelectron spectroscopy. Compared with Pd₁/ECN and Pd₂/ECN, the presence of a bridge site in Pd₃/ECN favoured the adsorption of alkynes, greatly enhancing the activity for their semi-hydrogenation⁸⁵. It has been observed that as the number of metal atoms in a nanocluster increases – and depending on the strength of interaction with the support material – the geometry of the metal nanocluster can change from 2D to 3D^{116–118}. Such a transformation will alter the coordination number and electronic structure of supported metal clusters as well as their interaction with reactant molecules. For example, atomically dispersed zero-valent Pt_{*n*} (*n* = 5–12) nanoclusters were utilized for the hydrogenation of styrene³⁷ (Fig. 5d). Interestingly, Pt₁₀ nanocluster exhibited a remarkable catalytic performance compared with the other clusters. DFT calculations revealed that Pt₁₀ exhibited a much lower activation barrier for the rate-determining step, α-insertion, compared with Pt₈ or Pt₉ nanoclusters. This distinct catalytic activity can be attributed to the geometric coordination effect as Pt₈ and Pt₉ favour quasi-2D structures, whereas Pt₁₀ prefers a rigid pyramidal structure. As a result, electron-rich Pt atoms at the vertices of the pyramidal Pt₁₀ can effectively activate the C=C bond in styrene.

The catalytic performance of SCCs is greatly influenced by the characteristics of the metal species, as it may introduce new atomic orbitals with varying orbital hybridization^{119–122}. The electronic properties of various bimetallic dimers anchored on N-doped carbon have been investigated, revealing that a considerable charge is located between the metal atoms and coordinating N atoms¹²². Among all the bimetallic dimers, NiCo-N₆C exhibits the lowest transition state energy barrier and highest rate for H₂O dissociation. Investigating the relationship between the 3*d* band centre of SCCs and the kinetic barrier of H₂O dissociation uncovered a linear correlation. The calculated *d*-band centres of Co and Ni atoms in NiCo-N₆C (–0.87 eV) are closer to the Fermi level than other SCCs, which facilitate H₂O dissociation and enhance proton adsorption for boosting hydrogen evolution reaction (Fig. 5e).

Metal clusters are typically anchored on supports through covalent bonding and electrostatic interactions⁶⁶. Engineering supports with desired properties can modulate the geometric, electronic and catalytic properties of nanoclusters. Gaining atomic insights into chemical bonding configurations between metal clusters and their supports, particularly during reactions, is a prerequisite for establishing structure–performance relationships of SCCs. However, obtaining detailed insights into the catalytic role of the underlying supports in different systems remains a considerable challenge. Therefore, investigating the metal cluster–support interactions and resulting catalytic performance is of paramount importance. Single-metal clusters on different supports may exhibit different adsorption geometries with varying catalytic behaviours⁶⁶. For example, gas-phase Pt₃ with a trigonal bipyramid geometry adopts a planar configuration upon deposition on MgO, mainly owing to electron transfer from the support¹²³. In contrast, gas-phase Pt₄ species with a tetrahedral configuration retain similar structures upon deposition on MgO because of a slight dominance of intracluster bonding over the coordination to the support¹²⁴. However, Pt₄ supported on TiO₂(110) exhibits a square-planar shape with increased support interactions. In addition to the adsorption geometry effect, charge transfer from the metal cluster and the support also

impacts the catalytic performance of SCCs. The total amount of charge transfer can be tuned by changing the chemical identity or modifying the doping and defect density of the support. In addition to the support, the catalytic environment, for example, pressure, temperature, potential and interaction with gas-phase or liquid-phase reactants, electrolytes or solvents can also cause rearrangement of the atoms in SCCs affecting the size and shape, and many such circumstances have been reported^{125–130}.

Stability

Stability is a crucial factor in determining the viability of catalysts. Studies have reported the potentially enhanced stability of SCCs compared with SACs, which can be influenced by several factors such as the metal–support interaction, electronic confinement, ensemble dynamics and associated coordination of reactive intermediates (Fig. 4d). For example, investigations regarding Ni₁ and Ni₁Cu₂ on graphitic carbon nitride catalysts revealed varying chemical stabilities owing to differences in the dynamic structures induced by C₂H₂ adsorption³⁰. DFT calculations predicted that, upon C₂H₂ adsorption, one Ni–support bond is broken with a small energy barrier followed by the cleavage of the second Ni–support bond with a similar barrier leading to the formation of Ni nanoparticles on graphitic carbon nitride. However, acetylene adsorption over Ni₁Cu₂ on graphitic carbon nitride is much stronger, and although it causes the breakage of two Ni–support bonds, spatial confinement by two adjacent Cu atoms makes the cleavage of the Cu–O support bond extremely endothermic (by more than 4 eV, 385 kJ mol^{–1}). Consequently, Ni₁Cu₂ on this support exhibits exceptional stability in acetylene hydrogenation (Fig. 5f). Although initial results suggested that SCCs may have an improved stability compared with SACs, the evaluation of SCC stability is still in its early stages and requires more in-depth experimental and theoretical analysis. Developing stability maps under operando conditions can help identify the most stable SCC structures, as not all SCCs are guaranteed to exhibit enhanced stability. For example, Au clusters anchored on a TiO₂(110) surface can agglomerate in a CO/O₂ mixture at 300 K in ultrahigh-vacuum systems, which is completely different from Au clusters that remain stable in either CO or O₂ environments, indicating the synergistic effect of CO and O₂ in initiating the Ostwald ripening of supported Au clusters¹²⁷. A comprehensive review on doping, alloying, cluster sintering, adsorbate and support influence on the stability can be found elsewhere¹³¹.

Reactivity discovery

With an increasing interest in atomically precise SCCs, there is a growing need for developing strategic approaches to discover new reactivity for these highly efficient catalysts. Here, we explore the potential of bio-inspired and artificial intelligence (AI)-guided design to inspire and uncover new catalytic architectures leading to enhanced activity, selectivity and stability of SCCs as well as the implications of structural dynamics in the design.

Enzyme-inspired design

Nature has long been an expert in catalysis, as evidenced by numerous redox reactions catalysed by metalloenzymes containing multinuclear metal active sites^{132–135} (Fig. 6). Therefore, bio-inspired design strategies hold great potential for developing highly efficient and novel SCCs by drawing inspiration from natural enzymes, which regulate the local environment and electronic configuration of metal centres. Understanding the types of metal species present in enzymes, such as iron, cobalt, copper and manganese, provides valuable insights for designing

highly active and selective SCCs on the basis of non-noble metals. For example, researchers successfully fabricated an MOF incorporating Co and Re species for photocatalytic syngas generation¹³⁶. The study demonstrated that the host efficiently delivers energy to active sites akin to the enzymatic process. By studying these examples, we can develop SCCs with tailored active sites and unique electronic structures, guided by the importance of secondary coordination spheres in enzymes. However, replicating the intricate structures and mechanisms found in nature in SCCs and ensuring stability under catalytic conditions remains an important challenge, highlighting the need for innovative approaches and interdisciplinary collaborations.

