Strategies for Stabilizing Atomically Dispersed Metal Catalysts

Ruixuan Qin, Pengxin Liu, Gang Fu, and Nanfeng Zheng*

Atomically dispersing metal atoms on supports provides an ideal strategy for maximizing metal utilization for catalysis, which is particularly important for fabricating cost-effective catalysts based on Earth-scarce metals. However, due to the high surface energy and thus instability of single atoms, it remains challenging to fabricate stable atomically dispersed metal catalysts. Here, strategies for stabilizing atomically dispersed metal catalysts on various supports are summarized. Based on strategies to enhance the interaction between the metal and the support to prevent the sintering of metal atoms, several approaches to stabilize supported atomically dispersed metal catalysts are then extensively discussed. To close, the importance of the interface species surrounding single atoms in determining the catalytic properties of atomically dispersed metal catalysts is discussed, together with a summary of the prospects for the development of the field.

1. Introduction

Catalysts play important roles in the chemical industry; nearly 80% of chemicals are produced based on catalytic processes. Typically, catalysts are classified into three types, namely homogeneous catalysts, heterogeneous catalysts, and biocatalysts (i.e., enzymes). Both homogeneous catalysts and biocatalysts usually consist of metal centers surrounded by various ligands or protein matrices with well-defined coordination environments. In these cases, the catalytic performances (activity and selectivity) can be readily regulated through ligand design or bioengineering. However, the poor stability of both homogenous catalysts and biocatalysts largely restricts their applications.

In heterogeneous metal catalysts, metal species are often deposited on supports with high surface areas to enhance both metal utilization and their chemical/thermal stability. A typical conventional approach to prepare supported metal catalysts involves the deposition of metal precursors on supports by impregnation (IMP), co-precipitation, or deposition–precipitation, followed by calcination and/or reduction.[1] Unfortunately, supported metal catalysts made by these conventional methods usually consist of ill-defined catalytic sites such that the reaction may undergo different catalytic pathways at different sites with different structural features.[2] The catalytic performance of a typical supported metal catalyst depends on numerous parameters, such as the composition, size, and shape of the metal nanoparticles, the nature of the supports, and the metal–support interactions, making it highly challenging to identify the catalytic site and thus simultaneously achieve high activity and high selectivity.[3] That is to say, conventional heterogeneous metal catalysts are still far away from the requirement of green chemistry, in which the reaction selectivity is crucial. Atomically dispersed metal catalysts have attracted more and more attention as they have maximal atomic utilization as well as uniform coordination environments, thus providing an ideal model for mechanistic investigation.[4] However, isolated metal atoms have extremely high surface energy so that they tend to aggregate to form nanoparticles, especially under harsh preparation or catalysis conditions.[5]

During the past decades, several strategies have been developed to stabilize single-site metal catalysts on various supports. As shown in **Figure 1**, anchoring organometallic catalysts onto the surface of supports through organic linkers or weak interactions (e.g., hydrogen bonds and electrostatic interactions) and encapsulating organometallics in the micropores of the support represent two early approaches to immobilize single-atom metal catalysts and thus enhance their stabilities for catalysis. The metal centers of the catalysts prepared by these two methods do not have direct interactions with supports. The knowledge learned from homogeneous catalysts can be easily migrated into heterogeneous systems. Since there have been already nice review articles on heterogenized organometallic catalysts,[6] these early-studied catalysts are not included in the scope here. Readers should also refer to some excellent reviews in the literature for a more comprehensive view on atomically dispersed metal catalysts.[7] Here, we mainly discuss how to stabilize single metal atoms on supports through direct chemical interactions and focus on the following three different classes of atomically dispersed catalysts:

(i) *Surface-Dispersed Mononuclear Organometallic Catalysts*: Metal centers in this class of catalysts are co-stabilized by both supports and organic ligands. To prepare this type of catalysts, mononuclear organometallic catalysts with labile ligands are usually used as precursors to allow the direct deposition of catalytic metal atoms onto oxide supports through metal–oxygen interactions. The easy reaction between the labile ligands on the organometallic precursors and the

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surface —OH groups on the supports is the main driving force for the deposition, thus often leading to the presence of less-labile ligands on the isolated metal centers.

(ii) *Micropore-Confined Single-Metal-Atom Catalysts*: In this class of catalysts, micropores are used to confine and stabilize individual metal atoms from aggregating into nanoparticles. Single metal atoms can simply be confined physically within the micropores or chemically grafted onto the frameworks of microporous matrices such as zeolites, metal–organic frameworks (MOFs), or covalent-organic frameworks (COFs).

(iii) *Surface-Stabilized Single-Metal-Atom Catalysts*: In this class of catalysts, surface species on the supports serve as "ligands" to isolate and stabilize metal atoms. No extra ligands are introduced to stabilize the catalytic metal atoms, which is different from surface-dispersed organometallics and thus requires the development of strategies to prevent the easy aggregation of the metal atoms during the preparation of the catalysts and also during the catalysis process.

In the following sections, we will first briefly discuss the preparation strategies for surface-dispersed mononuclear organometallic catalysts and micropore-stabilized single-metal-atom catalysts. Then, the recent development of surface-stabilized single-metal-atom catalysts on various supports will be discussed in depth. We will focus on the stabilizing strategies of single-metal-atom catalysts on supports containing metal atoms and no metals. In the last part, the importance of the interface species surrounding the catalytic metal atoms in determining the overall catalysis of atomically dispersed metal catalysts will be discussed, together with a summary of the prospects for the development of the field.

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2. Surface-Dispersed Mononuclear Organometallic Catalysts

In the surface-dispersed mononuclear organometallic catalysts discussed in this section, all the metal centers are co-stabilized by both supports and organic ligands, which are different from surface-grafted organometallics through organic linkers.[8] As shown in **Figure 2**a, by taking advantage of the high surface reactivity of the oxide support, systematic investigations have been carried out to deposit mononuclear catalytic organometallics on the surface nonporous silica by various groups.[9] Aerosil silica with pendant silanol groups (≡SiOH) has been widely used to anchor molecular complexes, forming catalysts with single metal atoms as active sites. As shown in Figure 2b, a typical example is silica-supported zirconium hydride with a tripodal grafting configuration.[10] The catalyst showed unexpected catalytic activity in the hydrogenolysis of low alkanes under mild conditions. By using the same protocol, organometallics of other transition-metal ions like Ta, Mo, W, and Re have also been successfully grafted onto silica.[9c]

