ACES Asian Chemical Editorial Society

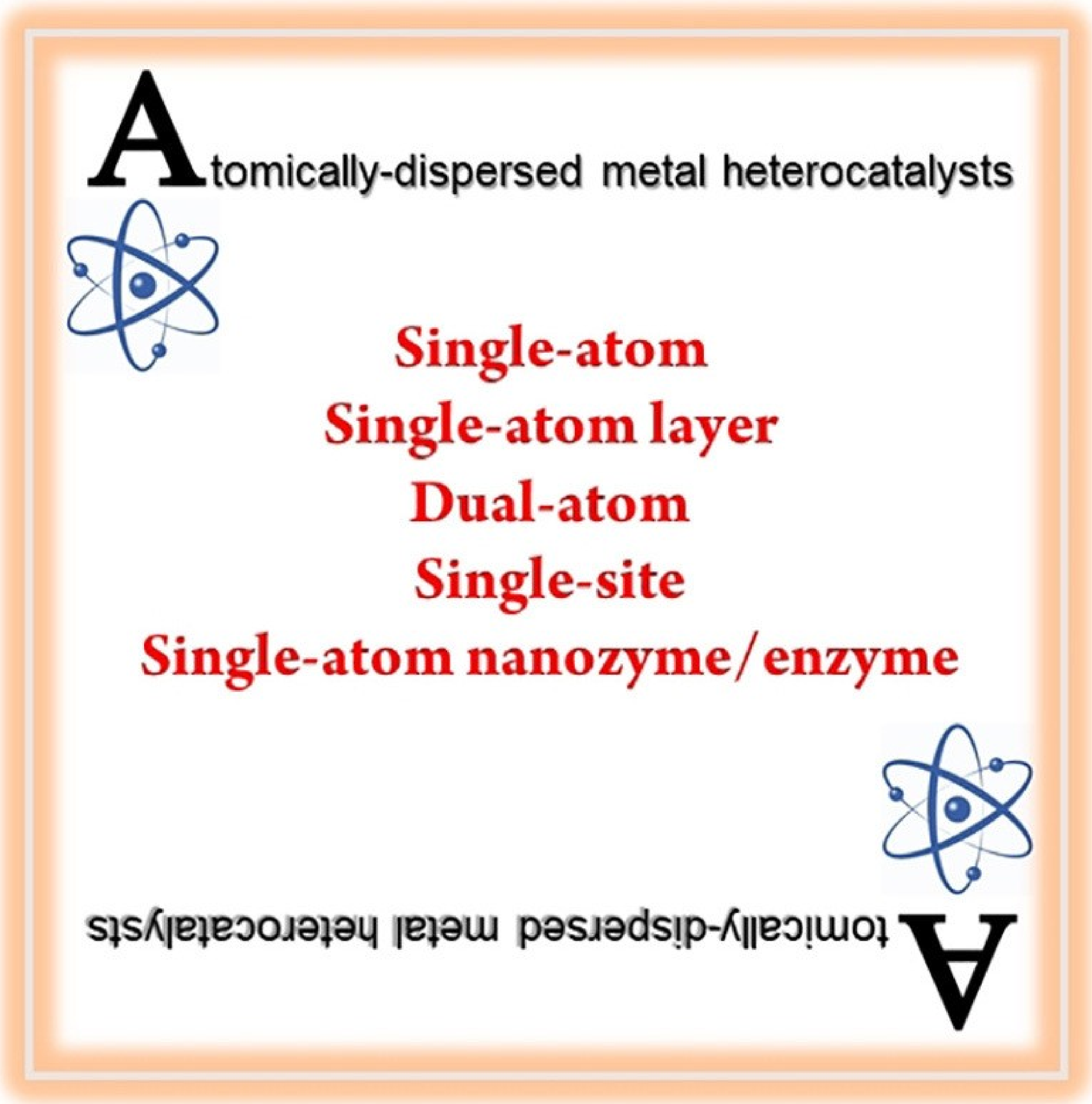
doi.org/10.1002/cnma.202300399

CHEMNANOMAT
Review

www.chemnanomat.org

Atomically-Dispersed Metal Heterocatalysts: A Practical Step Toward Sustainability

Majid Vafaeezadeh*[a] and Werner R Thiel*[a]



Atomically-dispersed heterogeneous metal catalysts can be considered as an "upgraded" version of classical solid metal catalysts. Unlike traditional heterogeneous metallic catalysts that contain nanoparticles or bulk micro-sized transition metal species, the active sites of these novel types of catalysts are atomically distributed on the support's surface. This provides several advantages compared to classical catalysts such as higher activity and need for just very small amounts of metal precursors for the catalyst preparation. The latter issue is a key point in green chemical processes and of importance to achieve low-cost pathways for industrial-scale synthesis. The atomically dispersed metal sites permit a maximum of metal dispersion and additionally allow to achieve more reproducible heterogeneous catalysts. This review summarizes an overview on breakthrough findings in synthesis, applications and characterization techniques developed in the area of single-atom, dual-atom, single-atom-layer, single-site as well as single-atom nanozyme/enzyme catalysis. The characteristics and properties of each system provide an appropriate understanding for designing a nanomaterial that is optimized for a specific requirement.

1. Introduction

Homogeneous catalysts based on soluble metal complexes have traditionally been used in a wide variety of chemical transformations in industries as well as in research laboratories.[1–3] Nevertheless, as a result of the limited abundance and increasing the price of noble metals such as rhodium, palladium, ruthenium, iridium, gold, etc., efforts have been made to immobilize homogeneous (organo)metallic compounds on solid supports to find a way for an easier separation and reusing of the catalysts. However, the resulting heterogenized metal catalysts often did not provide a comparable performances as their homogeneous counterparts. Poor turnover numbers, noticeable leaching of the metal centers, and in consequence contamination of the products with the transition metal were among the difficulties related in using of the initial generation of immobilized catalysts.[4] The mentioned drawbacks were solved to some extent through a covalent immobilization of metal complexes by employing the concept of "chemistry in the interphase".[5] However, the idea of a perfect immobilization of metal catalysts still is not realized properly in these catalysts. For example, in palladium-catalyzed C–C bond formation reactions (i.e. Suzuki, Heck and Sonogashira couplings), in most cases, the immobilized metal complexes convert to the corresponding nanoparticles during the reaction or the catalyst recovery. Although these palladium nanoparticles are still active in the recycled catalyst, only few good economic reasons remain for pursuing the classical immobilization concept using (expensive) metal complexes and carrier materials.

To take more advantage of using supported metal catalysts, one may think to increase the number of surface-loaded metal centers and simultaneously reduce the size of the active species to a sub-nanometer dimension with the aim of employing lower amounts of the expensive metal precursors.[6] Attempts to develop atomically-dispersed metal catalysts led to emerge a new class of heterogeneous nanocatalysts. Conceptually, in such systems only very small amounts of metal precursors are needed. The metal sites are uniformly distributed and robustly fixed on the surface. Such catalysts regularly demonstrate high performances, which are on par with that of molecular catalysts and superior to bulk metals. The ultimate goal in the chemistry of this type of catalysts is to maximize the productivity of each single atom center to achieve more sustainable and cost-effective catalytic chemical transformations. This review highlights pros and cons of the most recent and breakthrough findings related to the preparation and the application of atomically-dispersed heterogeneous catalysts in different classifications including single-atom, single-atom-layer, dual-atom, single-site and single-atom nanozyme/enzyme. In the case of single-atom, dual-atom and single-atom-layer catalysis, most of the recent efforts have been made to design and develop new nanomaterials with distinguished metal atom centers on a relatively bare surface. Alternatively, in single-site catalysis, the employed metal centers are located on isolated sites with their associated ionic or neutral ligand(s), which can induce a dramatic effects in catalytic activity and selectivity. Single-atom nanozyme/enzyme catalytic systems combine the benefit of single-atom catalysts and enzymes or enzyme-mimicked structures to achieve high selectivity and to overcome their intrinsic problems such as poor stability and reusability.

Heterogeneous catalysts based on surface organometallic chemistry (SOMC) are a sub-class of single-site catalysts and have found widespread applications.[7–10] This strategy gives the possibility to prepare various well-defined isolated metallic sites on the surface.[11] Furthermore, it is possible to generate metal-alloy clusters or nanoparticles in close proximity to the isolated metal sites in which the obtained materials show synergistic effects in distinct chemical reactions.[7–11] This goal can be achieved by employing the thermolytic molecular precursor (TMP) approach.[9] However, catalysts based on the SOMC strategy are out of the scope of this review.

2. Single-Atom Catalysis

Shortly after their discovery, single-atom catalysts (SACs) have been developed for various transition metals in the periodic table[12–14] with a wide diversity of host materials and the use of versatile synthetic strategies[15–21] that even work in large scale

---

[a] Dr. M. Vafaeezadeh, Prof. Dr. W. R Thiel
Fachbereich Chemie
RPTU Kaiserslautern-Landau
Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern (Germany)
E-mail: vafaeezadeh@chemie.uni-kl.de
thiel@chemie.uni-kl.de

processes.[22,23] Some notable examples for catalytic applications and characteristics of SACs are summarized in Table 1.[24–37] Single atoms are prone to agglomerate into clusters or nanoparticles through the Ostwald ripening phenomenon.[38] Hence, selection of the host support in SACs is a critical issue. Furthermore, it was found that the coordination environments delivered by the support can have a dramatic effect on the catalytic performance of a single-atom system.[39] For example, the atom-to-nanoparticle transition is an undesirable phenomenon that changes the product distribution of the carbon dioxide hydrogenation on copper catalysts.[40] Methanol was the major product of the CO_2 hydrogenation when single-atom Cu/ZrO_2 is used as the catalyst, while the reaction over copper clusters produced carbon monoxide. Furthermore, large-size copper nanoparticles on the ZrO_2 support showed no catalytic activity for CO_2 conversion at all. However, a point that should be taken into consideration in this context is that SACs do not always show superior activity compared to nano-clusters and nanoparticles.[41] Besides disclosing the described strategies in Table 1, efforts have been made for more simple and general synthetic procedures to prepare SACs. To address this, Hutchings et al. developed the wet impregnation method for the synthesis of a series of SACs with high loading and dispersion onto activated carbon.[42] The employed metal precursors were soluble in an organic solvent, which is a significant technical benefit for the preparation of various SACs.