High-throughput screening and AI-guided design

Similar to SACs, SCCs are ideal for computational screening of heterogeneous catalysts with atomically precise active centres owing to their uniformly dispersed and well-defined atomically precise active

centres. A number of theoretical studies have been conducted for two-atom and three-atom SCCs^{137–139}, and with large-scale computational modelling and simulations, it is now possible to search for excellent SCCs with robust performance for desired reactions¹⁴⁰. The application of AI in catalysis presents another exciting opportunity for accelerating the discovery of novel SCCs (Fig. 6b). By leveraging machine-learning algorithms and large experimental or theoretical data sets, AI will rapidly be able to identify promising candidates for targeted catalytic applications^{141–144}. The workflow for catalyst AI model construction involves the creation of SCC data sets with diverse properties, such as composition, support, size and shape, followed by the extraction of SCC characteristics using features that capture their electronic, geometric and support properties. AI models can then identify patterns and correlations between SCC structures and reactivity, enabling the design of SCCs with desired properties. However, challenges exist in developing accurate and robust machine-learning

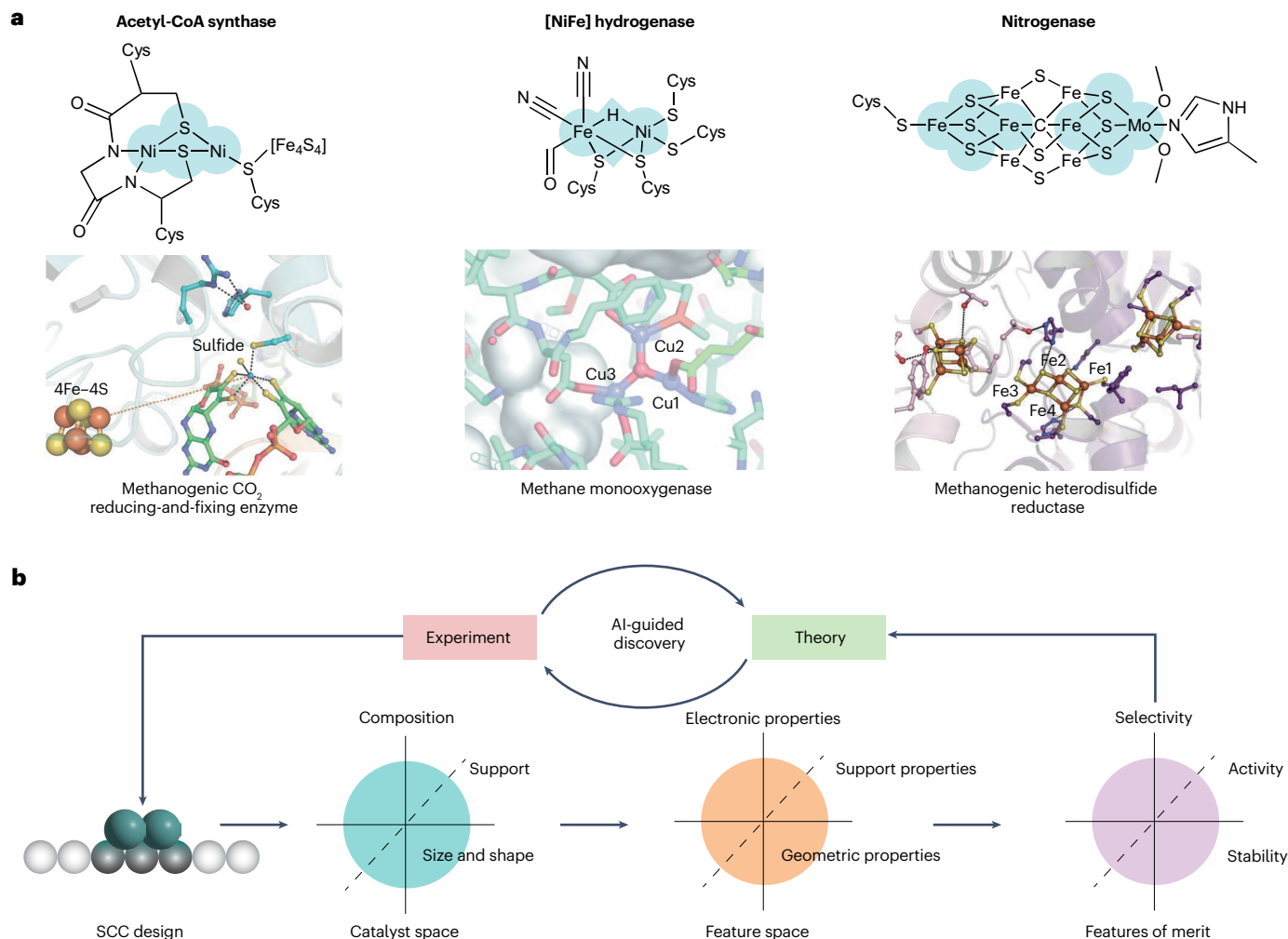


Fig. 6 | Conceptual strategies for discovering new reactivity of single-cluster catalysts. a, Bio-inspired design: the structure of single-metal cluster sites in enzymes, such as acetyl-CoA synthase, [NiFe] hydrogenase, nitrogenase, methanogenic CO₂ reducing-and-fixing enzyme, methane monooxygenase and methanogenic heterodisulfide reductase, can provide a blueprint for designing single-cluster catalysts (SCCs). Blue spheres were used to highlight

the cluster structure in enzymes. **b**, Artificial intelligence (AI) techniques including machine-learning algorithms, data analysis and predictive modelling can also help identify new SCCs by automating and accelerating the discovery process. Part **a**, bottom left adapted with permission from ref. 133, AAAS. Part **a**, bottom middle adapted with permission from ref. 134, Wiley. Part **a**, bottom right adapted with permission from ref. 135, AAAS.

models that can account for the complexity and diversity of catalytic systems. Additionally, the interpretation of AI-guided results can be non-trivial, requiring further experimental validation to confirm predicted properties.

Dynamic structure evolution upon reaction

Understanding the structural dynamics of SCCs is critical for advancing their design^{135,145,146}. As for other classes of supported metal catalysts, it has been observed that reactive environments, such as exposure to temperature, pressure, electrical potential and the interaction with gas-phase or liquid-phase reactants and solvents, can induce the formation of SCCs from SACs or MNCs owing to the thermodynamic or kinetic preferences of different structures under reaction conditions (Fig. 7). However, it is unknown whether such processes are reversible upon removal from the specific environment triggering the transformation. Furthermore, the dynamic evolution of SCC structures can lead to instability and even deactivation of their catalytic activity, for example, if they induce metal nanoparticle formation or volatilization of the active phase^{125,126,147}. Many theoretical studies focus on understanding these dynamics. For example, Pt clusters can thermally populate many low-energy metastable isomers¹⁴⁸. Pt clusters deposited on electrified graphite exist as statistical ensembles of multiple states, whose fluxionality is greatly affected by the applied potential, electrolyte and adsorbate coverage¹⁴⁹. It has been suggested that clusters can occupy a dynamic ensemble of states with varying reactivities, not only can they form an equilibrium of coexisting structural configurations, with various isomers exhibiting different chemical reactivities, but also has the fluxionality to adapt its structure, promoting the reaction to proceed on the most favourable free-energy path¹⁵⁰. Advanced in situ or operando electron microscopy and spectroscopy techniques are needed to gain a deeper understanding of the dynamic structural transformation of SCCs. Therefore, further research is required to understand and optimize the performance of SCCs in various catalytic reactions.

Opportunities and challenges ahead

Looking ahead, the increasing diversity of stable SCCs offers tremendous opportunities for designing advanced catalysts with tailored

performance in various thermocatalytic, electrocatalytic and photocatalytic reactions. The ability to manipulate geometric properties, such as the number and arrangement of adsorption sites and the 3D environment, along with the electronic structure, including oxidation and spin states, orbital configurations and energy levels, presents exciting prospects for these materials to access specific reactivity and high metal utilization, complementary to existing metal catalysts such as MNCs and SACs¹⁵¹. Still, research is needed to address the challenges and scientific questions in the field of SCCs. Key areas of focus include material synthesis and characterization, in which advancements are needed to improve our understanding and control of SCC structures and properties (Fig. 8).