It has been well documented that the surface density of ≡SiOH groups is a key parameter in surface organometallic chemistry. In early studies, aerosil silica with a moderate surface area (≈200 m² g⁻¹) was used as a support, and the concentration of ≡SiOH groups was merely around 0.7 nm⁻². Recently, mesoporous silica, which has exceptional high surface areas (usually 600–1000 m² g⁻¹), controllable pore diameters, and a much higher surface concentration of ≡SiOH groups (typically 1–2 nm⁻²), has been adopted as a support.[9c] For instance, a four-coordinated Ti^{IV} catalyst was readily prepared by anchoring a titanocene dichloride precursor [Ti(Cp)₂Cl₂] (Cp = C₅H₅) onto the inner walls of MCM-41 silica (Figure 2c).[11] In situ X-ray characterization revealed the structural evolution of the active center from ≡Ti(Cp)₂ to ≡Ti(Cp) to ≡TiOH after the removal of the Cp ligands. The resulting four-coordinated Ti was identified as the active center for the epoxidation of alkenes. By using similar precursors, other single-site catalysts with V, Cr, and Mo have also been successfully prepared.[12] Organometallic catalysts can also be grafted onto oxide supports based on the protonolysis reaction.[13] As shown in Figure 2d, tris(*tert*-butoxy)siloxy titanium complex can react with the ≡SiOH groups on the silica surface to form an Si—O bond and release an HOtBu molecule.[14] Meanwhile, besides silica, mesoporous aluminosilicates, and aluminophosphates,[15] dehydrated metal oxides (e.g., MgO[16] and Al₂O₃[17]) have also been used as supports in many studies.

3. Micropore-Confined Single-Metal-Atom Catalysts

Although single-site catalysts are easily obtained by surface reactions of organometallic catalysts with oxide supports that
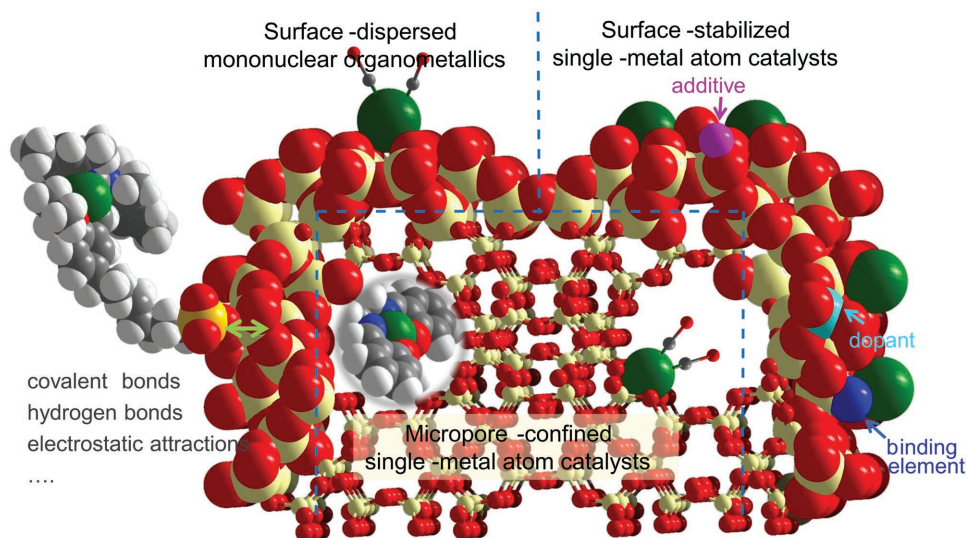
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Figure 1. Illustration of three different classes of atomically dispersed catalysts. Color codes: green, catalytic metal; yellow, metal of support; cyan, dopant metal; red, O; purple, additive; blue, nitrogen or other binding element; gray, C; white, H.
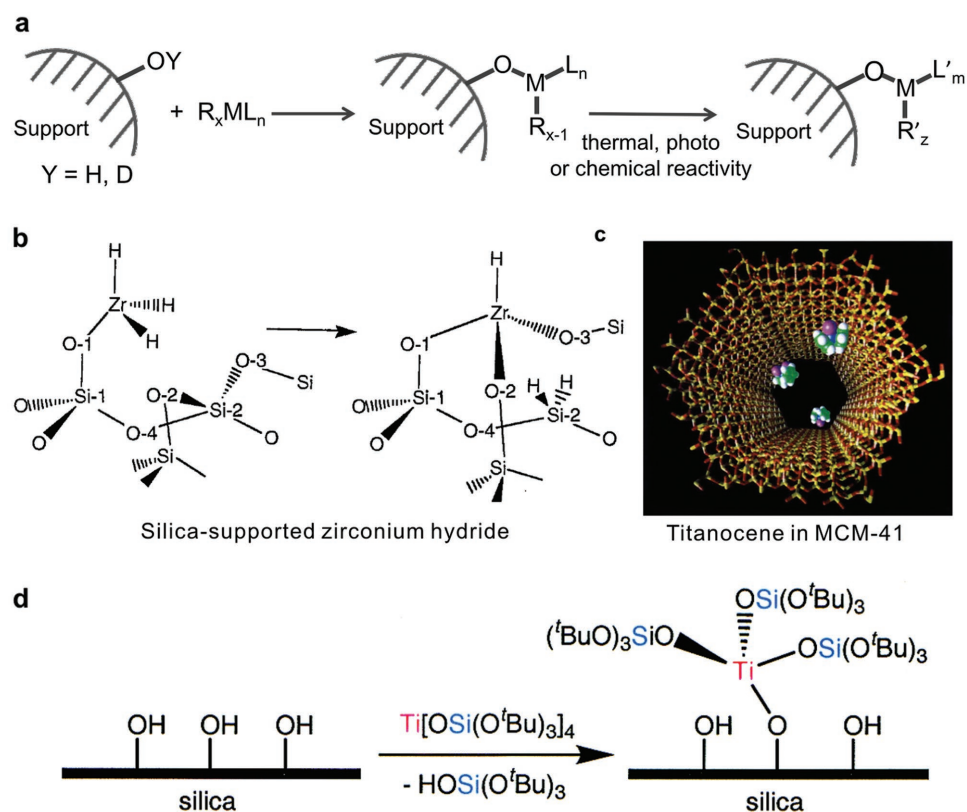

Figure 2. Surface-dispersed mononuclear organometallic catalysts. a) General mechanism of grafting surface complexes. Reproduced with permission.[9c] Copyright 2003, Wiley-VCH. b) Silica-supported zirconium hydride with a tripodal grafting configuration. Reproduced with permission.[10b] Copyright 1996, American Association for the Advancement of Science. c) Illustration of the accommodation (diffusion/adsorption) of molecules of titanocene dichloride inside a pore of MCM-41: Si (yellow); O (red); C (green); H (white); Cl (purple); and Ti (blue). Reproduced with permission.[11b] Copyright 1995, Nature Publishing Group. d) The tris(tert-butoxy)siloxy titanium complex can react with the ≡SiOH groups on silica surface. Reproduced with permission.[14] Copyright 2002, American Chemical Society.

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are either nonporous or contain macropores/mesopores, the leaching and aggregation of active metal sites is still a big concern, especially when the catalysts are applied in liquid-phase reactions. One effective strategy to prevent the leaching or aggregation of catalytic metal centers is to confine the metal centers into micropores to restrict their migration. For this purpose, microporous materials, such as zeolites, MOFs, and COFs, have been widely used as supports for the preparation of atomically dispersed metal catalysts.