In general, SACs with relatively weak bonds to the supports have higher intrinsic activity compared to those that are attached on the surface with strong covalent bonds.[43] However, this is a double-edged sword that means active species with relatively weaker interaction (better activity) to the surface of the support suffer from higher leaching of the metallic centers and likely can cause metal agglomerations and products' contaminations with heavy metals. However, there are some interesting reports on the preparation of surface stable and yet active SACs. One protocol describes the preparation of a single-atom platinum catalyst via a temperature-induced phase transition of single-atom Pt/Mn_3O_4 to Pt/Mn_2O_3.[44] It was found that the incorporation of the metal single-atoms into the van der Waals gaps of the 2D materials is a way to achieve an optimum level of both stability and catalytic performance of the intercalated metallic species.[43] Here, the resulting atomic species have higher stability compared to physically adsorbed species. Alternatively, a platinum SAC was prepared by the immobilization of an atomic platinum precursor on the vacancy of $Ti_{3-x}C_2$TyMXene nanosheets.[45] The catalyst was successfully employed for the fixation of carbon dioxide and was used for the *N*-formylation of aniline with CO_2 in the presence of Et_3SiH.[45] Another example of surface-bound ultra-stable and active SAC refers to the synthesis of a platinum SAC in the form of a PtGa–Pb/SiO_2 material, which is applied for propane dehydrogenation.[46] High efficiency accompanied by durability of the material up to 96 h at 600 °C was observed.

Recently, promising progress was achieved for employing SACs in organic synthesis.[47] In 2022, Beller et al. prepared a cheap single-atom iron catalyst based on zeolitic imidazolate frameworks and employed the material for the selective ammoxidation of various alcohols to nitriles (Scheme 1a).[48] The catalyst could be reused for six runs with preservation of its activity. This is a very practical example of using cheap starting materials for the green synthesis of nitriles. A common method for nitrile synthesis with a more expensive strategy is the palladium catalysed cyanation of aryl halides using some highly toxic cyanide sources.[49] In addition, the traditional methods suffers from the deactivation of the palladium catalyst in the presence of the applied cyanide sources.[50]

As shown in Table 1, an iridium SAC was successfully applied as the active component to produce H_2 in a water splitting reaction.[29] However, it was also found that this iridium SAC can efficiently participate in a carbenoid O–H bond insertion reaction (Scheme 1b).[51] Compared to a homogeneous analogue, the catalyst showed higher turnover numbers (TON: 1456 *vs.* 462, respectively).

The oxidation of glucose is an attractive biomass transformation for the synthesis of value-added chemicals such as glucaric acid. A platinum SAC anchored on defective TiO_2 is an illustrative example of how both, the catalyst and the support participate in a catalytic reaction.[52] Interaction of absorbed water on the disordered TiO_2 generates OH radicals as the active species to cleave a hydrogen atom from the C1–H and C1–O–H bonds. On the other hand, the platinum catalyst can selectively perform the oxidation of primary alcohols (Scheme 1c). The whole reaction was carried out in a photoelectrochemical oxidation process.[52]

Majid Vafaeezadeh received his PhD in Chemistry at Sharif University of Technology, Tehran, Iran. In 2018, he joined in the group of Prof. Werner R. Thiel at the RPTU Kaiserslautern-Landau as a postdoctoral researcher financially supported by a Georg Forster Research Fellowship from the Alexander von Humboldt foundation. Currently, he is working as a research scientist in this research group. His current research is the synthesis and applications of heterogeneous nanocatalysts for green chemical transformation.

Werner R. Thiel received his PhD in 1990 in Chemistry at TU München with Wolfgang A. Herrmann. After a postdoctoral fellowship in the group of Didier Astruc at Université de Bordeaux I, he started his academic career back in Munich. In 1997 he habilitated, in 2000 he was appointed associate professor at TU Chemnitz and in 2004 he became full professor at TU Kaiserslautern. Since 2020 he is vice-president for research and technology at this university. His research is focussed on fundamental aspects of homogeneous and single-site heterogeneous catalysis.

Table 1. Summary of key examples of recent findings for the synthesis and applications of SACs.

Elements	Applications	Remarks	Ref.
Ag	Photocatalytic hydrogen evolution	Carbon nitride is used as the support. The effect of the catalyst is due to a reduction of the hydrogen evolution barrier, an improvement of the charge transfer of carbon nitride and an expansion of the range of the light absorption.	[24]
Au	Acetylene hydrochlorination	The catalyst is composed of gold on carbon (Au/C). The activity of the single-site cationic gold species correlates with an adjustment of the ratio of Au(I) vs. Au(III).	[25]
Co	Hydrogen evolution reaction (HER)/ oxygen evolution reaction (OER)	Ruthenium oxide (RuO_2) spheres are used as the support. The single cobalt atoms modify the electronic structure of the surrounding Ru atoms to achieve a better catalytic activity.	[26]
Cu	Electroreduction of CO_2 to acetone	Nitrogen-doped porous carbon is used as the support. Density functional theory (DFT) calculations proposed that copper with four pyrrole N-atoms is the main active site.	[27]
Ga	Electrochemical CO_2 reduction to CO	The support was prepared by the reaction of ZIF-8 with a polymer containing the elements nitrogen, phosphorous, and sulfur.	[28]
Ir	Water splitting reaction for H_2 production under visible light	The single-atom iridium catalyst was immobilized on hematite (α-Fe_2O_3).	[29]
Mo	Oxygen reduction reaction (ORR) and OER	Multilayered porous hollow tubes containing the elements oxygen and sulfur were used as the support. The material showed a high power density and a better cycling stability in a zinc–air battery.	[30]
Nb	Catalytic conversion of lithium polysulfides in Li–S batteries	Nitrogen-doped carbon matrices are used as the support.	[31]
Ni	Electrochemical ORR	The reaction occurs at the solid-liquid electrochemical interface over single-atom nickel active sites.	[32]
Os	HER	Single-atom osmium with local charges ranging from $+0.9$ to $+2.9$ were synthesized. Osmium with a local charge of $+1.3$ showed the best catalytic activity.	[33]
Pd	Ammonia electrosynthesis	The catalyst was prepared by the incorporation of copper into single-atom palladium sites on the surface of a nitrogen-doped carbon material. One major effect of copper on the single-atom palladium is to improve the chemisorption of nitrogen on the palladium surface to reduce the activation energy for the hydrogenation reaction.	[34]
Pt	Selective oxidation of C_2–C_4 polyols to primary carboxylic acids	A platinum SAC was robustly immobilized on hydroxyapatite using the hydrothermal method. The catalyst showed high selectivity for the reaction and high resistance against leaching.	[35]
Rh	Gas-phase ethylene hydroformylation	Rhodium atoms were stabilized on oxygen-defective SnO_2. Excellent turnover frequency ($>100\ h^{-1}$) and selectivity (99%) were achieved.	[36]
V	HER	Single-atom vanadium sites were prepared on the surface of a monolayer tungsten disulfide employing a one-step chemical vapor deposition strategy.	[37]

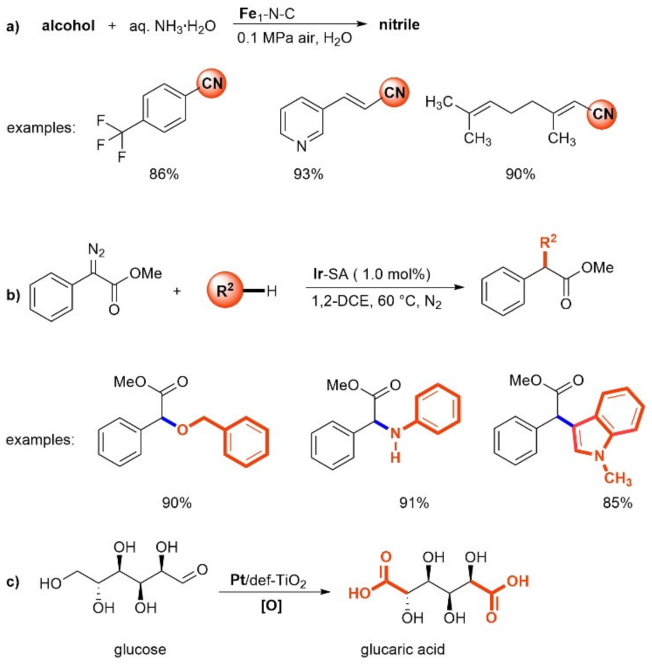
Parallel to the progress in the synthesis and application of SACs, experimental techniques supported by density functional theory (DFT) simulations were developed to visualize their active sites and obtain detailed information on reaction mechanisms.[53] An appealing example for a precise characterization of a SAC that was formed by the deposition of gold adatoms on a Ag(111) surface was reported by Schiffrin et al. in 2022.[54] Note: an adatom is an atom that lies on the surface of a crystal. In this work, the interaction of the gold sites with two molecules of 9,10-dicyanoanthracene (DCA) and the formation of the organometallic species DCA–Au–DCA via C–H bond activation was investigated.