As researchers refine the design guidelines and achieve greater control over the atomic and electronic structures of SCCs, new challenges emerge that require further exploration. Currently, the number of stable SCCs reported with high metal contents (>0.5 wt%) remains quite small and innovative approaches are required to extend this range.

Dedicated efforts to prepare suitable supports and precursors will have a key role in the efficient fabrication of SCCs with well-defined atomic and electronic structures and high stability. Exploiting synergistic effects between SCCs and other catalysts (such as SACs and MNCs) is also promising, and pioneering works in this direction have demonstrated the great potential to extend the catalytic applications of SCCs¹⁵². To develop novel synthesis strategies, a deep understanding of the interplay between different metal clusters and their supports is keenly required. Precisely controlling the properties of active metal sites of SCCs is another frontier during synthesis where different properties such as coordination number, bond length, electronic properties and proximity can be regulated. Another challenge is the synthesis of SCCs on a larger scale. Current routes often involve multiple-step chemical syntheses, which can be costly and not economically viable for SCC fabrication. Moreover, the synthesis of non-noble metal-based SCCs that outperform noble-metal-based SCCs remains a challenge.

One challenge of SCCs on certain supports is to discern where metal clusters coordinate as the local environment of a cluster is often unclear. Thus, accurately identifying the atomic structures of metal clusters on supports is essential to establishing reliable structure–property relationships. State-of-the-art characterization techniques

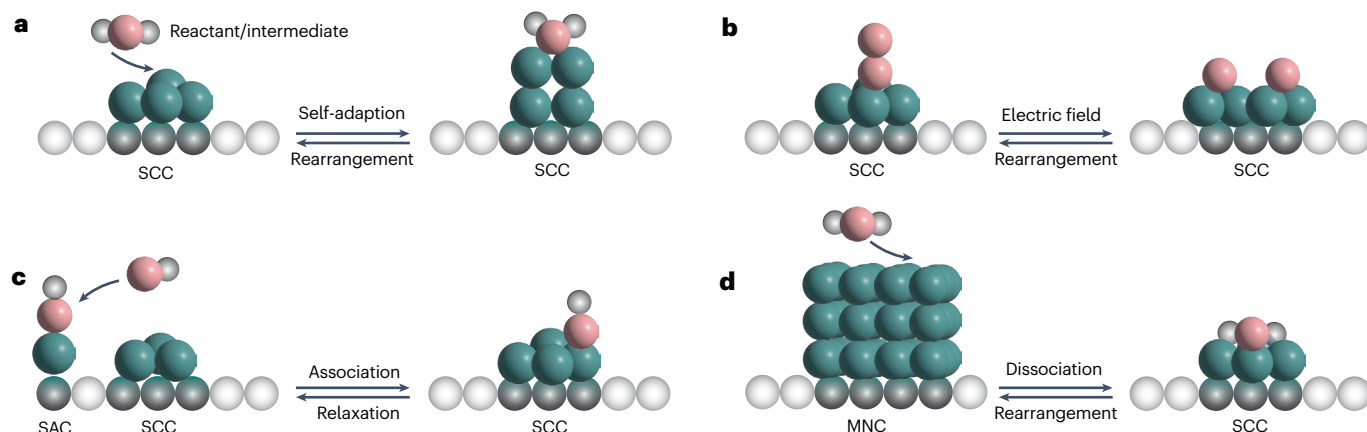


Fig. 7 | Structural dynamics of single-cluster catalysts. Schemes illustrating changes in the geometric structure of single-cluster catalysts (SCCs) induced by the adsorption of reactive intermediates or the reaction environment in panel **a** or by the application of an electric field in panel **b**. **c**, SCCs may also form through

rearrangement of metal species in single-atom catalysts (SACs) or redistribution of metal nanoparticle catalysts (MNCs) depending on the reaction conditions and environment as shown in panel **d**.

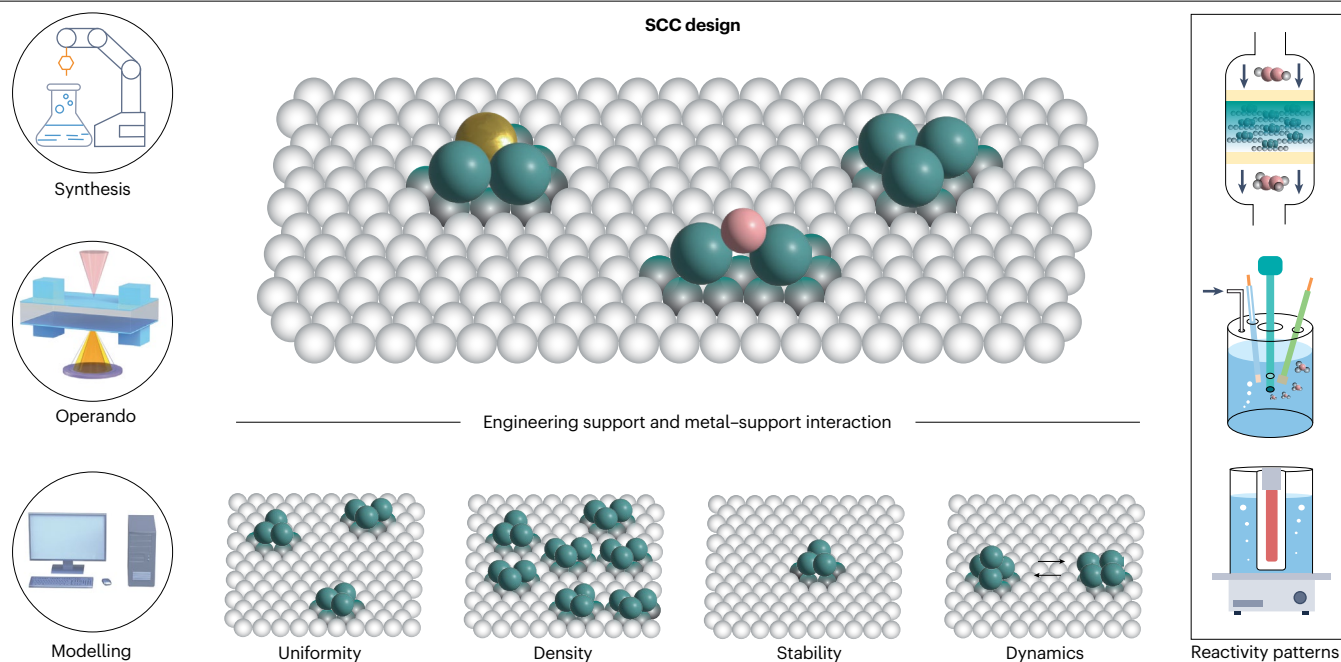


Fig. 8 | Roadmap for single-cluster catalyst development. Current challenges and future directions in the synthesis, characterization and application of SCCs. Schematic illustrations depict promising applications of SCCs in thermocatalysis, electrocatalysis and photocatalysis.

such as aberration-corrected-high-angle annular dark-field scanning transmission electron microscopy (STEM) and X-ray absorption fine structure have been widely used to visualize the spatial arrangement and probe the local structure of metal clusters in SCCs. However, the interpretation of the results from these techniques can be challenging owing to factors such as atom overlap owing to the 2D projections of 3D objects in TEM, insufficient resolution or chemical sensitivity, degradation of samples owing to the analysis method and uncertainty in estimates of cluster sizes and structure. The potential of environmental TEM for in situ or operando visualizations of single-atom dynamics in SACs has been demonstrated^{153–155}. Besides, digital tools such as machine learning and computational simulations have emerged as powerful tools for interpreting and analysing complex data from these techniques. For example, machine-learning algorithms can be trained on large data sets of STEM images to extract valuable information on cluster size, shape and composition¹⁵⁶. Similarly, computational simulations can provide insights into the dynamic behaviour of SCCs and their catalytic activity under various conditions. With the rapid development of these digital tools and intelligent synthesis methods, we can anticipate more SCCs with well-defined atomic and electronic structures that can be designed and fabricated as model catalysts to investigate the structure–property–function relationship further.