3.1. Confining Single Metal Atoms within the Micropores of Zeolites

In early studies of such a strategy, a so-called ship-in-bottle technique was developed to encapsulate molecular catalysts in the micropores of zeolites, forming isolated catalytic sites.[18]

In this method, the metal ions and ligands are small enough to diffuse through the pore windows of the cages of the zeolites. Once metal complexes are formed inside the cages, they are trapped therein. Examples like cobalt (II) phthalocyanine molecules (**Figure 3**a) and *cis*-[Mn(bpy)₂]²⁺ (bpy: bipyridine) encapsulated in zeolites have been successfully demonstrated.[19] In general, the catalytic metal centers in the catalysts obtained by the "ship-in-bottle" strategy do not chemically interact with the frameworks of microporous supports.

To have metal atoms grafted to the framework while confined in micropores, organometallics that have labile ligands and also a diameter smaller than that of the window size of the micropores can be used as the metal precursors. For example, metal complexes with acetylacetonate (acac) ligands have been extensively used to prepare grafted single-site catalysts within micropores of zeolites. Gates et al. demonstrated that $Rh(CO)_2(acac)$ was able to be deposited on the dealuminated HY zeolite, leading
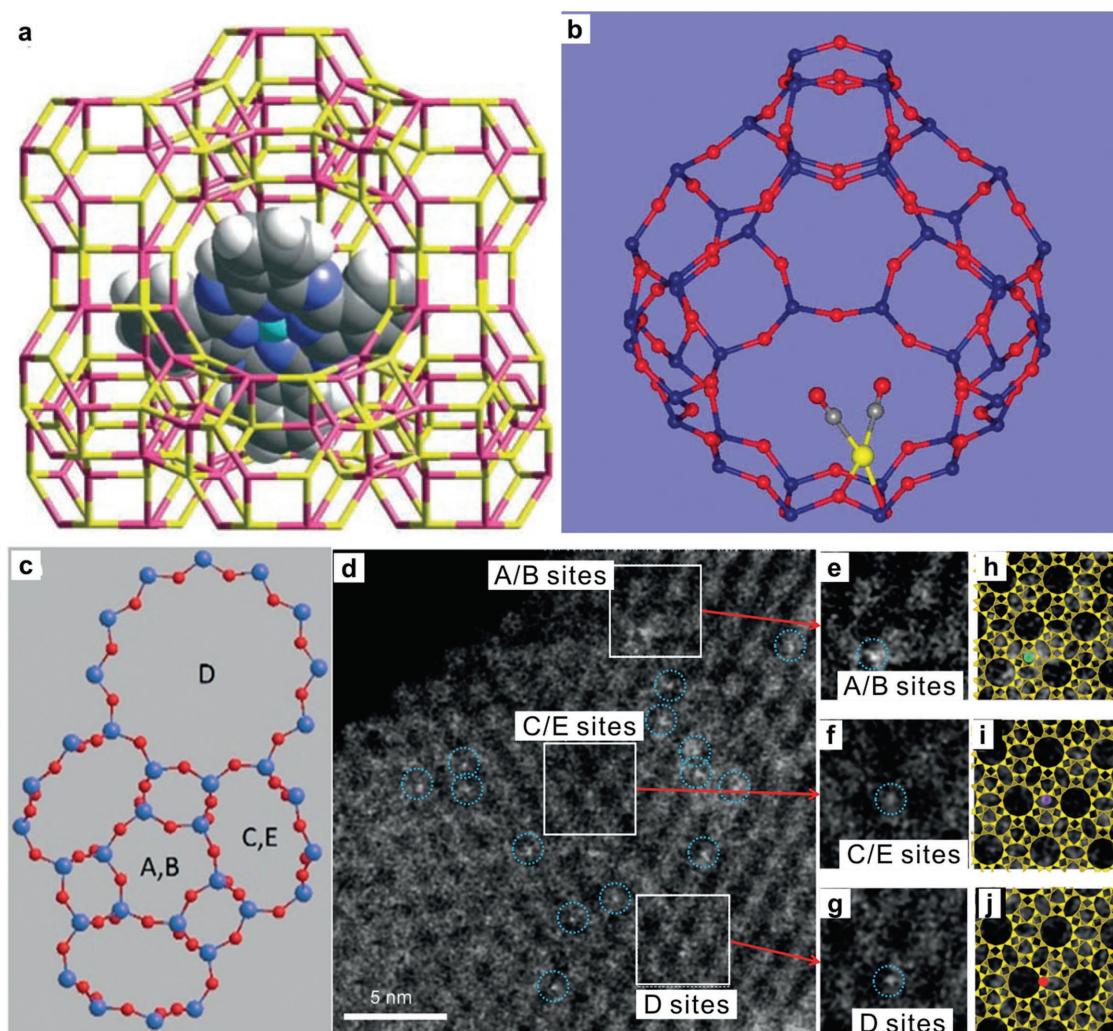

Figure 3. Confining single metal atoms within micropores of zeolites. a) Cobalt phthalocyanines housed within zeolite Y. Reproduced with permission.[19] Copyright 2003, American Chemical Society. b) Structural model representing the location of a rhodiumdicarbonyl complex at a faujasite four-ring unit. Reproduced with permission.[20] Copyright 2003, Royal Society of Chemistry. c,d) Model of c) zeolite LTL and d) STEM images of site-isolated Pt atoms in different sites inside the pores of zeolite KLTL. e–g) Magnified views of the highlighted regions in panel (d), and h–j) the corresponding simulated Pt location in the rings. c–j) Reproduced with permission.[26] Copyright 2014, Wiley-VCH.

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to the formation of the Rh(CO)$_2$ active structure (Figure 3b).[20] After acac was removed, each Rh atom would be bound with two oxygen atoms from the zeolite framework, resulting in two Rh−O bonds. By using Fourier transform infrared (FTIR) spectroscopy, they observed a very sharp peak attributed to the carbonyl group, proving the uniformity of the supported species. This method was successfully extended to other acetylacetonate precursors, such as Ir(C$_2$H$_4$)$_2$(acac),[21] Ru(C$_2$H$_4$)$_2$(acac)$_2$,[22] and Au(CH$_3$)$_2$(acac).[23] Zeolite-HY-supported isostructural mononuclear Rh and Ir complexes exhibit tunable catalytic activity and selectivity by ligand modification.[24]