Figure 1a shows an optimized structure of the organometallic *trans* DCA–Au–DCA dimer. The simulated non-contact atomic force microscopy (ncAFM) image corresponds to the optimized structure of the dimer (Figure 1b) and shows very good agreement with the experimental ncAFM image (Figure 1c). Understanding the nature of such C–H bond activation reactions will have significant effect for developing modern organic and organometallic chemistry.

3. Single-Atom-Layer Catalysis

Due to the lack of a universally approved procedure for the preparation of robust and active SACs, fearless increasing the amounts of the metallic precursors during the synthesis with the aim of improving the loading of the metallic centers on a support may cause agglomeration and consequently deactivation of the catalysts. Hence, development of new strategies for improving the activity of SACs is necessary.[55] This can be overcome to some extent by employing an interesting alternative "single-atom alloy catalysts". A single-atom alloy consists of a reactive metallic dopant that is atomically dispersed on the surface of a less reactive support such as gold, silver or copper.[56] Despite remarkable achievements in the synthesis and application of single-atom alloy catalysts,[56–58] this sub-class of SACs suffers from some restrictions such as the use of rather expensive supports[56,59,60] and distinct difficulties in the preparation of *"non-precious"* metal single-atom alloy catalysts.[61]

One improvement in the design of atomically-dispersed catalysts was obtained by covering the surface of the supports with metal layers having a thickness of one-atom-dimeter. Taking the advantages of the support's defect, Lu et al.



Scheme 1. a) Application of single-atom iron catalyst for the selective ammoxidation of various alcohols to nitriles. b) Carbenoid O–H bond insertion reaction using an iridium SAC. c) Photoelectrochemical oxidation of glucose to glucaric acid using a platinum SAC on a defective TiO_2 support.

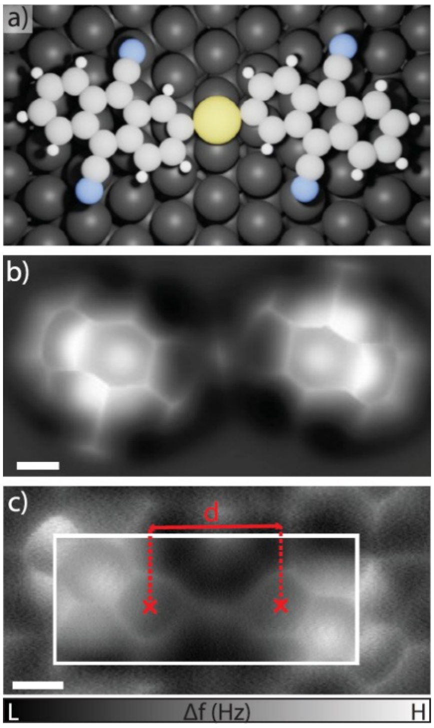


Figure 1. a) Ball and stick model of the structure of DCA–Au–DCA obtained by DFT calculations. b) Simulated ncAFM image of the optimized structure and c) experimental ncAFM image of the DCA–Au–DCA dimer. More details are provided in ref [54]. Reprinted with permission from ref [54]. Copyright 2022 American Chemical Society.

prepared a single-atomic layer of platinum on a defective CeO_2–Al_2O_3 support.[62] Surprisingly, this single-atom-layer catalyst showed an activity up to 70 times higher than a single-atom platinum catalyst in the oxidation of CO to CO_2. Currently, single-atom-layer systems are not as well developed as SACs. However, they should not be overlooked since sometimes they demonstrate not only better performance than SACs, but also are more efficient than a multilayer counterpart. To address the latter point, doping of magnetic cobalt ions into a two-dimensional monolayer of MoS_2 led to a catalyst for the electrochemical hydrogen evolution that has a doubled activity compared to the multilayer one.[63] However, information about the activity of single-atom-layer catalysts is rather limited at the moment and there are no explicit correlations between the numbers of the atomic layers and the catalytic activity.

To address the effect of the numbers of layers on the activity of the catalyst, Doustkhah et al. reported that silicate sheets with six atomic layers of palladium with approximately 1 nm thickness, showed higher activities in the selective dehydrogenation of formic acid for hydrogen production in water compared to isotropic palladium nanoparticles and a single-atom palladium catalyst.[64] Zenobi et al. used tip-enhanced Raman spectroscopy to visualize the active sites of a (sub)monolayer of palladium deposited on the surface of Au(111) with the aim of a better understanding of the reaction mechanism.[65] The results indicated that for the hydrogenation of chloronitrobenzenethiol, the reactive regions are not limited on the palladium regions, but extend up to ~20 nm into the gold regions as a result of hydrogen spillover.[66–70] The catalyst showed higher activity than Pd/Au alloy system.

4. Dual-Atom Catalysis

In an ideal dispersion, all of the atomic centers in a SAC are randomly distributed on the surface with no interaction to the neighboring metal atoms. Interests to upgrade single-atom catalysis with diverse atomic centers led to unveil correlated SACs.[71] In this type of catalyst, there is a spatial correlation among the metal single-atom sites with or without a bridging atom. Correlated SAC having two metal centers are called dual-atom (also known as double-atom) catalysts.[72–74] Dual-atom catalysts (DACs) are introduced in different modes such as two separated heterometallic sites, two linked homometallic sites and two linked heterometallic sites.[75] Each of them has its own electronic characteristics and properties. The synergetic effect between these homo- or heterobimetallic pairs such as orbital coupling of the metal sites in dual-atom catalysis,[76] is a key factor for the improvement of their catalytic performance.[77–79]

One interesting strategy to achieve a DAC is through the structural reconstruction mechanism (Figure 2) from dual-site SACs under OER conditions, which was approved using in situ X-ray absorption spectroscopy.[80] Almost at the same time, Chen et al. discovered that under OER conditions, cobalt, iron and nickel SACs can be converted to double-atom catalysts by e.g. incorporating iron ions from an electrolyte.[81]

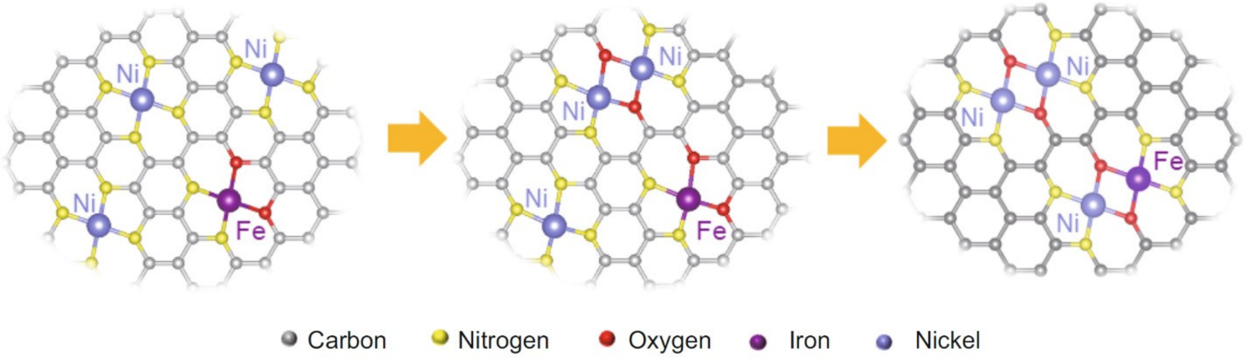


Figure 2. Structural reconstruction of NiFe–CNG (CNG = N-doped graphene nanosheets prepared with glucose) during OER from isolated nickel and iron centers to Ni–O–Fe and Ni–O–Ni moieties. Reprinted and adapted under the terms of a Creative Commons CC-BY 4.0 License from ref [80]. Copyright 2021 Springer Nature.

Further attempts to monitor the synthetic steps from the metal precursor to the DAC disclosed an interesting mechanism. Zhang et al. employed in situ environmental scanning transmission electron microscopy (ESTEM) to analyse the surface of a nickel catalyst for the transition from the metal precursor to the dual-atom nickel catalyst from room temperature (RT) up to 800 °C (Figure 3).[82] In the first step, the nickel precursor converts to nickel nanoparticles at 200 °C. These nanoparticles grow bigger by increasing the temperature up to 500 °C through the Ostwald ripening process.

Further heating the material led to reorganize the bulk metal to the dual-atom system in an atomization process (Figure 3). It was also found that bulk iron could convert to a single-atom iron catalyst at room temperature by employing the electrochemical filtration method.[83]

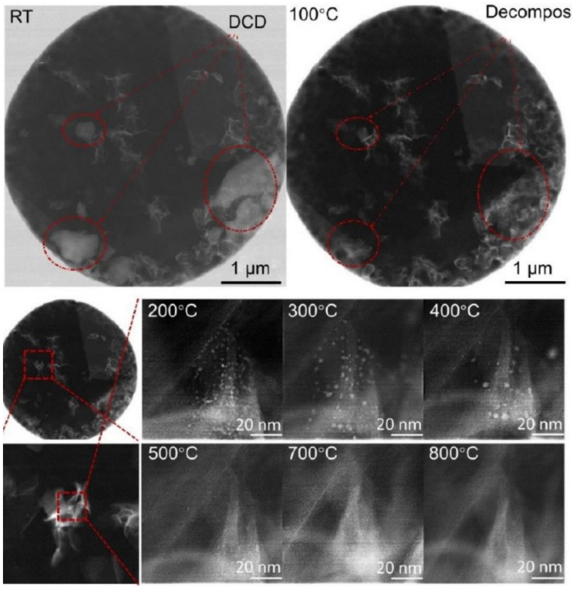


Figure 3. In-situ ESTEM images for the transition from the metal precursor to the dual-atom nickel catalyst from room temperature (RT) up to 800 °C. DCD represents dicyandiamide. Reprinted with permission from ref [82]. Copyright 2022 Springer Nature. The rights in the material are owned by a third party.