Early examples have already shown the great potential of SCCs for various thermocatalytic, electrocatalytic and photocatalytic transformations, such as hydrogenations, couplings, ammonia synthesis and water splitting. For example, Ni₁Cu₂ clusters anchored on graphitic carbon nitride exhibit extraordinary catalytic performance in terms of activity, selectivity and stability for the semi-hydrogenation of acetylene in excess ethylene³⁰. Moreover, Ru₃O₂ clusters on reduced graphene oxide efficiently catalyse coupling reactions involving three reactants, as demonstrated in the synthesis of imines and Cavosonstat

derivative (a F508del-CFTR mutation treatment medicine) via the Friedländer reaction⁶². Similarly, Au₄Pd₂ on graphene and Pd-Cu dimer on N-doped carbon demonstrate high yield production of NH₃ via electrocatalysis^{24,157}. Co-O-Pt dimers on TiO₂ exhibit an ultra-high and stable photocatalytic water-splitting activity with a rate of 43.467 mmol g⁻¹ h⁻¹ and external quantum efficiency of ≈83.4% at 365 nm²⁹. Future research efforts should focus on further exploring the catalytic performance of SCCs in these reactions and optimizing their properties to outperform both traditional MNCs and SACs.

To fully exploit the potential of SCCs, it is crucial to also consider other aspects beyond their catalytic activity, such as their scalability, sustainability, cost-effectiveness, durability and potential for integration with other processes. One key advantage of SCCs is their high specific metal utilization, which can enable efficient reactions even at low metal concentrations. However, current synthesis approaches for SCCs primarily focus on obtaining atomically precise architectures rather than scalable, sustainable and cost-effective methods. Thus, there is a need to develop efficient and environmentally friendly approaches for large-scale synthesis and recycling of SCCs. In addition, the development of non-noble metal-based SCCs with high catalytic activity and selectivity is an area of considerable interest. Furthermore, the durability of SCCs must be considered, as they may be subject to degradation over time, for example, owing to poisoning by feedstock impurities or substantial structural changes upon exposure to certain reaction conditions. Demonstrating their stability over extended periods under industrially relevant conditions is important to better understand their scope and potential. Overall, continued research and development are necessary to optimize SCCs for industrial use and enable their widespread adoption in the chemical industry.

In conclusion, the field of SCCs is still in its early stages. Because of the atomically precise and spatially isolated nature, there are vast

opportunities to explore their unique properties, especially with various atomic compositions and geometric structures. Two-atom SCCs as the simplest form have already demonstrated rich catalytic advantages, as exemplified by their applications in the cross-coupling reactions of C–X (X = C, N, O, S) bonds using recently discovered heterogeneous geminal-atom catalysts¹⁵⁸. With continued research efforts, we anticipate that SCCs will revolutionize the field of heterogeneous catalysis, opening new reaction paths and paving the way for more sustainable and catalytically efficient industrial processes.