In addition to the strategy to use organometallics as precursors, single-metal-atom catalysts confined within the micropores of zeolites can be prepared by ion change as well.[25] For example, atomically dispersed Pt in the KLTL zeolite was successfully prepared by treating the KLTL zeolite with aqueous [Pt(NH$_3$)$_4$](NO$_3$)$_2$ to have [Pt(NH$_3$)$_4$]$^{2+}$ complexes exchanged into the micropores. The complexes then were oxidized at 633 K in the presence of flowing 10% O$_2$ in He to give an atomically dispersed Pt catalyst that catalyzed the CO oxidation (Figure 3c–j),[26] and Au^I in the NaY zeolite[27] showed a relatively high activity and durability in CO oxidation. The atomically dispersed species were bound to the Al sites in the zeolite rings through two M−O bonds, which inhibited them from agglomerating. Moreover, supported atomically dispersed species have also been obtained by using highly siliceous chabazite,[28] and pure porous siliceous MCM-22[29] and ZSM-5 as supports.[30] Although small amount of isolated species was present on the outer surface,[30] the catalysts with metal atoms dispersed inside micropores of zeolites effectively catalyzed size-selective reactions.[29] In addition to the 3D porous structure, recently nanocavities created on 2D thin films were demonstrated to be effective physical barriers to form highly stable atomically dispersed metal catalysts.[31] However, it should be noted that the supported single-atomic dispersed Pt in those pure porous siliceous materials was only stable in an O$_2$ atmosphere and existed in an oxidation state. Once treated with H$_2$ at high temperature, the atomically dispersed species would be reduced and aggregated into fine nanoparticles inside the pores.[28,32]

3.2. Stabilizing Single Metal Atoms in Micropores with Organic Frameworks

MOFs and COFs have been emerging as new porous materials during the past two decades. Different from pure, inorganic porous materials, both MOFs and COFs consist of organic linkers and inorganic nodes. When catalytically active metal atoms are introduced onto the complex-like building blocks of the frameworks, these MOFs and COFs readily serve as single-site heterogeneous catalysts.[33] The immobilized organometallic single-site catalysts and MOF-based single-site catalysts are a prosperous research field that has had remarkable progress in recent years. Readers can refer to several excellent reviews on this topic.[34]

In the literature, there are three major strategies to prepare atomically dispersed metal catalysts based on MOFs or COFs. The first strategy is to confine catalytic organometallics within the pores using the ship-in-a-bottle approach discussed above.[35] As shown in **Figure 4**a, [Mn(bpy)$_2$]$^{2+}$ complexes were successfully synthesized and immobilized in the network of a microporous COF synthesized by polymerization of [B(C$_6$F$_4$Br)$_4$]$^−$.[35b] The catalyst exhibited excellent catalysis for the oxidation of styrene. The second strategy is to anchor catalytic metal atoms on the organic components of the frameworks of MOFs or COFs through post-treatments.[36] As a nice recent example, Rh- and Ir-mono(phosphine) complexes were successfully incorporated into a porous triarylphosphine-based MOF through postsynthetic metalation (Figure 4b).[37] The catalyst displayed stable and excellent activity in various reactions, such as the hydrosilylation of ketones and alkenes, the hydrogenation of alkenes, and the C−H borylation of arenes. COFs containing phosphine motifs were also successfully prepared by copolymerization of a vinyl-functionalized biphephos ligand with tris(4-vinphenyl)phosphine and other ligands, and used as a porous matrix for the incorporation of single atoms of Rh and Pd.[38] The catalysts exhibited excellent catalytic performances in the hydroformylation of olefins and Suzuki–Miyaura coupling of aryl chlorides. COFs with pyridine-type ligands containing C≡C bonds have also been synthesized to anchor Pd atoms for selective oxidative Heck reactions.[39] The third strategy is to incorporate catalytic metal atoms into the inorganic nodes of MOFs. Catalytically active metal sites can be incorporated either during the synthesis of MOFs or after synthesis through post-treatment. Metal sites in the as-prepared MOFs are typically coordinatively saturated. Partial removal of labile ligands on metal sites is typically required to start the catalysis.[40] For example, the coordinated water molecules in the frameworks of [Cu$_3$(btc)$_2$(H$_2$O)$_3$] (HKUST-1) and [Cr$_3$F(H$_2$O)$_2$O(bdc)$_3$] (MIL-101) are easily removed to expose their Cu(II) and Cr(III) sites, which readily serve as Lewis acids to catalyze the cyanosilylation of benzaldehyde or acetone.[41] As an alternative, catalytically active metal species can be introduced through post-treatment by anchoring extra metal ions onto the inorganic nodes of the MOFs. As shown in Figure 4c, a sintering-resistant single-site nickel catalyst (denoted as Ni-AIM) was successfully prepared by loading Ni ions onto the inorganic nodes of a Zr-based MOF (NU-1000) using atomic-layer deposition (ALD).[42] After being treated with 3% H$_2$/Ar at 200 °C, the Ni-AIM was highly active for ethylene hydrogenation with a per-nickel-atom turnover frequency of 0.9 s^{-1}. Moreover, the resulting catalyst was highly stable in the stream for 2 weeks.