There are some examples showing that diatomic centres can persist in combination with isolated mono atomic centers.[84,85] Nevertheless, such a blended SAC/DAC system showed better performance than its single-atom analogue.[85] Similar to the SACs, the supports' characteristics such as the surface state (surface state is the electronic states found at the surface of materials) have significant influence on the catalytic properties of DACs.[86] In electrocatalysis, most of the DACs have demonstrated superior activities compared to single-atom systems.[72] As an example in organic synthesis, a homometallic dual-atom platinum catalyst was used for the hydrogenation of organic compounds such as nitrobenzene and benzaldehyde as well as for the epoxidation of styrene with potential of industrial applications.[79] Compounds composed of three or more metal atoms possessing metal–metal interactions are generally considered as metal clusters.[87]

5. Single-Site Catalysis

This section deals with the synthesis and applications of site-isolated organometallic complexes and molecular catalysts (this type of the catalyst should not be confused with SOMC-based catalysts).[7–11] Organic ligands such as phosphines or *N*-heterocyclic carbenes (NHCs) have a great influence on metal-catalyzed organic synthesis in terms of improving the activity and selectivity of the reaction.[88] However, the preparation of single-/dual-atom catalysts accompanied by an organic ligand is not a simple task. The reason is that most of the established procedures for the synthesis of single-/dual-atom catalysts proceed through a thermal treatment step in which the associated ligands (if any) decompose at the employed temperature. In our opinion, the lack of adequate metal-chiral ligand pairs in SACs and DACs is the major reason that asymmetric organic synthesis based on these catalysts is not developed. Immobilization of metal complexes on the surface of a support is a relatively simple, efficient and well-known approach for the synthesis of single-site catalysts. In these single-site catalysts, each metal-ligand combination can separately be located on the surface of the support as shown in Figure 4a (herein, the

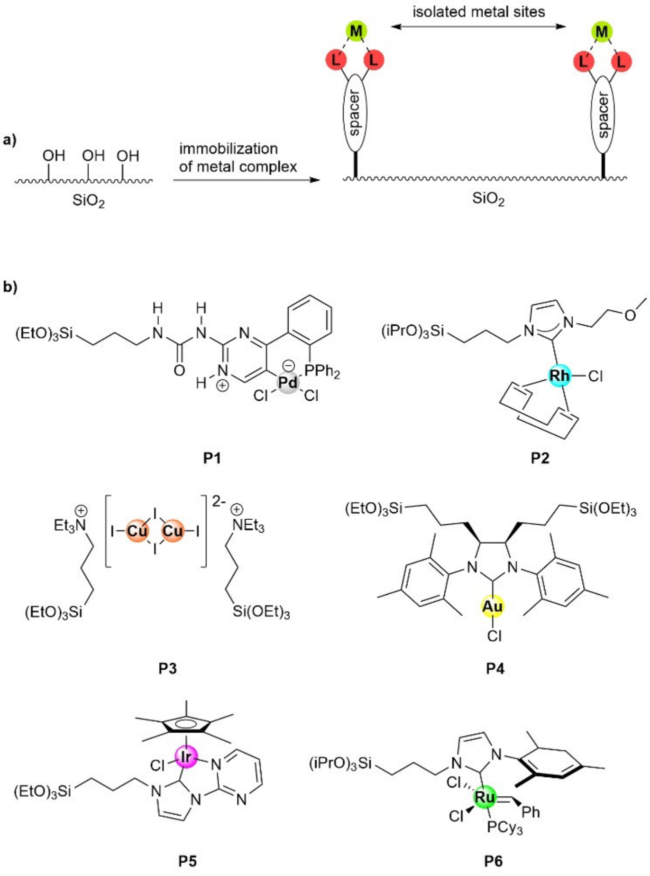
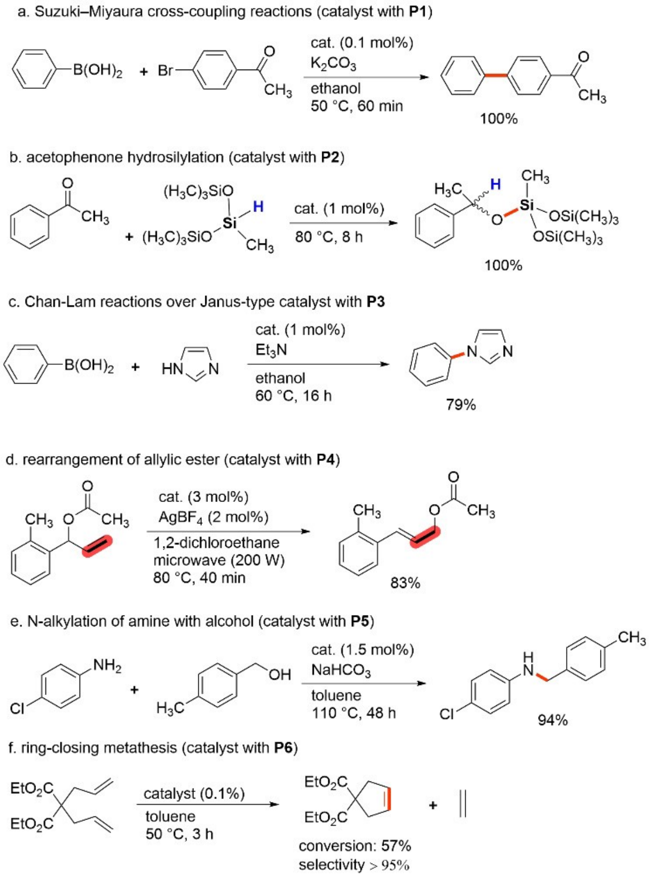


Figure 4. a) Schematic illustration of the site-isolation in immobilized metal complexes (L = ligand). b) Examples of some silane precursors for the immobilization on the surface of silica-based materials to form surface-isolated single-site catalysts.



Scheme 2. Applications of single-site catalysts derived from precursors **P1**–**6**.

supports are mainly mesoporous silica-based materials). Consequently, this class of material can be considered as a member of the atomically-dispersed metal catalysts. A major characteristic of these single-site catalysts is the role of the accompanying ligand on improving activity and stability of the metallic catalyst, while in SACs and DACs, the surface-metal interaction is the important parameter affecting the reaction efficiency.

Some examples of such single-site metal precursors are shown in Figure 4b.[89–94] The final catalysts can be prepared by immobilization of these metal precursors on the surface of porous silica-based material.

The catalysts, which were prepared based on this concept, were successfully participated in various organic reactions. For example, precursor **P1** was prepared and covalently grafted on the surface of SiO_2 and the mesoporous silica MCM-41 and the resulting catalyst was used for Suzuki-Miyaura cross-coupling reactions of iodo- and bromobenzene with phenylboronic acid (Scheme 2a).[89] MCM-41 modified with rhodium precursor **P2** showed excellent activity for acetophenone hydrosilylation, even for the recovered catalyst (Scheme 2b).[90] Recently, we showed that the dinuclear copper complex **P3** immobilized on the surface of a Janus-type material efficiently catalyses various organic transformations such as the copper-catalysed azide–alkyne cycloaddition (CuAAC click reaction) and the Chan-Lam C–N coupling reaction (Scheme 2c).[91] Thanks to the unique anisotropic structure of the employed Janus-type material[95–99] the catalyst shows an excellent compatibility with water, organic solvents as well as with reactions under solvent-free conditions.[91] In another example, a hybrid silica material containing the disilylated *N*-heterocyclic carbene gold complex **P4** was used as an efficient catalyst for the rearrangement of allylic esters and for the cycloisomerization of γ-alkynoic acids (Scheme 2d).[92]

A noticeable feature of immobilized precious metal catalysts is their multiple recycling and reusability that strongly reduces the reaction costs. It was shown that the catalyst that was obtained by the immobilization of precursor **P5** onto the surface of a mesoporous SBA-15 material can be reused twelve times for the *N*-alkylation of amines with alcohol (Scheme 2e).[93] Each reaction run was conducted at 110 °C for 48 hours and the catalyst tolerated such harsh conditions.

Copéret et al. showed that a heterogeneous catalyst containing complex **P6**, which was attached to the surface of a mesostructured silica support with a flexible linker has a high stability.[94] The catalyst is stabilized through the interaction with the surface and hence showed a delayed deactivation. The material was tested for several olefin metathesis reactions such as ring-closing metathesis (Scheme 2f).[94]

Tannic acid is one of the most abundant phenolic compounds in nature. It contains lots of hydroxyl groups on its structure. Taking advantage from chelating properties and the strong surface adhesion of tannic acid, Luo et al. described a general strategy for the preparation of a "single-atom coating" of cobalt catalysts on the surface of different materials such as carbon, TiO_2 and MoS_2.[100] In the first step of the material preparation, tannic acid molecules were reacted with formaldehyde to form a polymer matrix on the surface of the supports followed by chelating the desired metal ions with the resulting materials to form site-isolated metallic centers (Figure 5a). Finally, the material was pyrolyzed in an ammonia atmosphere at 600 °C to realize a nitrogen-doped porous carbon coating. The cobalt SAC on a TiO_2 support, which was prepared according to this method, showed higher activity for the tetracycline photodegradation compared to a simple Co–SAC and a physically mixture of a Co–SAC and TiO_2.