Published online: 09 October 2023

References

- Mistry, H., Varela, A. S., Kühl, S., Strasser, P. & Cuenya, B. R. Nanostructured electrocatalysts with tunable activity and selectivity. *Nat. Rev. Mater.* **1**, 16009 (2016).
- Liu, L. & Corma, A. Metal catalysts for heterogeneous catalysis: from single atoms to nanoclusters and nanoparticles. *Chem. Rev.* **118**, 4981–5079 (2018).
- Mitchell, S., Qin, R., Zheng, N. & Pérez-Ramírez, J. Nanoscale engineering of catalytic materials for sustainable technologies. *Nat. Nanotechnol.* **16**, 129–139 (2021).
This paper examines how nanoscale engineering can enhance the selectivity and stability of heterogeneous catalysts.
- Zhao, Z.-J. et al. Theory-guided design of catalytic materials using scaling relationships and reactivity descriptors. *Nat. Rev. Mater.* **4**, 792–804 (2019).
- Pérez-Ramírez, J. & López, N. Strategies to break linear scaling relationships. *Nat. Catal.* **2**, 971–976 (2019).
- Zhang, J., Yang, H. B., Zhou, D. & Liu, B. Adsorption energy in oxygen electrocatalysis. *Chem. Rev.* **122**, 17028–17072 (2022).
- Seh, Z. W. et al. Combining theory and experiment in electrocatalysis: insights into materials design. *Science* **355**, eaad4998 (2017).
- Zhao, X., Levell, Z. H., Yu, S. & Liu, Y. Atomistic understanding of two-dimensional electrocatalysts from first principles. *Chem. Rev.* **122**, 10675–10709 (2022).
- Li, X. et al. Ordered clustering of single atomic Te vacancies in atomically thin PtTe₂ promotes hydrogen evolution catalysis. *Nat. Commun.* **12**, 2351 (2021).
- Guo, Y., Wang, M., Zhu, Q., Xiao, D. & Ma, D. Ensemble effect for single-atom, small cluster and nanoparticle catalysts. *Nat. Catal.* **5**, 766–776 (2022).
- Liu, L. & Corma, A. Confining isolated atoms and clusters in crystalline porous materials for catalysis. *Nat. Rev. Mater.* **6**, 244–263 (2021).
- Yang, H. et al. Catalytically active atomically thin cuprate with periodic Cu single sites. *Nat. Sci. Rev.* **10**, nwa100 (2023).
- Heiz, U. & Schneider, W.-D. Size-selected clusters on solid surfaces. *Crit. Rev. Solid State Mater. Sci.* **26**, 251–290 (2001).
- Lei, Y. et al. Increased silver activity for direct propylene epoxidation via subnanometer size effects. *Science* **328**, 224–228 (2010).
- Vajda, S. & White, M. G. Catalysis applications of size-selected cluster deposition. *ACS Catal.* **5**, 7152–7176 (2015).
- Valden, M., Lai, X. & Goodman, D. W. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science* **281**, 1647–1650 (1998).
- Yoon, B. et al. Charging effects on bonding and catalyzed oxidation of CO on Au₈ clusters on MgO. *Science* **307**, 403–407 (2005).
- Mitchell, S. & Pérez-Ramírez, J. Atomically precise control in the design of low-nuclearity supported metal catalysts. *Nat. Rev. Mater.* **6**, 969–985 (2021).
- Sun, L., Reddu, V. & Wang, X. Multi-atom cluster catalysts for efficient electrocatalysis. *Chem. Soc. Rev.* **51**, 8923–8956 (2022).
- Tyo, E. C. & Vajda, S. Catalysis by clusters with precise numbers of atoms. *Nat. Nanotechnol.* **10**, 577–588 (2015).
This paper summarizes work on size-selected supported clusters to provide a mechanistic understanding of their catalytic properties.
- Liu, J.-C. et al. Heterogeneous Fe₂ single-cluster catalyst for ammonia synthesis via an associative mechanism. *Nat. Commun.* **9**, 1610 (2018).
This paper is one of the earliest papers using the term of SCCs.
- Ma, X.-L., Liu, J.-C., Xiao, H. & Li, J. Surface single-cluster catalyst for N₂-to-NH₃ thermal conversion. *J. Am. Chem. Soc.* **140**, 46–49 (2018).
This paper first introduces the term SCC.
- Xing, D.-H., Xu, C.-Q., Wang, Y.-G. & Li, J. Heterogeneous single-cluster catalysts for selective semihydrogenation of acetylene with graphdiyne-supported triatomic clusters. *J. Phys. Chem. C* **123**, 10494–10500 (2019).
- Yao, C. et al. Atomically-precise dopant-controlled single cluster catalysis for electrochemical nitrogen reduction. *Nat. Commun.* **11**, 4389 (2020).
- Rong, H., Ji, S., Zhang, J., Wang, D. & Li, Y. Synthetic strategies of supported atomic clusters for heterogeneous catalysis. *Nat. Commun.* **11**, 5884 (2020).
This review presents the progress of the synthesis of supported atomic clusters and highlights how the structure affects catalytic properties.
- Han, A. et al. Construction of Co₄ atomic clusters to enable Fe–N₄ motifs with highly active and durable oxygen reduction performance. *Angew. Chem. Int. Ed. Engl.* **135**, e202303185 (2023).
- Tian, S. et al. Dual-atom Pt heterogeneous catalyst with excellent catalytic performances for the selective hydrogenation and epoxidation. *Nat. Commun.* **12**, 3181 (2021).
- Zhang, N. et al. A supported Pd₂ dual-atom site catalyst for efficient electrochemical CO₂ reduction. *Angew. Chem. Int. Ed. Engl.* **60**, 13388–13393 (2021).
- Wang, C. et al. Co and Pt dual-single-atoms with oxygen-coordinated Co–O–Pt dimer sites for ultrahigh photocatalytic hydrogen evolution efficiency. *Adv. Mater.* **33**, 2003327 (2021).
This paper is a representative paper about dual-atom catalysts, which can be seen as the simplest form of SCCs.
- Gu, J. et al. Synergizing metal–support interactions and spatial confinement boosts dynamics of atomic nickel for hydrogenations. *Nat. Nanotechnol.* **16**, 1141–1149 (2021).
This paper reports the enhanced stability of SCCs compared with SACs.
- Yang, Y. et al. O-coordinated W–Mo dual-atom catalyst for pH-universal electrocatalytic hydrogen evolution. *Sci. Adv.* **6**, eaba6586 (2020).
- Zhang, L. et al. Atomic layer deposited Pt–Ru dual-metal dimers and identifying their active sites for hydrogen evolution reaction. *Nat. Commun.* **10**, 4936 (2019).
- Ye, W. et al. Precisely tuning the number of Fe atoms in clusters on N-doped carbon toward acidic oxygen reduction reaction. *Chem* **5**, 2865–2878 (2019).
- Ren, W. et al. Isolated diatomic Ni–Fe metal–nitrogen sites for synergistic electroreduction of CO₂. *Angew. Chem. Int. Ed. Engl.* **58**, 6972–6976 (2019).
- Jiao, J. et al. Copper atom-pair catalyst anchored on alloy nanowires for selective and efficient electrochemical reduction of CO₂. *Nat. Chem.* **11**, 222–228 (2019).
- Bai, L., Hsu, C.-S., Alexander, D. T. L., Chen, H. M. & Hu, X. A cobalt-iron double-atom catalyst for the oxygen evolution reaction. *J. Am. Chem. Soc.* **141**, 14190–14199 (2019).
- Imaoka, T. et al. Platinum clusters with precise numbers of atoms for preparative-scale catalysis. *Nat. Commun.* **8**, 688 (2017).
- Wei, Y. S. et al. Fabricating dual-atom iron catalysts for efficient oxygen evolution reaction: a heteroatom modulator approach. *Angew. Chem. Int. Ed. Engl.* **59**, 16013–16022 (2020).
- Zhou, Y. et al. Revealing of active sites and catalytic mechanism in N-coordinated Fe, Ni dual-doped carbon with superior acidic oxygen reduction than single-atom catalyst. *J. Phys. Chem. Lett.* **11**, 1404–1410 (2020).
- Dai, S. et al. Platinum-trimer decorated cobalt–palladium core–shell nanocatalyst with promising performance for oxygen reduction reaction. *Nat. Commun.* **10**, 440 (2019).
- Wang, J. et al. Design of N-coordinated dual-metal sites: a stable and active Pt-free catalyst for acidic oxygen reduction reaction. *J. Am. Chem. Soc.* **139**, 17281–17284 (2017).
- Xie, C., Niu, Z., Kim, D., Li, M. & Yang, P. Surface and interface control in nanoparticle catalysis. *Chem. Rev.* **120**, 1184–1249 (2020).
- Xia, Y., Yang, H. & Campbell, T. C. Nanoparticles for catalysis. *Acc. Chem. Res.* **46**, 1671–1672 (2013).
- Yan, H. et al. Bottom-up precise synthesis of stable platinum dimers on graphene. *Nat. Commun.* **8**, 1070 (2017).
- Ji, S. et al. Confined pyrolysis within metal–organic frameworks to form uniform Ru₃ clusters for efficient oxidation of alcohols. *J. Am. Chem. Soc.* **139**, 9795–9798 (2017).
- Tian, S. et al. Carbon nitride supported Fe₂ cluster catalysts with superior performance for alkene epoxidation. *Nat. Commun.* **9**, 2353 (2018).
- Zhao, Y. et al. Stable iridium dinuclear heterogeneous catalysts supported on metal-oxide substrate for solar water oxidation. *Proc. Natl Acad. Sci. USA* **115**, 2902 (2018).
- Ji, S. et al. Atomically dispersed ruthenium species inside metal–organic frameworks: combining the high activity of atomic sites and the molecular sieving effect of MOFs. *Angew. Chem. Int. Ed. Engl.* **58**, 4271–4275 (2019).
- Li, X. et al. Microenvironment modulation of single-atom catalysts and their roles in electrochemical energy conversion. *Sci. Adv.* **6**, eabb6833 (2020).
- Zhang, L., Ren, Y., Liu, W., Wang, A. & Zhang, T. Single-atom catalyst: a rising star for green synthesis of fine chemicals. *Nat. Sci. Rev.* **5**, 653–672 (2018).
- Fortea-Pérez, F. R. et al. The MOF-driven synthesis of supported palladium clusters with catalytic activity for carbene-mediated chemistry. *Nat. Mater.* **16**, 760–766 (2017).
- Lu, Z. Y. et al. An isolated zinc–cobalt atomic pair for highly active and durable oxygen reduction. *Angew. Chem. Int. Ed.* **58**, 2622–2626 (2019).
- Liu, J., Cao, D., Xu, H. & Cheng, D. From double-atom catalysts to single-cluster catalysts: a new frontier in heterogeneous catalysis. *Nano Sel.* **2**, 251–270 (2021).
- Pei, W. et al. Immobilized trimeric metal clusters: a family of the smallest catalysts for selective CO₂ reduction toward multi-carbon products. *Nano Energy* **76**, 105049 (2020).
- Liu, J.-C., Xiao, H. & Li, J. Constructing high-loading single-atom/cluster catalysts via an electrochemical potential window strategy. *J. Am. Chem. Soc.* **142**, 3375–3383 (2020).
- Wang, Z. et al. Atomically dispersed Co₂–N₆ and Fe–N₄ costructures boost oxygen reduction reaction in both alkaline and acidic media. *Adv. Mater.* **33**, 2104718 (2021).
- Wang, Y. et al. Precisely constructing orbital coupling-modulated dual-atom Fe pair sites for synergistic CO₂ electroreduction. *ACS Energy Lett.* **7**, 640–649 (2022).
- Ling, C. et al. Atomic-layered Cu₅ nanoclusters on FeS₂ with dual catalytic sites for efficient and selective H₂O₂ activation. *Angew. Chem. Int. Ed. Engl.* **134**, e202200670 (2022).
- Yan, X. et al. Atomically dispersed Co₂MnN₈ triatomic sites anchored in N-doped carbon enabling efficient oxygen reduction reaction. *Adv. Mater.* <https://doi.org/10.1002/adma.202210975> (2023).
- Sun, X. et al. Palladium dimer supported on Mo₂Co₂(Mxene) for direct methane to methanol conversion. *Adv. Theory Simul.* **2**, 1800158 (2019).