Due to molecularly designable and controllable local coordination environments of metal centers, atomically dispersed metal catalysts based on MOF and COF catalysts are expected to serve as a nice bridge for homogeneous and heterogeneous metal catalysts. Besides their applications in simple hydrogenation, oxidation, coupling reactions, and acid/base-catalyzed reactions, the diversity of framework structures and compositions of both metal nodes and organic ligands makes it possible to incorporate multifunctional catalytic metal centers in MOFs for catalyzing tandem reactions.[43] Moreover, to overcome the diffusion problem caused by their microporous structures, some research effort has been recently directed to the preparation of atomically dispersed metal catalysts based on 2D MOFs.[44]
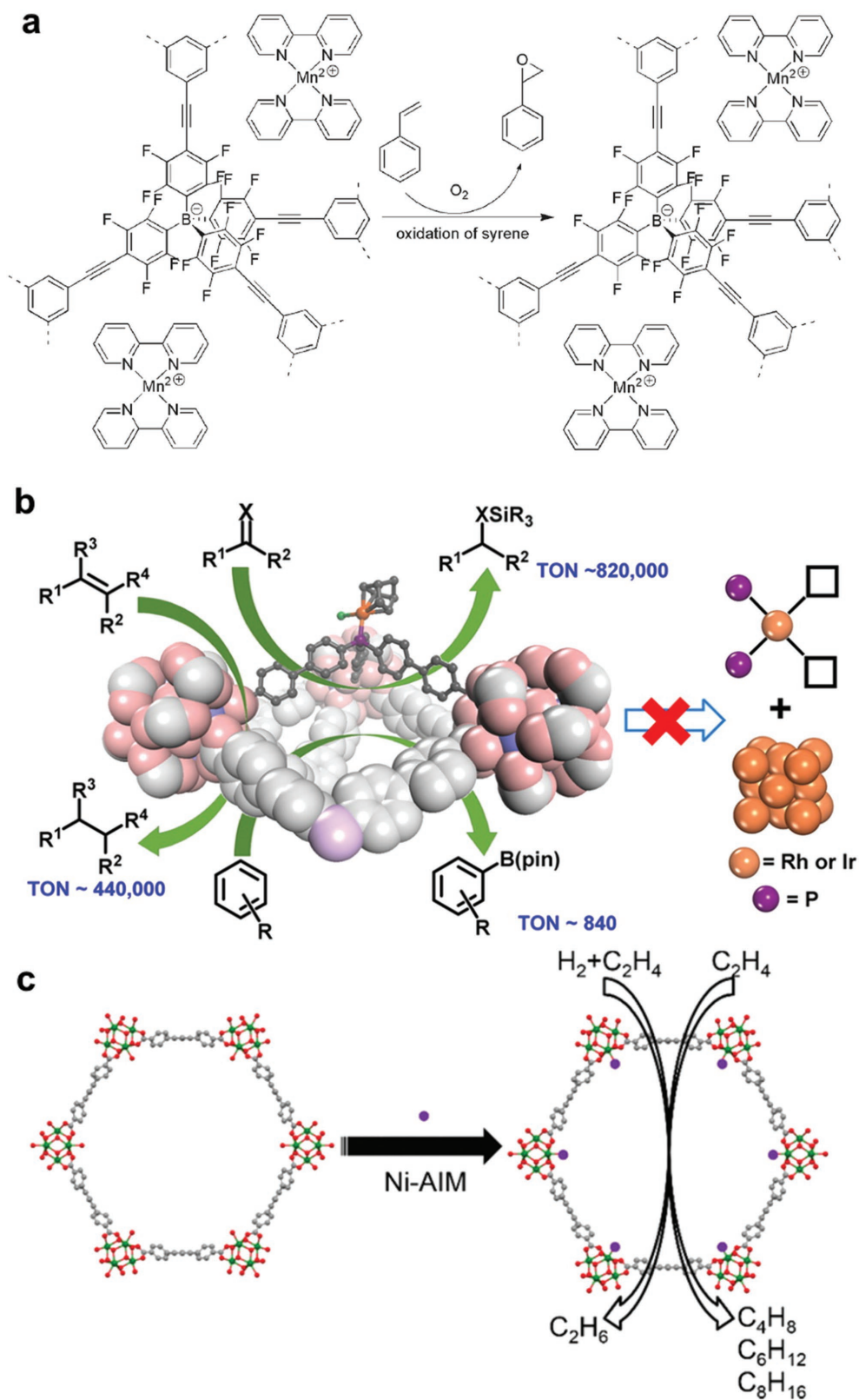
Figure 4. Stabilizing single metal atoms in micropores with organic frameworks. a) Immobilization of $[Mn(bpy)_2]^{2+}$ in the anionic borate network (ABN) COF. Reproduced with permission.[35b] Copyright 2013, Wiley-VCH. b) Anchored Rh- or Ir-mono(phosphine) complexes on the organic framework of a porous triarylphosphine-based MOF through postsynthetic metalation. Reproduced with permission.[37] Copyright 2016, American Chemical Society. c) Single-site nickel anchored at the inorganic nodes of a Zr-based MOF (NU-1000). Reproduced with permission.[42] Copyright 2016, American Chemical Society.

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4. Atomically Dispersed Metal Catalysts on Metal-Containing Supports

As easily observed by transmission electron microscopy (TEM), metal nanoparticles are often characterized on the surface of conventional supported metal catalysts and considered as their catalytically active species. However, recent studies have revealed that metal nanoparticles over several nanometers do not contribute to the activity in some catalytic reactions.[45] For example, the excellent catalysis of many Au nanocatalysts in CO oxidation was ascribed to oxide-supported Au bilayers or sub-nanometer to 1–2 nm Au nanoclusters.[46] In the water–gas

shift reaction, only oxidized Au species (atomically dispersed Au cations and sub-nanometer-sized clusters) were considered as the active sites.[47] Due to the rapid development of atomic-resolution characterization techniques, new insights into the active species of support metal catalysts have been emerging. For instance, high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) has revealed the copresence of atomically dispersed metal species and nanoparticles on supported catalysts (**Figure 5**a).[48] Both single-atom Au and Au nanoparticles were present on the Au/TiO$_2$ catalyst that was synthesized through a photodeposition method.[49] Surprisingly, it was demonstrated that the catalytic activity was
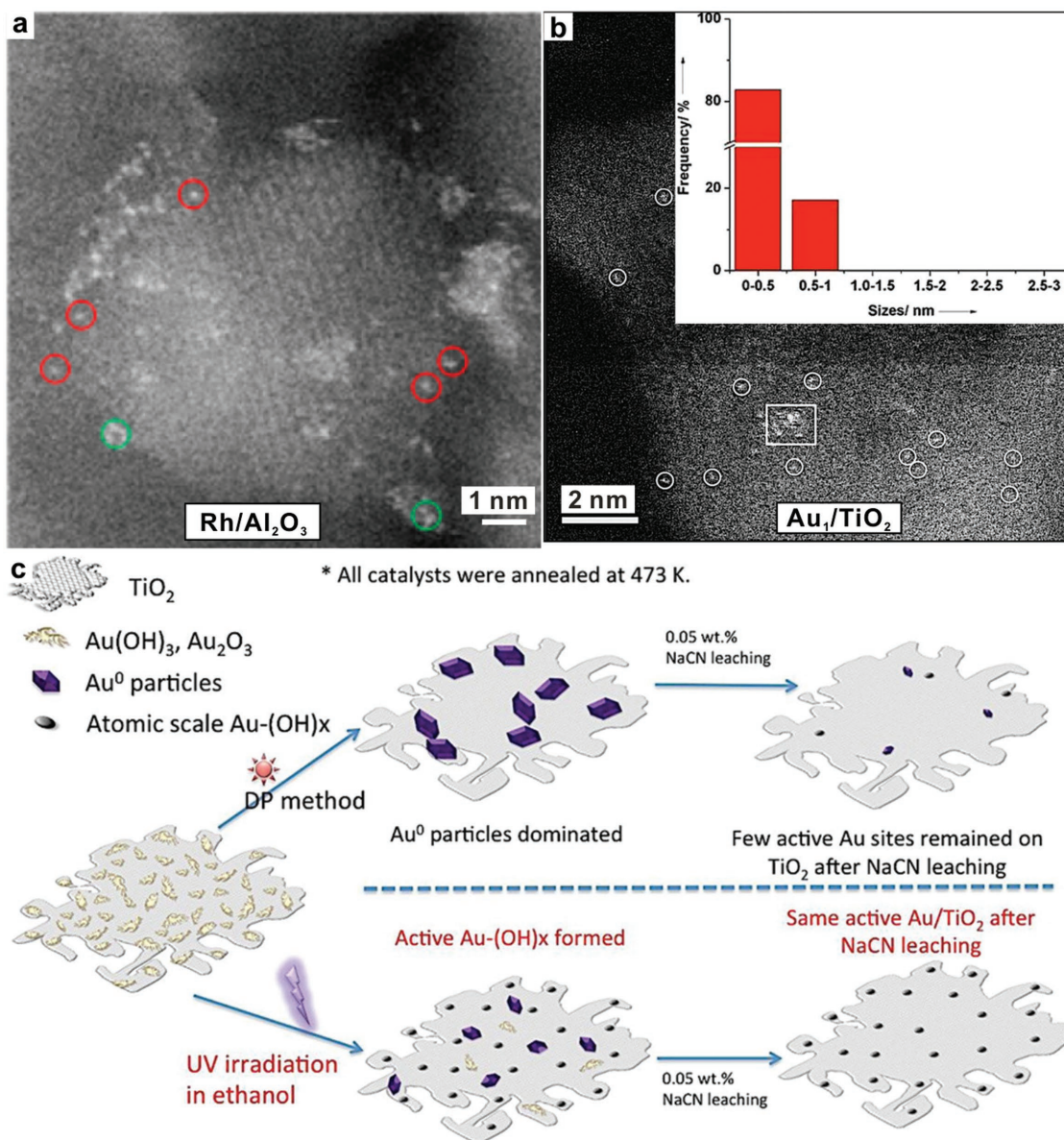