Surface-supported single-site molecular catalysts combine the benefits of both homogeneous and heterogeneous catalysts and hence tracking the interaction between the active sites and the reactant molecules is crucial. For this aim, Burke et al. used scanning tunneling microscopy (STM) and ncAFM to study the interaction between the immobilized Fe–terpyridine (Fe–tpy) with carbon monoxide (CO) and ethylene on a Ag(111) surface.[101] STM and ncAFM images of CO associated with Fe–tpy structures are shown in Figure 5 b–g. They found CO has two types of interaction with the Fe–tpy active sites: a CO prebond (i.e. CO approaching, Figure 5d) and a CO bond mode (Figure 5g). STM images revealed localized curved dark parts at the iron sites related to the Fe–typ interaction with CO for both, the CO bond and prebond modes, though for the CO bond mode, it is brighter (Figure 5b,e). The ncAFM for CO bond mode (Figure 5f) has a longer feature corresponding to the suggested configuration in Figure 5g, while the corresponding distance for CO prebond mode is shortened due to its standing-up configuration on the Ag surface (Figure 5c,d).

Electrochemical conversion of CO_2 into C_{2+} compounds (such as ethanol) is an interesting strategy for fuel production, especially when the reaction's electricity supply can be provided from renewable resources. Copper catalysts are well-known for this transformation by delivering ethylene as a by-product. The reaction selectivity for ethanol production could slightly be improved by doping of some elements such as silver.[102] In an interesting study, Sargent et al. functionalized the copper surface of a Cu/polytetrafluoroethylene electrode with single-site, porphyrin-based complexes containing iron or cobalt.[103] The resulting site-isolated porphyrin-based complexes efficiently catalyzed the conversion of CO_2 to CO. This is favorable to shift the selectivity of the reaction towards ethanol production. Consequently, in this system, the Faradaic efficiency for ethanol reached up to 41 %, which is due to the high local concentration of the produced carbon monoxide intermediate.[103] This work demonstrates an interesting example of a cooperativity between an immobilized single-site molecular catalyst and the catalytically active support.

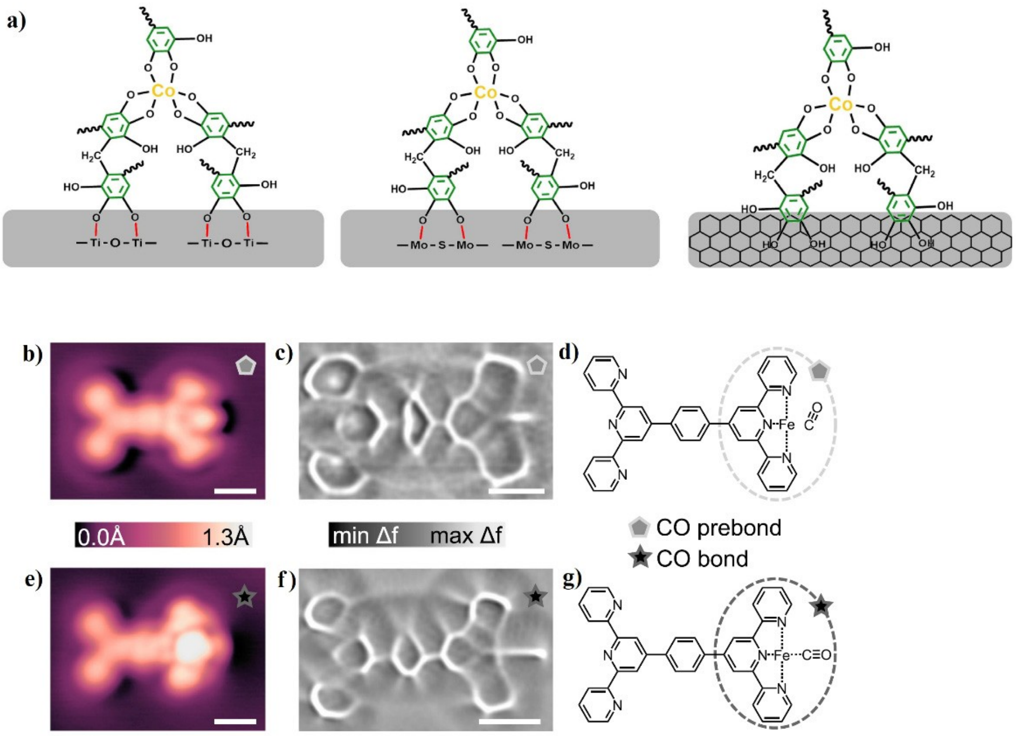


Figure 5. Proposed structure of a single-site Co-tannic acid/formaldehyde polymer on different types of supports. Reprinted and adapted with permission from ref [100]. Copyright 2021 Wiley-VCH. STM (b,e) and ncAFM (c,f) of CO associated Fe–tpy structures and their relevant proposed chemical structures for the CO prebond (d) and CO bond (g) modes. Reprinted and adapted under the terms of a Creative Commons CC-BY 4.0 License from ref [101]. Copyright 2022 Springer Nature.

6. Single-Atom Nanozyme/Enzyme Catalysis

In general, two types of relationships can be considered for the cooperation of single-atom and enzymatic architectures: a single-atom nanozyme and an anchoring of single-atoms on enzymes (single-atom/enzyme complex). Nanozymes – nanomaterials with enzyme-like characteristics – have integrated the advantages of enzymes and nanomaterials by overcoming the intrinsic limitations of enzymes-based catalysts such as high costs and low stabilities in chemical transformations.[104] Recently, the combination of atomically-dispersed metal catalysts and enzymes in the form of either an enzyme-mimicked single-atom nanozyme or single-atom/enzyme combinations attracted increasing attentions, especially in tumor therapy. For briefly addressing, metal-single atom nanozymes containing cobalt or manganese single-atom moieties were successfully employed for tumor treatment via the generation of cytotoxic superoxide and hydroxyl radicals ($^{\bullet}O_2^{-}$ & $^{\bullet}OH$), respectively.[105,106] Recently, the group of Li et al. reported an iron single-atom nanozyme catalyst coordinated to phosphorus and nitrogen atoms (FeN_3P).[107]

The structure of the catalyst is inspired by the similarities of the chemical environments of the enzyme horseradish peroxidase (Figure 6a). As a proof of concept, a comparative activity assessment showed that for the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) with H_2O_2, the specific activity of the FeN_3P single-atom nanozyme is 30 times higher than the activity of the most widely utilized Fe_3O_4 nanozyme catalyst and 10 times higher than the activity of a phosphorous-free FeN_4 single-atom nanozyme (Figure 6b).

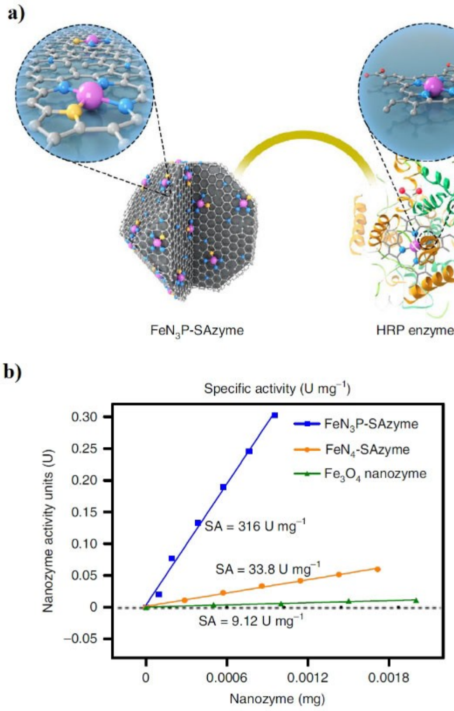


Figure 6. a) The structure of an iron single-atom nanozyme catalyst mimicked from the active Fe center of horseradish peroxidase. b) The results of the TMB oxidation with H_2O_2 using different catalysts. Reprinted and Adapted with permission from ref [107]. Copyright 2021 Springer Nature. The rights in the material are owned by a third party.

Moreover, the material was found to have a catalytic efficiency and selectivity comparable to the natural horseradish peroxidase. In 2022, Ge et al. employed a photochemical method for the fabrication of a stable enzyme–metal hybrid catalyst.[108] Figure 7a shows a general demonstration for the immobilization of a palladium SAC on the surface of an enzyme–polymer compound.