61. Zhang, S. et al. Catalysis on singly dispersed bimetallic sites. *Nat. Commun.* **6**, 7938 (2015).
62. Li, X. et al. Atomically precise single metal oxide cluster catalyst with oxygen-controlled activity. *Adv. Funct. Mater.* **32**, 2200933 (2022).
63. Baxter, E. T., Ha, M.-A., Cass, A. C., Alexandrova, A. N. & Anderson, S. L. Ethylene dehydrogenation on Pt_{4,7,8} clusters on Al₂O₃: strong cluster size dependence linked to preferred catalyst morphologies. *ACS Catal.* **7**, 3322–3335 (2017).
64. Ren, Y., Yang, Y., Zhao, Y.-X. & He, S.-G. Conversion of methane with oxygen to produce hydrogen catalyzed by triatomic Rh₃-cluster anion. *JACS Au* **2**, 197–203 (2021).
65. Watanabe, Y. Atomically precise cluster catalysis towards quantum controlled catalysts. *Sci. Technol. Adv. Mater.* **15**, 063501 (2014).
66. Jimenez-Izal, E. & Alexandrova, A. N. Computational design of clusters for catalysis. *Annu. Rev. Phys. Chem.* **69**, 377–400 (2018).
67. Li, H. et al. Synergistic interaction between neighbouring platinum monomers in CO₂ hydrogenation. *Nat. Nanotechnol.* **13**, 411–417 (2018).
68. Kwon, G. et al. Size-dependent subnanometer Pd cluster (Pd₄, Pd₆, and Pd₁₇) water oxidation electrocatalysis. *ACS Nano* **7**, 5808–5817 (2013).
69. Halder, A. et al. Water oxidation catalysis via size-selected iridium clusters. *J. Phys. Chem. C* **122**, 9965–9972 (2018).
70. Xiao, M. et al. Identification of binuclear Co₂N₂ active sites for oxygen reduction reaction with more than one magnitude higher activity than single atom CoN₄ site. *Nano Energy* **46**, 396–403 (2018).
71. Liu, D. et al. Distinguished Zn,Co-N₂-C-S₂ active sites confined in dentric carbon for highly efficient oxygen reduction reaction and flexible Zn-air batteries. *Nano Energy* **58**, 277–283 (2019).
72. Wang, J. et al. Synergistic effect of well-defined dual sites boosting the oxygen reduction reaction. *Energy Environ. Sci.* **11**, 3375–3379 (2018).
73. Jiang, M. et al. Rationalization on high-loading iron and cobalt dual metal single atoms and mechanistic insight into the oxygen reduction reaction. *Nano Energy* **93**, 106793 (2022).
74. Zhang, T. et al. Dual-atom nickel moieties of Ni(II)₂(μ₂-N)₂ anchored on alfalfa-derived developed porous N-doped carbon for high-performance Li-S battery. *Small* **18**, 22001996 (2022).
75. Zeng, X. et al. Single-atom to single-atom grafting of Pt₁ onto Fe-N₄ center: Pt₁@Fe-N-C multifunctional electrocatalyst with significantly enhanced properties. *Adv. Energy Mater.* **8**, 1701345 (2018).
76. Jin, R., Zeng, C., Zhou, M. & Chen, Y. Atomically precise colloidal metal nanoclusters and nanoparticles: fundamentals and opportunities. *Chem. Rev.* **116**, 10346–10413 (2016).
77. Wang, X. et al. Confined Fe-Cu clusters as sub-nanometer reactors for efficiently regulating the electrochemical nitrogen reduction reaction. *Adv. Mater.* **32**, 2004382 (2020).
78. Kaden, W. E., Wu, T., Kunkel, W. A. & Anderson, S. L. Electronic structure controls reactivity of size-selected Pd clusters adsorbed on TiO₂ surfaces. *Science* **326**, 826 (2009).
79. Lu, J. et al. Effect of the size-selective silver clusters on lithium peroxide morphology in lithium-oxygen batteries. *Nat. Commun.* **5**, 4895 (2014).
80. Liu, C. et al. Carbon dioxide conversion to methanol over size-selected Cu₄ clusters at low pressures. *J. Am. Chem. Soc.* **137**, 8676–8679 (2015).
81. Yang, B. et al. Copper cluster size effect in methanol synthesis from CO₂. *J. Phys. Chem. C* **121**, 10406–10412 (2017).
82. Taketoshi, A. & Haruta, M. Size- and structure-specificity in catalysis by gold clusters. *Chem. Lett.* **43**, 380–387 (2014).
83. Judai, K., Abbet, S., Wörz, A. S., Heiz, U. & Henry, C. R. Low-temperature cluster catalysis. *J. Am. Chem. Soc.* **126**, 2732–2737 (2004).
84. Rötzer, M. D. et al. Nanotuning via local work function control: ethylene hydrogenation on supported Pt nanoclusters. *ACS Catal.* **10**, 1799–1809 (2020).
85. Vorobyeva, E. et al. Atom-by-atom resolution of structure–function relations over low-nuclearity metal catalysts. *Angew. Chem. Int. Ed. Engl.* **58**, 8724–8729 (2019).
86. Zhang, G. et al. A general route via formamide condensation to prepare atomically dispersed metal–nitrogen–carbon electrocatalysts for energy technologies. *Energy Environ. Sci.* **12**, 1317–1325 (2019).
87. Han, X. et al. Atomically dispersed binary Co-Ni sites in nitrogen-doped hollow carbon nanocubes for reversible oxygen reduction and evolution. *Adv. Mater.* **31**, 1905622 (2019).
88. Zhu, X. et al. Harnessing the interplay of Fe-Ni atom pairs embedded in nitrogen-doped carbon for bifunctional oxygen electrocatalysis. *Nano Energy* **71**, 104597 (2020).
89. George, S. M. Atomic layer deposition: an overview. *Chem. Rev.* **110**, 111–131 (2010).
90. Qian, H., Zhu, M., Wu, Z. & Jin, R. Quantum sized gold nanoclusters with atomic precision. *Acc. Chem. Res.* **45**, 1470–1479 (2012).
91. Ni, B. & Wang, X. Chemistry and properties at a sub-nanometer scale. *Chem. Sci.* **7**, 3978–3991 (2016).
92. Park, H., Shin, D. J. & Yu, J. Categorization of quantum dots, clusters, nanoclusters, and nanodots. *J. Chem. Educ.* **98**, 703–709 (2021).
93. Taylor, K. J., Pettiette-Hall, C. L., Cheshnovsky, O. & Smalley, R. E. Ultraviolet photoelectron spectra of coinage metal clusters. *J. Chem. Phys.* **96**, 3319–3329 (1992).
94. Prats, H. & Stamatakis, M. Atomistic and electronic structure of metal clusters supported on transition metal carbides: implications for catalysis. *J. Mater. Chem. A* **10**, 1522–1534 (2022).
95. Zhao, W. et al. Triggering Pt active sites in basal plane of van der Waals PtTe₂ materials by amorphization engineering for hydrogen evolution. *Adv. Mater.* **35**, 2301593 (2023).
96. Ding, T. et al. Atomically precise dinuclear site active toward electrocatalytic CO₂ reduction. *J. Am. Chem. Soc.* **143**, 11317–11324 (2021).
97. Nørskov, J. K., Bligaard, T., Rossmeisl, J. & Christensen, C. H. Towards the computational design of solid catalysts. *Nat. Chem.* **1**, 37–46 (2009).
98. Montemore, M. M., van Spronsen, M. A., Madix, R. J. & Friend, C. M. O₂ activation by metal surfaces: implications for bonding and reactivity on heterogeneous catalysts. *Chem. Rev.* **118**, 2816–2862 (2018).
99. Du, Y., Sheng, H., Astruc, D. & Zhu, M. Atomically precise noble metal nanoclusters as efficient catalysts: a bridge between structure and properties. *Chem. Rev.* **120**, 526–622 (2020).
100. Medford, A. J. et al. From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. *J. Catal.* **328**, 36–42 (2015).
101. Xie, C. et al. Insight into the design of defect electrocatalysts: from electronic structure to adsorption energy. *Mater. Today* **31**, 47–68 (2019).
102. Kress, P. L. et al. A priori design of dual-atom alloy sites and experimental demonstration of ethanol dehydrogenation and dehydration on PtCrAg. *J. Am. Chem. Soc.* **145**, 8401–8407 (2023).
103. Zhang, S., Sykes, E. C. H. & Montemore, M. M. Tuning reactivity in trimetallic dual-atom alloys: molecular-like electronic states and ensemble effects. *Chem. Sci.* **13**, 14070–14079 (2022).
104. Zhou, P. et al. Synergistic interaction between neighboring platinum and ruthenium monomers boosts CO oxidation. *Chem. Sci.* **10**, 5898–5905 (2019).
105. Liu, M. et al. Tuning the site-to-site interaction in Ru-M (M = Co, Fe, Ni) diatomic electrocatalysts to climb up the volcano plot of oxygen electroreduction. *ACS Nano* **16**, 10657–10666 (2022).
106. Shi, H. et al. Atomically dispersed indium-copper dual-metal active sites promoting C-C coupling for CO₂ photoreduction to ethanol. *Angew. Chem. Int. Ed. Engl.* **61**, e202208908 (2022).
107. Li, F., Liu, X. & Chen, Z. 1+1 > 2: Heteronuclear biatom catalyst outperforms its homonuclear counterpartners for CO oxidation. *Small Methods* **3**, 1800480 (2019).
108. Giulimondi, V. et al. Controlled formation of dimers and spatially isolated atoms in bimetallic Au-Ru catalysts via carbon-host functionalization. *Small* **18**, 2200224 (2022).
109. Wang, J. et al. N-coordinated dual-metal single-site catalyst for low-temperature CO oxidation. *ACS Catal.* **10**, 2754–2761 (2020).
110. Xiao, M. et al. Climbing the apex of the ORR volcano plot via binuclear site construction: electronic and geometric engineering. *J. Am. Chem. Soc.* **141**, 17763–17770 (2019).
111. Sarkar, S. et al. Unravelling the role of Fe-Mn binary active sites electrocatalyst for efficient oxygen reduction reaction and rechargeable Zn-air batteries. *Inorg. Chem.* **59**, 5194–5205 (2020).
112. Jia, G. et al. Asymmetric coupled dual-atom sites for selective photoreduction of carbon dioxide to acetic acid. *Adv. Funct. Mater.* **32**, 2206817 (2022).
113. Zhu, J. et al. Quasi-covalently coupled Ni-Cu atomic pair for synergistic electroreduction of CO₂. *J. Am. Chem. Soc.* **144**, 9661–9671 (2022).
114. Wan, X.-K., Wang, J.-Q., Nan, Z.-A. & Wang, Q.-M. Ligand effects in catalysis by atomically precise gold nanoclusters. *Sci. Adv.* **3**, e1701823 (2017).
115. DeRoshia, D. E. et al. Planar three-coordinate iron sulfide in a synthetic [4Fe-3S] cluster with biomimetic reactivity. *Nat. Chem.* **11**, 1019–1025 (2019).
116. Watanabe, Y., Wu, X., Hirata, H. & Isomura, N. Size-dependent catalytic activity and geometries of size-selected Pt clusters on TiO₂(110) surfaces. *Catal. Sci. Technol.* **1**, 1490–1495 (2011).
117. Yang, C.-T., Wood, B. C., Bhethanabotla, V. R. & Joseph, B. The effect of the morphology of supported subnanometer Pt clusters on the first and key step of CO₂ photoreduction. *Phys. Chem. Chem. Phys.* **17**, 25379–25392 (2015).
118. Wang, J., Wang, G. & Zhao, J. Density-functional study of Au_n (n = 2–20) clusters: lowest-energy structures and electronic properties. *Phys. Rev. B* **66**, 035418 (2002).
119. Li, X., Zhong, W., Cui, P., Li, J. & Jiang, J. Design of efficient catalysts with double transition metal atoms on C₂N layer. *J. Phys. Chem. Lett.* **7**, 1750–1755 (2016).
120. Zhao, J., Zhao, J., Li, F. & Chen, Z. Copper dimer supported on a C₂N layer as an efficient electrocatalyst for CO₂ reduction reaction: a computational study. *J. Phys. Chem. C* **122**, 19712–19721 (2018).
121. Li, Y., Su, H., Chan, S. H. & Sun, Q. CO₂ electroreduction performance of transition metal dimers supported on graphene: a theoretical study. *ACS Catal.* **5**, 6658–6664 (2015).
122. Kumar, A. et al. Moving beyond bimetallic-alloy to single-atom dimer atomic-interface for all-pH hydrogen evolution. *Nat. Commun.* **12**, 6766 (2021).
123. Shen, L., Dadras, J. & Alexandrova, A. N. Pure and Zn-doped Pt clusters go flat and upright on MgO(100). *Phys. Chem. Chem. Phys.* **16**, 26436–26442 (2014).
124. Dadras, J., Shen, L. & Alexandrova, A. Pt-Zn clusters on stoichiometric MgO(100) and TiO₂(110): dramatically different sintering behavior. *J. Phys. Chem. C* **119**, 6047–6055 (2015).
125. Parkinson, G. S. et al. Carbon monoxide-induced adatom sintering in a Pd-FeO₄ model catalyst. *Nat. Mater.* **12**, 724–728 (2013).
126. Corma, A. et al. Exceptional oxidation activity with size-controlled supported gold clusters of low atomicity. *Nat. Chem.* **5**, 775–781 (2013).
127. Yang, F., Chen, M. S. & Goodman, D. W. Sintering of Au particles supported on TiO₂(110) during CO oxidation. *J. Phys. Chem. C* **113**, 254–260 (2009).
128. Moliner, M. et al. Reversible transformation of Pt nanoparticles into single atoms inside high-silica chabazite zeolite. *J. Am. Chem. Soc.* **138**, 15743–15750 (2016).