Figure 5. Atomically dispersed metal catalysts on metal-containing supports. a) Representative HAADF–STEM images of Rh/Al$_2$O$_3$, showing the copresence of nanoparticles and atomically dispersed Pt species. Reproduced with permission.[83] Copyright 2014, American Chemical Society. b) HAADF/STEM images of atomically dispersed Au catalysts prepared by UV-induced deposition, followed by leaching of the metallic Au nanoparticles by sodium cyanide and leaving the Au cation species atomically dispersed on TiO$_2$. c) The detailed synthetic scheme. b,c) Reproduced with permission.[49] Copyright 2013, American Chemical Society.

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maintained even after Au nanoparticles were leached by cyanide (Figure 5b,c). The result clearly indicated that the catalytic sites should be the atomically dispersed Au. Although atomically dispersed metals on oxide might be present in supported metal catalysts obtained by conventional preparation methods, it remains challenging to prepare catalysts with only single-metal-atom species on supports due to their high surface energy, as compared to their nanoparticulate counterparts. The developed strategies to stabilize single metal atoms on metal-containing supports are summarized in the following sections.

4.1. Reducing the Surface Loading Density of Metal Atoms

To prepare atomically dispersed catalysts, an intuitive strategy is to reduce the metal loading so that the sintering of metal atoms into nanoparticles is effectively prevented. Following this strategy, Pt_1/FeO_x catalysts with 0.17 wt% Pt loading were successfully synthesized through a coprecipitation procedure by Zhang and co-workers (**Figure 6**a,b).[50] The atomically dispersed nature of the supported Pt was confirmed by means of HAADF–STEM, extended X-ray absorption (XAS) fine structure (EXAFS) measurements, and in situ diffuse reflectance infrared Fourier transform spectroscopy. By contrast, Pt clusters were present on the 2.5 wt% Pt/FeO_x sample. The atomically dispersed Pt catalyst exhibited higher catalytic activity for the CO oxidation and preferential oxidation of CO in H_2 than the supported Pt clusters catalyst. The superior activity of Pt_1/FeO_x was attributed to the regulated electronic structure of the atomically dispersed Pt on the FeO_x surface. With the developed strategy, a number of atomically dispersed catalysts have been reported.[51]

In order to reduce the density of metal atoms on supports, an alternative way to synthesize atomically dispersed catalysts is to increase the specific surface area (or binding sites) of the oxide supports. In this regard, newly developed 2D ultrathin materials have great potential and promising prospects. As demonstrated in Figure 6c,d, using ethylglycolate (EG)-capped ultrathin $TiO_2(B)$ nanosheets as the support and taking advantage of their semiconductor nature, atomically dispersed Pd (Pd_1/TiO_2) was readily obtained upon UV irradiation.[52] It was revealed that the EG groups on the surface not only protected the ultrathin structure of $TiO_2(B)$, but also promoted the dechlorination of adsorbed $[PdCl_4]^{2-}$ to form isolated Pd species. Benefiting from the ultrahigh specific
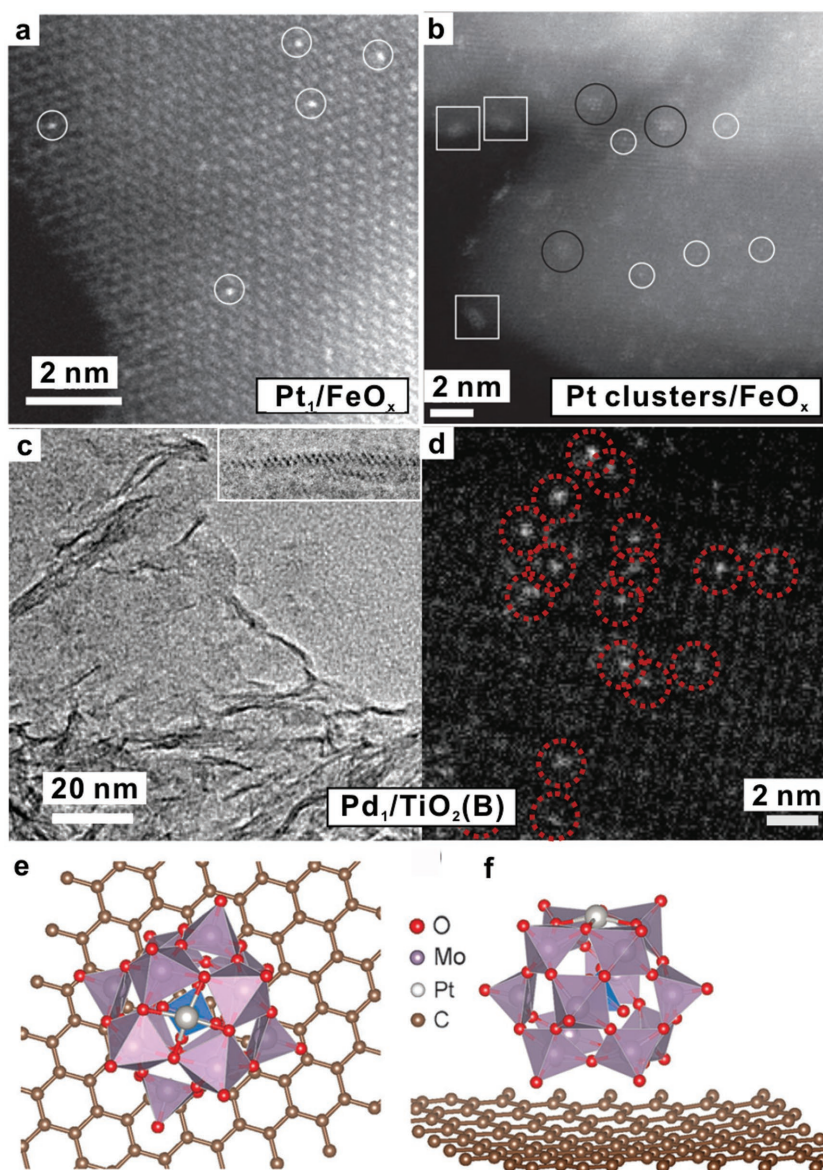