In the first step, the palladium atom attaches to two oxygen atoms of an amino acid of the enzyme. UV irradiation led to the formation of a carbon radical on the surface followed by an attack of the radical species to the palladium center and a removal of the chlorido ligands (Figure 7b). Unlike common examples that utilized rigid supports for the immobilization of metal SACs, the enzyme–polymer support has a relatively flexible configuration and is assumed to act as a semi-heterogeneous SAC. The resulting catalyst was used for the alkyl–alkyl cross-coupling reaction between 1-bromohexane and *B*-n-hexyl-9-BBN (BBN= 9-borabicyclo[3.3.1]nonane). Surprisingly, the turnover frequency of the catalyst was found to be 300 times higher than that of the homogeneous $Pd(OAc)_2$ catalyst with the additional benefit of a catalyst reusability of up to ten times. A note that should be considered here is that the pure enzyme only has a poor binding capability and therefore is not suitable to stabilize metal single atom catalysts.[108]

7. Summary and Outlook

An overview of different forms of atom-size metal catalysts together with their applications was presented here. These types of heterogeneous nanocatalysts have shown excellent flexibility to be involved in different types of supports ranging from non-functionalized materials to organic-inorganic hybrid systems and enzyme(−like) structures. Atom-scaled metal catalysts define a new opportunity in applications of heterogeneous catalysts in green chemical transformations. The authors believe that the nearly forgotten heterogeneous bulk metal

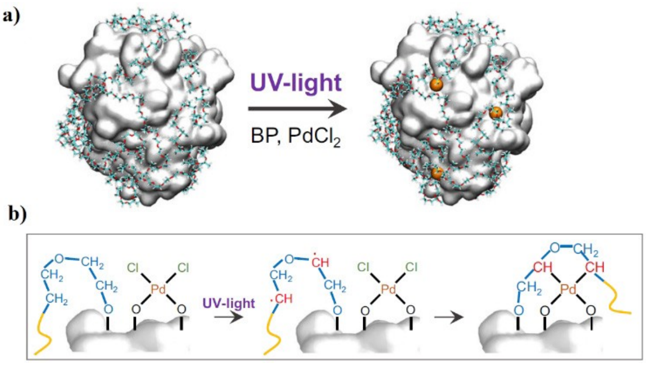


Figure 7. a) Schematic synthesis and b) the mechanism for the synthesis of a palladium-anchored enzyme. Reprinted and adapted under the terms of a Creative Commons CC-BY 4.0 License from ref [108]. Copyright 2022 Springer Nature.

catalysts can be resuscitated by introducing atomically-dispersed metal heterocatalysts. It was discussed that some of the atom-size heterogeneous catalysts have found noticeable improvement in activity compared to homogeneous ones. The most promising atomically-dispersed metal catalysts are those, which bring two properties together: Surface stability and yet high activity of the metal species. These catalysts have found widespread applications in different chemical transformations ranging from gas-phase reactions to various organic syntheses. Nonetheless, some challenges are remaining, for example for the asymmetric organic syntheses with single-atom, dual-atom and single-atom-layer catalysts. One promising solution, which is proposed here, is to prepare atomically-dispersed metal catalysts based on helical mesoporous supports since it was found that an un-functionalized helical material can introduce chirality in some organic transformations.[109] In addition, it was reported that asymmetric synthesis over enzyme-metal single-atom hybrid catalyst could proceed well[110] that is an insightful finding for developing asymmetric synthesis over SACs and other related atom-size catalysts.

Modifying the surface of the self-propelled particles (the particles that consume energy from chemical substances for their movements)[111,112] with atom-size metallic species will be another attractive subject for the future development of atomically dispersed nanocatalysts. In case of single-atom-layer catalysts, it is necessary to provide correlations between the numbers of the atomic layers and the catalytic activity. Furthermore, the effect of a full or a partial coverage of the surface with atomic layers on the reaction efficiency should be taken into account. A successful example of a partial surface coverage is a controllable doping of mono layer metal islands on the surface of MoS_2.[113] While the ultimate goal of the titled concept is to gain the maximum productivity of any single atom, the key question that remains is: can a single atomic site always act as a catalyst? Not always. Some chemical reactions can only proceed with more than one metal atom in the form of metal ensemble catalysts.[114,115]

Prior to the synthesis, various aspects of these materials such as the effect of the surface and of surface functionalities on the target reactions and the intrinsic activity of the metal centers should be carefully explored to select the most appropriate catalytic systems. In general, the discussed atom-sized architectures are sensitive to minor changes in the central metal atoms and in the electronic and steric properties of the supports. In other words, such precise catalytic systems may seriously suffer from reproducibility in their preparation as well as the results of their activity assessments. Hence, achieving general synthetic procedures for SACs, DACs, single-atom-layer and single-atom nanozyme/enzyme systems with well-defined mechanisms and a high degree of reproducibility of the resulting catalysts is still unsolved and thus an open subject of future research.

Like any homogeneous and heterogeneous catalysts, large-scale synthesis of the materials is an important factor that should be considered parallel to the newly established preparation methods. Two important subjects i.e. spillover phenomena and the employment of Janus-type materials may have significant effects on further development of new materials for this family of catalysts.

Overall, atomically-dispersed metal catalyst may not currently be a utopia in catalyst design. In contrast, their exponential progress shows that they have very high potential for further development and rapid spreading into the various chemical transformations with perspective for industrial applications in the near future.

Acknowledgements

We wish to thank the Carl-Zeiss-Stiftung for financial support (project "*Smart batch processes*"). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

This is a review article. For additional data, readers may refer to the original works that are cited in the references section.

Keywords: single-atom catalysts · dual-atom catalysts · single-atom-layer catalysts · single-atom nanozymes · single-site catalysts

[1] Y. G. Shelke, A. Yashmeen, A. V. A. Gholap, S. J. Gharpure, A. R. Kapdi, *Chem. Asian J.* **2018**, *13*, 2991–3013.
[2] T. A. Bender, J. A. Dabrowski, M. R. Gagné, *Nat. Chem. Rev.* **2018**, *2*, 35–46.
[3] A. Kumar, P. Daw, D. Milstein, *Chem. Rev.* **2022**, *122*, 385–441.
[4] S. Hübner, J. G. de Vries, V. Farina, *Adv. Synth. Catal.* **2016**, *358*, 3–25.
[5] E. Lindner, T. Schneller, F. Auer, H. A. Mayer, *Angew. Chem. Int. Ed.* **1999**, *38*, 2154–2174.
[6] Z. W. Chen, L. X. Chen, C. C. Yang, Q. Jiang, *J. Mater. Chem. A* **2019**, *7*, 3492–3515.
[7] C. Copéret, *Nat. Energy* **2019**, *4*, 1018–1024.
[8] L. Rochlitz, K. Searles, J. Alfke, D. Zemlyanov, O. V. Safonova, C. Copéret, *Chem. Sci.* **2020**, *11*, 1549–1555.
[9] C. Copéret, *Acc. Chem. Res.* **2019**, *52*, 1697–1708.
[10] E. Lam, G. Noh, K. Larmier, O. V. Safonova, C. Copéret, *J. Catal.* **2021**, *394*, 266–272.
[11] A. H. Mason, A. Motta, A. Das, Q. Ma, M. J. Bedzyk, Y. Kratish, T. J. Marks, *Nat. Commun.* **2022**, *13*, 7187.
[12] L. Han, H. Cheng, W. Liu, H. Li, P. Ou, R. Lin, H. Wang, C. Pao, A. R. Head, C. Wang, X. Tong, C. Sun, W. Pong, J. Luo, J. Zheng, H. Xin, *Nat. Mater.* **2022**, *21*, 681–688.
[13] P. Kumar, T. A. Al-Attas, J. Hu, M. G. Kibria, *ACS Nano* **2022**, *16*, 8557–8618.
[14] Y. Wang, F. Chu, J. Zang, Q. Wang, T. Naren, Y. Li, Y. Cheng, Y. Lei, F. Wu, *ACS Nano* **2021**, *15*, 210–239.
[15] S. Mitchell, E. Vorobyeva, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2018**, *57*, 15316–15329.
[16] A. Wang, J. Li, T. Zhang, *Nat. Chem. Rev.* **2018**, *2*, 65–81.
[17] X. Liang, N. Fu, S. Yao, Z. Li, Y. Li, *J. Am. Chem. Soc.* **2022**, *144*, 18155–18174.
[18] S. Ji, Y. Chen, X. Wang, Z. Zhang, D. Wang, Y. Li, *Chem. Rev.* **2020**, *120*, 11900–11955.