129. Wang, Y.-G., Mei, D., Glezakou, V.-A., Li, J. & Rousseau, R. Dynamic formation of single-atom catalytic active sites on ceria-supported gold nanoparticles. *Nat. Commun.* **6**, 6511 (2015).
130. Liu, J.-C., Wang, Y.-G. & Li, J. Toward rational design of oxide-supported single-atom catalysts: atomic dispersion of gold on ceria. *J. Am. Chem. Soc.* **139**, 6190–6199 (2017).
131. Chavez, S. et al. Studying, promoting, exploiting, and predicting catalyst dynamics: the next frontier in heterogeneous catalysis. *J. Phys. Chem. C* **127**, 2127–2146 (2023).
This review summarizes the doping, alloying, cluster sintering, adsorbate and support influence on the stability of catalysts.
132. Bullock, R. M. et al. Using nature's blueprint to expand catalysis with earth-abundant metals. *Science* **369**, eabc3183 (2020).
133. Wagner, T., Ermler, U. & Shima, S. The methanogenic CO₂ reducing-and-fixing enzyme is bifunctional and contains 46 [4Fe-4S] clusters. *Science* **354**, 114–117 (2016).
134. Chan, S. I. et al. Redox potentiometry studies of particulate methane monooxygenase: support for a trinuclear copper cluster active site. *Angew. Chem. Int. Ed. Engl.* **46**, 1992–1994 (2007).
135. Wagner, T., Koch, J., Ermler, U. & Shima, S. Methanogenic heterodisulfide reductase (HdrABC-MvhAGD) uses two noncubane [4Fe-4S] clusters for reduction. *Science* **357**, 699–703 (2017).
136. Stanley, P. M. et al. Photocatalytic CO₂-to-syngas evolution with molecular catalyst metal-organic framework nanozymes. *Adv. Mater.* **35**, 2207380 (2023).
137. Chen, J.-C. et al. Heterogeneous two-atom single-cluster catalysts for the nitrogen electroreduction reaction. *J. Phys. Chem. C* **125**, 19821–19830 (2021).
138. Liu, N., Ma, X.-L., Li, J. & Xiao, H. Singly dispersed bimetallic sites as stable and efficient single-cluster catalysts for activating N₂ and CO₂. *J. Phys. Chem. C* **125**, 27192–27198 (2021).
139. Liu, J.-C. et al. Computational prediction of graphdiyne-supported three-atom single-cluster catalysts. *ACS Chem.* **5**, 152–163 (2022).
140. Liu, J.-C. et al. Metal affinity of support dictates sintering of gold catalysts. *J. Am. Chem. Soc.* **144**, 20601–20609 (2022).
141. Xu, J., Xie, W., Han, Y. & Hu, P. Atomistic insights into the oxidation of flat and stepped platinum surfaces using large-scale machine learning potential-based grand-canonical Monte Carlo. *ACS Catal.* **12**, 14812–14824 (2022).
142. Kitchin, J. R. Machine learning in catalysis. *Nat. Catal.* **1**, 230–232 (2018).
143. Esterhuizen, J. A., Goldsmith, B. R. & Lincic, S. Interpretable machine learning for knowledge generation in heterogeneous catalysis. *Nat. Catal.* **5**, 175–184 (2022).
144. Ma, S. & Liu, Z.-P. Machine learning for atomic simulation and activity prediction in heterogeneous catalysis: current status and future. *ACS Catal.* **10**, 13213–13226 (2020).
145. Wang, Y.-G., Yoon, Y., Glezakou, V.-A., Li, J. & Rousseau, R. The role of reducible oxide-metal cluster charge transfer in catalytic processes: new insights on the catalytic mechanism of CO oxidation on Au/TiO₂ from ab initio molecular dynamics. *J. Am. Chem. Soc.* **135**, 10673–10683 (2013).
146. Mekker, M. J. et al. Dry reforming of methane over single-atom Rh/Al₂O₃ catalysts prepared by exsolution. *Catal. Sci. Technol.* **13**, 2255–2260 (2023).
147. Shrestha, S., Liu, Y. & Mustain, W. E. Electrocatalytic activity and stability of Pt clusters on state-of-the-art supports: a review. *Catal. Rev. Sci. Eng.* **53**, 256–336 (2011).
148. Zandkarimi, B., Poths, P. & Alexandrova, A. N. When fluxionality beats size selection: acceleration of Ostwald ripening of sub-nano clusters. *Angew. Chem.* **133**, 12080–12089 (2021).
149. Munarriz, J., Zhang, Z., Sautet, P. & Alexandrova, A. N. Graphite-supported Pt_n cluster electrocatalysts: major change of active sites as a function of the applied potential. *ACS Catal.* **12**, 14517–14526 (2022).
150. Häkkinen, H., Abbet, S., Sanchez, A., Heiz, U. & Landman, U. Structural, electronic, and impurity-doping effects in nanoscale chemistry: supported gold nanoclusters. *Angew. Chem. Int. Ed. Engl.* **42**, 1297–1300 (2003).
This paper reveals that clusters can occupy a dynamic ensemble of states with varying reactivities.
151. Sun, T. et al. Ferromagnetic single-atom spin catalyst for boosting water splitting. *Nat. Nanotechnol.* **18**, 763–771 (2023).
152. Li, X. et al. Single cobalt atoms anchored on porous N-doped graphene with dual reaction sites for efficient fenton-like catalysis. *J. Am. Chem. Soc.* **140**, 12469–12475 (2018).
153. Boyes, E. D. & Gai, P. L. Visualizing reacting single atoms in chemical reactions: advancing the frontiers of materials research. *MRS Bull.* **40**, 600–609 (2015).
154. Gai, P. L. & Boyes, E. D. Advances in atomic resolution in situ environmental transmission electron microscopy and 1 Å aberration corrected in situ electron microscopy. *Microsc. Res. Tech.* **72**, 153–164 (2009).
155. Gai, P. L., Lari, L., Ward, M. R. & Boyes, E. D. Visualisation of single atom dynamics and their role in nanocatalysts under controlled reaction environments. *Chem. Phys. Lett.* **592**, 355–359 (2014).
156. Mitchell, S. et al. Automated image analysis for single-atom detection in catalytic materials by transmission electron microscopy. *J. Am. Chem. Soc.* **144**, 8018–8029 (2022).
157. Han, L. et al. Modulating single-atom palladium sites with copper for enhanced ambient ammonia electrocatalysis. *Angew. Chem. Int. Ed. Engl.* **60**, 345–350 (2021).
158. Hai, X. et al. Geminal-atom catalysis for cross-coupling. *Nature* <https://doi.org/10.1038/s41586-023-06529-z> (2023).