Figure 6. Reducing the surface loading density of metal atoms. a,b) HAADF–STEM images of a) 0.17 wt% Pt/FeO_x and b) 2.5 wt% Pt/FeO_x with dispersed single Pt atoms. a,b) Reproduced with permission.[50] Copyright 2011, Nature Publishing Group. c) Representative TEM image of Pd_1/TiO_2. The inset is an aberration-corrected STEM image for cross sections of ultrathin $TiO_2(B)$, showing that it was composed of only two layers of Ti atoms. d) HAADF–STEM image of Pd_1/TiO_2. The sample was calcined in air at 350 °C for better contrast. c,d) Reproduced with permission.[52a] Copyright 2016, American Association for the Advancement of Science. e) Top view and f) side view of the most stable configuration of Pt_1 on PMA/graphene, based on DFT calculations. e,f) Reproduced with permission.[55] Copyright 2016, Wiley-VCH.

surface area, the loading of Pd on Pd_1/TiO_2 could reach up to 1.5 wt% (≈0.3 Pd atoms nm^{-2}). The surface monolayer EG groups not only were bound with the TiO_2 surface and isolated Pd atoms, but also created physical and chemical barriers to prevent the Pd atoms from aggregating. Moreover, the EG groups on the surface play a crucial role in the catalytic hydrogenation. H_2 was activated on Pd through a heterolytic route, resulting in the formation of $H^{\delta+}$ and $H^{\delta-}$. Such an activation pathway made the Pd_1/TiO_2 catalyst much more efficient than

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Pd nanoparticles' atom by atom in the hydrogenation of both C=O. The developed photochemical strategy was also recently applied for the synthesis of atomically dispersed Pd catalysts on anatase-TiO_2 nanosheets with a major exposure of TiO_2 (001), and on commercial TiO_2 nanoparticles (P25).[53]

Following the idea of increasing the surface area of supports, a better approach is to use small oxide clusters as a support. As demonstrated in gas-phase heteroatomic oxide clusters generated by laser ablation,[54] the catalytic behavior of the heteroatomic oxide clusters was quite similar to that of supported atomically dispersed species. However, oxide clusters fabricated under those delicate conditions prevented them from being used as realistic catalysts. A more practical way is to use polyoxometalate clusters to trap isolated metal species on specific sites, followed by loading the decorated clusters on high-surface-area supports. As shown in Figure 6e,f, using phosphomolybdic acid (PMA)-modified active carbon as the support, positively charged isolated Pt atoms were stabilized by four oxygen atoms within the fourfold hollow sites in the PMA.[55] Even with high Pt loading (1 wt%) on these small polyoxometalate clusters, the as-prepared catalysts exhibited excellent performance in catalytic hydrogenation of nitrobenzene and cyclohexanone.

The use of ultrathin nanomaterials and ultrasmall clusters as supports not only helps to reduce the surface dispersion of metal atoms and thus enhance the stability of the prepared atomically dispersed metal catalysts, but also facilitates the molecular-level characterization of metal-binding structures. With the recent rapid development of 2D nanomaterials and atomically precise nanoclusters, we expect that the research of atomically dispersed metal catalysts with these materials as supports will continuously provide model catalysts for decoding the catalytic mechanisms of complicated supported metal catalysts.

4.2. Utilizing Defects to Stabilize Single Metal Atoms

In heterogeneous catalysis, the strong metal–support interaction (SMSI) commonly accounts for enhanced metal dispersion and stability, altered electronic state, and catalytic performance in catalysis.[56] It has been revealed that the SMSI is associated with reduced surface metal cations,[57] or more commonly with the oxygen vacancies (O_v).[58] Under harsh conditions, the cations around the O_v would also migrate or form vacant cationic sites. In fact, the existence of vacancies can alter the electronic structure of the supported metal species. When the atomically dispersed species is nested in these

vacancies, this interaction will be far stronger than those on a vacancy-free oxide surface.[57]

Reducible oxides (e.g., TiO_2 and CeO_2) are often considered as active supports and are extensively used in industrial catalysts. For example, in the three-way catalyst,[59] it has been well demonstrated that the surface vacancies and step edges on CeO_2 play a crucial role in catalysis.[60] As illustrated in **Figure 7**a–c, by aging physically mixed Pt/Al_2O_3 and CeO_2 at 800 °C, Pt nanoparticles on the Al_2O_3 form PtO_2 species in situ and are transferred to CeO_2 nanorods and polyhedral-CeO_2, forming atomically dispersed Pt on CeO_2.[61] As reported, the Pt atoms are strongly bound at the step-edge sites such that the sintering and bulk diffusion of Pt were nicely inhibited.[62] Structurally, the Pt cations prefer the octahedral coordination[61] that enhances their stability but suppresses their catalytic activity. As a result, the Pt_1/CeO_2 displays poor activity for CO oxidation without the assistant of water.[63]
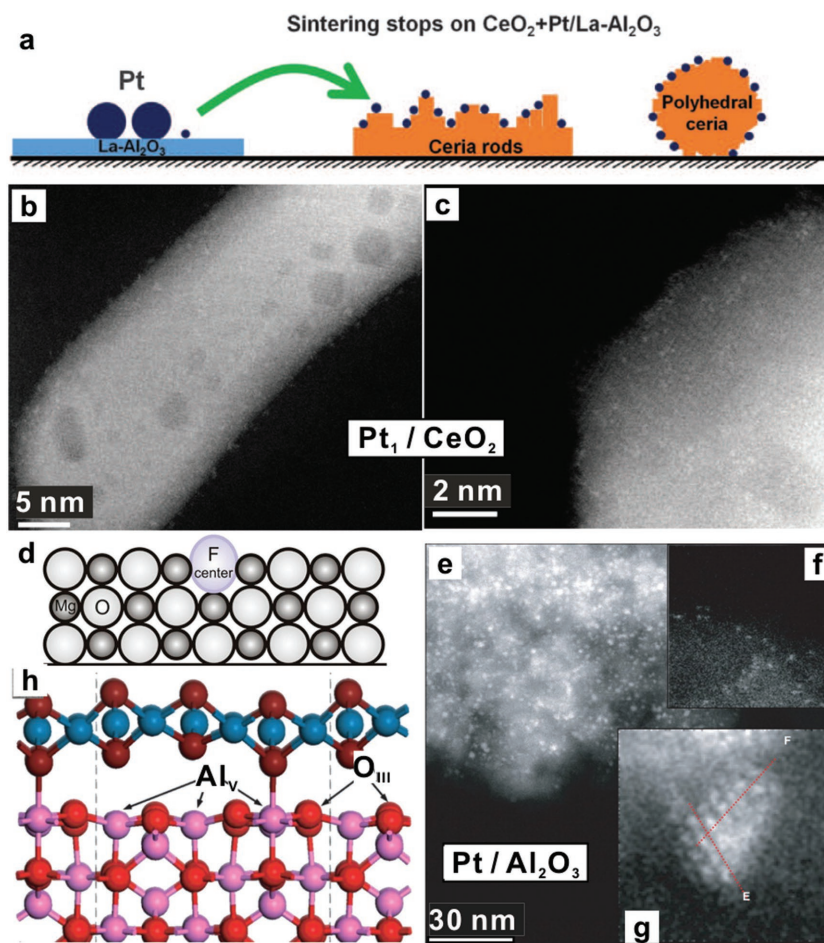
Figure 7. Utilizing defects to stabilize single-metal atoms. a) Illustration of how polyhedral ceria can trap the mobile Pt to suppress sintering. b,c) Representative AC–STEM images of b) 1 wt% Pt/CeO_2 rod and c) 1 wt% Pt/CeO_2 polyhedra after aging at 800 °C for 10 h in flowing air. a–c) Reproduced with permission.[61] Copyright 2016, American Association for the Advancement of Science. d) Illustration of the F center on MgO surface. Reproduced with permission.[70a] Copyright 2011, Beilstein Institute. e) STEM images of 10 wt% $Pt/\gamma-Al_2O_3$. f,g) The presence of f) atomically dispersed Pt and g) the raft-like Pt species. h) Side view of the optimized structure of raft-like Pt on $\gamma-Al_2O_3$(100). e–h) Reproduced with permission.[75] Copyright 2009, American Association for the Advancement of Science.