[19] W. Zheng, R. Zhu, H. Wu, T. Ma, H. Zhou, M. Zhou, C. He, X. Liu, S. Li, C. Cheng, *Angew. Chem. Int. Ed.* **2022**, *61*, e202208667.
[20] A. Iemhoff, M. Vennewald, R. Palkovits, *Angew. Chem. Int. Ed.* **2023**, *62*, e202212015.
[21] X. Fu, X. Zhao, T. Lu, M. Yuan, M. Wang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202219242.
[22] Q. Sun, W. Ren, Y. Zhao, C. Zhao, *Chem. Commun.* **2021**, *57*, 1514–1517.
[23] H. Yang, L. Shang, Q. Zhang, R. Shi, *Nat. Commun.* **2019**, *10*, 4585.
[24] X. Jiang, L. Zhang, H. Liu, D. Wu, F. Wu, L. Tian, L. Liu, J. Zou, S. Luo, B. Chen, *Angew. Chem. Int. Ed.* **2020**, *59*, 23112–23116.
[25] G. Malta, S. A. Kondrat, S. J. Freakley, C. J. Davies, L. Lu, S. Dawson, A. Thetford, E. K. Gibson, D. J. Morgan, W. Jones, P. P. Wells, P. Johnston, C. R. A. Catlow, C. J. Kiely, G. J. Hutchings, *Science* **2017**, *355*, 1399–1403.
[26] K. Shah, R. Dai, M. Mateen, Z. Hassan, Z. Zhuang, C. Liu, M. Israr, W. Cheong, B. Hu, R. Tu, C. Zhang, X. Chen, Q. Peng, C. Chen, Y. Li, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114951.
[27] K. Zhao, X. Nie, H. Wang, S. Chen, X. Quan, H. Yu, W. Choi, G. Zhang, B. Kim, J. G. Chen, *Nat. Commun.* **2020**, *11*, 2455.
[28] Z. Zhang, J. Zhu, S. Chen, W. Sun, D. Wang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215136.
[29] Q. Guo, Q. Zhao, R. Crespo-Otero, D. D. Tommaso, J. Tang, S. D. Dimitrov, M. Titirici, X. Li, A. B. J. Sobrido, *J. Am. Chem. Soc.* **2023**, *145*, 1686–1695.
[30] Y. Zhao, Z. Zhang, L. Liu, Y. Wang, T. Wu, W. Qin, S. Liu, B. Jia, H. Wu, D. Zhang, X. Qu, G. Qi, E. P. Giannelis, M. Qin, S. Guo, *J. Am. Chem. Soc.* **2022**, *144*, 20571–20581.
[31] Y. Zhang, C. Kang, W. Zhao, Y. Song, J. Zhu, H. Huo, Y. Ma, C. Du, P. Zuo, S. Lou, G. Yin, *J. Am. Chem. Soc.* **2023**, *145*, 1728–1739.
[32] H. Su, W. Zhou, H. Zhang, W. Zhou, X. Zhao, Y. Li, M. Liu, W. Cheng, Q. Liu, *J. Am. Chem. Soc.* **2020**, *142*, 12306–12313.
[33] D. Cao, H. Xu, H. Li, C. Feng, J. Zeng, D. Cheng, *Nat. Commun.* **2022**, *13*, 5843.
[34] L. Han, Z. Ren, P. Ou, H. Cheng, N. Rui, L. Lin, X. Liu, L. Zhou, J. Song, J. Sun, J. Luo, H. L. Xin, *Angew. Chem. Int. Ed.* **2021**, *60*, 345–350.
[35] H. Yan, M. Zhao, X. Feng, S. Zhao, X. Zhou, S. Li, M. Zha, F. Meng, X. Chen, Y. Liu, D. Chen, N. Yan, C. Yang, *Angew. Chem. Int. Ed.* **2022**, *61*, e202116059.
[36] M. G. Farpón, W. Henao, P. N. Plessow, E. Andrés, R. Arenal, C. Marini, G. Agostini, F. Studt, G. Prieto, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214048.
[37] A. Han, X. Zhou, X. Wang, S. Liu, Q. Xiong, Q. Zhang, L. Gu, Z. Zhuang, W. Zhang, F. Li, D. Wang, L. Li, Y. Li, *Nat. Commun.* **2021**, *12*, 709.
[38] A. K. Datye, H. Guo, *Nat. Commun.* **2021**, *12*, 895.
[39] W. Lai, H. Wang, L. Zheng, Q. Jiang, Z. Yan, L. Wang, H. Yoshikawa, D. Matsumura, Q. Sun, Y. Wang, Q. Gu, J. Wang, H. Liu, S. Chou, S. Dou, *Angew. Chem. Int. Ed.* **2020**, *59*, 22171–22178.
[40] H. Zhao, R. Yu, S. Ma, K. Xu, Y. Chen, K. Jiang, Y. Fang, C. Zhu, X. Liu, Y. Tang, L. Wu, Y. Wu, Q. Jiang, P. He, Z. Liu, L. Tan, *Nat. Catal.* **2022**, *5*, 818–831.
[41] M. D. Rossell, F. J. Caparrós, I. Angurell, G. Muller, J. Llorca, M. Seco, O. Rossell, *Catal. Sci. Technol.* **2016**, *6*, 4081–4085.
[42] X. Sun, S. R. Dawson, T. E. Parmentier, G. Malta, T. E. Davies, Q. He, L. Lu, D. J. Morgan, N. Carthey, P. Johnston, S. A. Kondrat, S. J. Freakley, C. J. Kiely, G. J. Hutchings, *Nat. Catal.* **2020**, *12*, 560–567.
[43] H. Jiang, W. Yang, M. Xu, E. Wang, Y. Wei, W. Liu, X. Gu, L. Liu, Q. Chen, P. Zhai, X. Zou, P. M. Ajayan, W. Zhou, Y. Gong, *Nat. Commun.* **2022**, *13*, 6863.
[44] D. Yan, J. Chen, H. Jia, *Angew. Chem. Int. Ed.* **2020**, *59*, 13562–13567.
[45] D. Zhao, Z. Chen, W. Yang, S. Liu, X. Zhang, Y. Yu, W. Cheong, L. Zheng, F. Ren, G. Ying, X. Cao, D. Wang, Q. Peng, G. Wang, C. Chen, *J. Am. Chem. Soc.* **2019**, *141*, 4086–4093.
[46] Y. Nakaya, J. Hirayama, S. Yamazoe, K. Shimizu, S. Furukawa *Nat. Commun.* **2020**, *11*, 2838.
[47] V. B. Saptal, V. Ruta, M. A. Bajada, G. Vilé, *Angew. Chem. Int. Ed.* **2023**, *62*, e202219306.
[48] K. Sun, H. Shan, H. Neumann, G. Lu, M. Beller, *Nat. Commun.* **2022**, *13*, 1848.
[49] P. Anbarasan, T. Schareina, M. Beller, *Chem. Soc. Rev.* **2011**, *40*, 5049–5067.
[50] S. Erhardt, V. V. Grushin, A. H. Kilpatrick, S. A. Macgregor, W. J. Marshall, D. C. Roe, *J. Am. Chem. Soc.* **2008**, *130*, 4828–4845.
[51] J. Zhao, S. Ji, C. Guo, H. Li, J. Dong, P. Guo, D. Wang, Y. Li, F. D. A. Toste, *Nat. Catal.* **2021**, *4*, 523–531.
[52] Z. Tian, Y. Da, M. Wang, X. Dou, X. Cui, J. Chen, R. Jiang, S. Xi, B. Cui, Y. Luo, H. Yang, Y. Long, Y. Xiao, Chen, *Nat. Commun.* **2023**, *14*, 142.
[53] A. J. Therrien, A. J. R. Hensley, M. D. Marcinkowski, R. Zhang, F. R. Lucci, B. Coughlin, A. C. Schilling, J. McEwen, E. C. H. Sykes, *Nat. Catal.* **2018**, *1*, 192–198.
[54] B. Lowe, J. Hellerstedt, A. Matěj, P. Mutombo, D. Kumar, M. Ondráček, P. Jelinek, A. Schiffrin, *J. Am. Chem. Soc.* **2022**, *144*, 21389–21397.
[55] H. Zhang, X. Jin, J. Lee, X. Wang, *ACS Nano* **2022**, *16*, 17572–17592.
[56] R. T. Hannagan, G. Giannakakis, M. Flytzani-Stephanopoulos, E. C. H. Sykes, *Chem. Rev.* **2020**, *120*, 12044–12088.
[57] R. T. Hannagan, G. Giannakakis, R. Réocreux, J. Schumann, J. Finzel, Y. Wang, A. Michaelides, P. Deshlahra, P. Christopher, M. Flytzani-Stephanopoulos, M, Stamatakis, E. C. H. Sykes, *Science* **2021**, *372*, 1444–1447.
[58] K. Ji, M. Xu, S. Xu, Y. Wang, R. Ge, X. Hu, X. Sun, H. Duan, *Angew. Chem. Int. Ed.* **2022**, *61*, e202209849.
[59] M. Ouyang, K. G. Papanikolaou, A. Boubnov, A. S. Hoffman, G. Giannakakis, S. R. Bare, M. Stamatakis, M. Flytzani-Stephanopoulos, E. C. H. Sykes, *Nat. Commun.* **2021**, *12*, 1549.
[60] Y. Jiang, Y. Ding, F. Li, S. Yin, D. Li, X. Li, Y. Chen, *J. Mater. Chem. A* **2022**, *10*, 24701–24707.
[61] J. Mao, J. Yin, J. Pei, D. Wang, Y. Li, *Nano Today* **2020**, *34*, 100917.
[62] S. Xie, L. Liu, Y. Lu, C. Wang, S. Cao, W. Diao, J. Deng, W. Tan, L. Ma, S. N. Ehrlich, Y. Li, Y. Zhang, K. Ye, H. Xin, *J. Am. Chem. Soc.* **2022**, *144*, 21255–21266.
[63] H. Duan, C. Wang, G. Li, H. Tan, W. Hu, L. Cai, W. Liu, N. Li, Q. Ji, Y. Wang, Y. Lu, W. Yan, F. Hu, W. Zhang, Z. Sun, Z. Qi, L. Song, S. Wei, *Angew. Chem. Int. Ed.* **2021**, *60*, 7251–7258.
[64] E. Doustkhah, N. Tsunoji, M. H. N. Assadi, Y. Ide, *Adv. Mater. Interfaces* **2023**, *10*, 2202368.
[65] H. Yin, L. Zheng, W. Fang, Y. Lai, N. Porenta, G. Goubert, H. Zhang, H. Su, B. Ren, J. O. Richardson, J. Li, R. Zenobi, *Nat. Catal.* **2020**, *3*, 834–842.
[66] A. Xiong, Z. Gao, Y. Qin, *ACS Catal.* **2021**, *11*, 3159–3172.
[67] J. Park, S. Lee, H. Kim, A. Cho, S. Kim, Y. Ye, J. W. Han, H. Lee, J. H. Jang, J. Lee, *Angew. Chem. Int. Ed.* **2019**, *58*, 16038–16042.
[68] A. J. Lachawiec, Jr., G. Qi, R. T. Yang, *Langmuir* **2005**, *21*, 11418–11424.
[69] W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, J. A. van Bokhoven, *Nature* **2017**, *541*, 68–71.
[70] J. Im, H. Shin, H. Jang, H. Kim, M. Choi, *Nat. Commun.* **2014**, *5*, 3370.
[71] J. Shan, C. Ye, Y. Jiang, M. Jaroniec, Y. Zheng, S. Qiao, *Sci. Adv.* **2022**, *8*, eabo0762.
[72] R. Li, D. Wang, *Adv. Energy Mater.* **2022**, *12*, 2103564.
[73] H. Liu, H. Rong, J. Zhang, *ChemSusChem* **2022**, *15*, e202200498.
[74] L. Wang, Y. Li, H. Wang, T. Yang, Y. Luo, S. Lee, M. G. Kim, T. T. T. Nga, C. Dong, H. Lee, *ACS Nano* **2023**, *17*, 7406–7416.
[75] L. Li, K. Yuan, Y. Chen, *Acc. Mater. Res.* **2022**, *3*, 584–596.
[76] Y. Wang, B. J. Park, V. K. Paidi, R. Huang, Y. Lee, K. Noh, K. Lee, J. W. Han, *ACS Energy Lett.* **2022**, *7*, 640–649.
[77] L. Pan, J. Wang, F. Lu, Q. Liu, Y. Gao, Y. Wang, J. Jiang, C. Sun, J. Wang, X. Wang, *Angew. Chem. Int. Ed.* **2023**, *62*, e202216835.
[78] Z. Yu, C. Si, A. P. LaGrow, Z. Tai, W. A. Caliebe, A. Tayal, M. J. Sampaio, J. P. S. Sousa, I. Amorim, A. Araujo, L. Meng, J. L. Faria, J. Xu, B. Li, L. Liu, *ACS Catal.* **2022**, *12*, 9397–9409.
[79] S. Tian, B. Wang, W. Gong, Z. He, Q. Xu, W. Chen, Q. Zhang, Y. Zhu, J. Yang, Q. Fu, C. Chen, Y. Bu, L. Gu, X. Sun, H. Zhao, D. Wang, Y. Li, *Nat. Commun.* **2021**, *12*, 3181.
[80] W. Wan, Y. Zhao, S. Wei, C. A. Triana, J. Li, A. Arcifa, C. S. Allen, R. Cao, G. R. Patzke, *Nat. Commun.* **2021**, *12*, 5589.
[81] L. Bai, C. Hsu, D. T. L. Alexander, H. M. Chen, X. Hu, *Nat. Energy* **2021**, *6*, 1054–1066.
[82] Q. Hao, H. Zhong, J. Wang, K. Liu, J. Yan, Z. Ren, N. Zhou, X. Zhao, H. Zhang, D. Liu, X. Liu, L. Chen, J. Luo, X. Zhang, *Nat. Synth.* **2022**, *1*, 719–728.
[83] Z. Wang, J. Yang, J. Cao, W. Chen, G. Wang, F. Liao, X. Zhou, F. Zhou, R. Li, Z. Yu, G. Zhang, X. Duan, Y. Wu, *ACS Nano* **2020**, *14*, 6164–6172.
[84] T. Gu, D. Zhang, Y. Yang, C. Peng, D. Xue, C. Zhi, M. Zhu, J. Liu, *Adv. Funct. Mater.* **2023**, *33*, 2212299.
[85] F. Huang, M. Peng, Y. Chen, X. Cai, X. Qin, N. Wang, D. Xiao, L. Jin, G. Wang, X. Wen, H. Liu, D. Ma, *J. Am. Chem. Soc.* **2022**, *144*, 18485–18493.
[86] W. Yang, Z. Jia, B. Zhou, L. Wei, Z. Gao, H. Li, *Commun. Chem.* **2023**, *6*, 6.
[87] E. Fernández, M. Boronat, *J. Phys. Condens. Matter.* **2019**, *31*, 013002.