Acknowledgements

J.Lu acknowledges the support from National Research Foundation, CRP programme (CRP29-2022-0038) and from Agency for Science, Technology and Research (A*STAR) under its MTC IRG Grant (M22K2c0082). S.M. and J.P.-R. acknowledge NCCR Catalysis (No. 180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation. X.L. acknowledges the support from the Natural Science Foundation of Shaanxi Province (No. 2023-JC-QN-0136), 'Young Talent Support Plan' of Xi'an Jiaotong University (No. ND6J026) and Qinchuangyuan High-Level Talent Project (No. QCYRCXM-2022-344). J.Li. acknowledges the financial support from the National Natural Science Foundation of China (Grant No. 22033005), NSFC Center for Single-Atom Catalysis, the National Key Research and Development Project (Grant Nos 2022YFA1503900 and 2022YFA1503000) and the Guangdong Provincial Key Laboratory of Catalysis (No. 2020B121201002). Y.F. acknowledges the financial support from the National Natural Science Foundation of China (No. 22005244) and Fundamental Research Funds for the Central Universities (No. D5000230127).

Author contributions

X.L. and S.M. contributed equally. All authors contributed substantially to the discussion of the content and structure, investigated the literature, wrote, reviewed and edited the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Peer review information *Nature Reviews Chemistry* thanks Aiqin Wang and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

© Springer Nature Limited 2023

¹Department of Environmental Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, China. ²Department of Chemistry, National University of Singapore, Singapore, Singapore. ³Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland. ⁴Department of Chemistry and Engineering Research Center of Advanced Rare-Earth Materials of Ministry of Education, Tsinghua University, Beijing, China. ⁵Department of Chemistry and Guangdong Provincial Key Laboratory of Catalytic Chemistry, Southern University of Science and Technology, Shenzhen, China. ⁶These authors contributed equally: Xinzhe Li, Sharon Mitchell.