[88] I. J. S. Fairlamb, J. M. Lynam, in book: *Organometallic Chemistry*. RSC Publishing, **2009**, [https://doi.org/10.1039/9781847551030].
[89] S. Farsadpour, L. T. Ghoochany, S. Shylesh, G. Dörr, A. Seifert, S. Ernst, W. R. Thiel, *ChemCatChem* **2012**, *4*, 401–407.
[90] G. Lázaro, M. Iglesias, F. J. Fernández-Alvarez, P. J. S. Miguel, J. J. Pérez-Torrente, L. A. Oro, *ChemCatChem* **2013**, *5*, 1133–1141.
[91] M. Vafaeezadeh, J. Schaumlöffel, A. Lösch, A. De Cuyper, W. R. Thiel, *ACS Appl. Mater. Interfaces* **2021**, *13*, 33091–33101.
[92] M. Ferré, X. Cattoën, M. W. C. Man, R. Pleixats, *ChemCatChem* **2016**, *8*, 2824–2831.
[93] D. Wang, X. Guo, C. Wang, Y. Wang, R. Zhong, X. Zhu, L. Cai, Z. Gao, X. Hou, *Adv. Synth. Catal.* **2013**, *355*, 1117–1125.
[94] M. K. Samantaray, J. Alauzun, D. Gajan, S. Kavitake, A. Mehdi, L. Veyre, M. Lelli, A. Lesage, L. Emsley, C. Copéret, C. Thieuleux, *J. Am. Chem. Soc.* **2013**, *135*, 3193–3199.
[95] D. Dedovets, Q. Li, L. Leclercq, V. Nardello-Rataj, J. Leng, S. Zhao, M. Pera-Titus, *Angew. Chem. Int. Ed.* **2022**, *61*, e202107537.
[96] W. Xue, H. Yang, Z. Du, *Langmuir* **2017**, *33*, 10283–10290.
[97] L. Ni, C. Yu, Q. Wei, D. Liu, J. Qiu, *Angew. Chem. Int. Ed.* **2022**, *61*, e202115885.
[98] M. Vafaeezadeh, W. R. Thiel, *Angew. Chem. Int. Ed.* **2022**, *61*, e202206403; *Angew. Chem.* **2022**, *134*, e202206403.
[99] Y. Liu, J. Wang, Y. Shao, R. Deng, J. Zhu, Z. Yang, *Prog. Mater. Sci.* **2022**, *124*, 100888.
[100] H. Wang, X. Li, Y. Jiang, M. Li, Q. Xiao, T. Zhao, S. Yang, C. Qi, P. Qiu, J. Yang, Z. Jiang, W. Luo, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200465.
[101] M. DeJong, A. J. A. Price, E. Mårsell, G. Tom, G. D. Nguyen, E. R. Johnson, S. A. Burke, *Nat. Commun.* **2022**, *13*, 7407.
[102] T. T. H. Hoang, S. Verma, S. Ma, T. T. Fister, J. Timoshenko, A. I. Frenkel, P. J. A. Kenis, A. A. Gewirth, *J. Am. Chem. Soc.* **2018**, *140*, 5791–5797.
[103] F. Li, Y. C. Li, Z. Wang, J. Li, D. Nam, Y. Lum, M. Luo, X. Wang, A. Ozden, S. Hung, B. Chen, Y. Wang, J. Wicks, Y. Xu, Y. Li, C. M. Gabardo, C. Dinh, Y. Wang, T. Zhuang, D. Sinton, E. H. Sargent, *Nat. Catal.* **2020**, *3*, 75–82.
[104] L. Jiao, H. Yan, Y. Wu, W. Gu, C. Zhu, D. Du, Y. Lin, *Angew. Chem. Int. Ed.* **2020**, *59*, 2565–2576.
[105] S. Cai, J. Liu, J. Ding, Z. Fu, H. Li, Y. Xiong, Z. Lian, R. Yang, C. Chen, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204502.
[106] Y. Zhu, W. Wang, J. Cheng, Y. Qu, Y. Dai, M. Liu, J. Yu, C. Wang, H. Wang, S. Wang, C. Zhao, Y. Wu, Y. Liu, *Angew. Chem. Int. Ed.* **2021**, *60*, 9480–9488.
[107] S. Ji, B. Jiang, H. Hao, Y. Chen, J. Dong, Y. Mao, Z. Zhang, R. Gao, W. Chen, R. Zhang, Q. Liang, H. Li, S. Liu, Y. Wang, Q. Zhang, L. Gu, D. Duan, M. Liang, D. Wang, X. Yan, Y. Li, *Nat. Catal.* **2021**, *4*, 407–417.
[108] X. Li, Y. Cao, K. Luo, L. Zhang, Y. Bai, J. Xiong, R. N. Zare, J. Ge, *Nat. Commun.* **2022**, *13*, 2189.
[109] M. Vafaeezadeh, W. R. Thiel, *Chem. Eur. J.* **2023**, *29*, e202204005.
[110] X. Li, Y. Cao, J. Xiong, J. Li, H. Xiao, X. Li, Q. Gou, J. Ge, *Chin. J. Catal.* **2023**, *44*, 139–145.
[111] Y. Ye, J. Luan, M. Wang, Y. Chen, D. A. Wilson, F. Peng, Y. Tu, *Chem. Eur. J.* **2019**, *25*, 8663–8680.
[112] C. Zhou, L. Yang, Y. Wu, M. Yang, Q. He, *Chem. Eur. J.* **2022**, *28*, e202202319.
[113] X. Li, S. Han, Z. Qiao, X. Zeng, D. Cao, J. Chen, *Chem. Eng. J.* **2023**, *453*, 139803.
[114] Y. Guo, M. Wang, Q. Zhu, D. Xiao, D. Ma, *Nat. Catal.* **2022**, *5*, 766–776.
[115] H. Jeong, S. Shin, H. Lee, *ACS Nano* **2020**, *14*, 14355–14374.

Manuscript received: August 29, 2023
Accepted manuscript online: September 15, 2023
Version of record online: October 16, 2023