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When TiO_2 was employed as a support, the metal dispersion, morphology, and catalytic activity critically depended on the nature of the surface defects.[64] TiO_2 is a supreme support to atomically dispersed metal atoms such as Pt, Pd, Rh, and Ru.[65] Similar to CeO_2, isolated Pt atoms have been predicted to situate at the step-edge sites on TiO_2. By contrast, in Rh-doped TiO_2 nanosheets, Rh atoms substitute the Ti^{4+} sites during the preparation.[66] In addition to CeO_2 and TiO_2, other reducible oxides support, such as CoO_x,[67] FeO_x,[50] WO_x,[68] and so on,[69] have also been reported to be suitable for anchoring and stabilizing atomically dispersed species, highlighting the significance of defects on the reducible oxides in the synthesis of atomically dispersed catalysts.

While the deoxygenation process often leads to the reduction of metal cations in reducible oxides, it creates anion defects or F centers on nonreducible oxides (Figure 7d).[70] It has been theoretically predicted that, on defected MgO(100), the transition-metal atom prefers to locate at F_s or F_s^+ centers rather than on O^{2-}.[71] Further calculations revealed that the single metal atom diffuses smoothly on the (100) terraces but stops at F_s and F_s^+ centers.[72] Interestingly, when the single atom is trapped by the F centers, the negative charge density will accumulate on the active metal center.[73] However, such an interaction is not so stable under oxidizing or humid conditions. For CO oxidation catalyzed by single-atom Pd supported on defective MgO, the $Pd(CO)O_2$ and $PdCO_3CO$ species that are produced during the catalytic processes will remedy the defects and induce migration and coalescence, leading to the formation of metal clusters.[74] The Al_2O_3 support has been widely used for various industrial applications. The critical roles of coordination-unsaturated Al^{3+} sites in stabilizing noble-metal atoms from sintering have been proposed.[75] It has been demonstrated theoretically and experimentally that the presence of surface pentacoordinated Al^{3+} sites (Al_{penta}^{3+}) will favor the formation of atomically dispersed Pt, both thermodynamically and kinetically.[76] The ratio of Pt_1/Al_{penta}^{3+} was found to be near 1, confirming the key role of Al_{penta}^{3+} (Figure 7e–g).

4.3. Introducing Additives/Dopants to Enhance Interactions between Supports and Metal Atoms

The binding sites of metal oxide supports mainly come from their surface anionic oxygen species (i.e., O^{2-} and OH^-) which are, however, not strong binders to many metal atoms for the preparation of atomically dispersed metal catalysts with relatively high metal loading. Once the metal loading is high, metal atoms tend to aggregate into nanoparticles. In many studies, specific additives or dopants are often introduced to enhance the interaction between metal atoms and supports, so that the loading of metal atoms can be increased.[77] For instance, alkali metals have been widely used as effective additives in catalysis to improve the metal dispersion and inhibit aggregation.[78] As shown in **Figure 8**a–d, the addition of Na^+ remarkably reduces the size of Pt clusters on SiO_2, which show high water-gas-shift (WGS) activity at low temperature.[79] With the addition of alkali ions, supported atomically dispersed Pt or Au has been achieved on a few oxide supports, such as TiO_2, SiO_2, and Al_2O_3.[80] The as-prepared catalysts also have high catalytic activity toward

WGS under mild conditions. The enhanced catalytic activities have been attributed to the formation of active surface M−OH species created by the introduction of alkali ions. Interestingly, different oxide-supported atomically dispersed Pt (or Au) catalysts have similar activation energies, indicating that these catalyst systems share similar active sites and similar mechanisms as well.[47c]

Different from surface additives, dopants in oxide supports can adjust the electronic interaction between the oxide and supported metal atoms, or structurally change the support's surface to produce more binding sites.[77] For example, lanthanum doping is commonly applied to enhance the stability of γ-Al_2O_3[81] and has also been proved as a promising strategy to stabilize atomically dispersed Pd species (Figure 8e–h).[82] Atomically dispersed Rh catalysts based on xSm_2O_3–γCeO_2–Al_2O_3 supports were also synthesized and applied in the methane steam reforming reaction.[83] Sn or Zr dopants were successfully confined in the brucite-like lattice of layered double hydroxide. The formation of electron-rich Sn or electron-deficient Zr sites provided additional strong binding sites for stabilizing atomically dispersed Pt atoms and small Pt clusters.[84]

4.4. Introducing Strong Binding Motifs to Enhance Interactions between Supports and Metal Atoms

Although the introduction of defects or cationic additive/dopants can enhance, to some extent, the interactions between metal atoms and oxygen species on metal oxide supports, much research effort has been directed toward enhancing the metal–support interaction by introducing nonoxygen binding motifs onto supports. For example, transition-metal disulfide materials (TMS), such as MoS_2 and WS_2, which have been widely applied in electrochemical energy storage/conversion,[85] are also used as supports to prepare atomically dispersed metal catalysts. Pt atoms have been nicely dispersed into TMS layers to offer enhanced hydrogen-evolution reaction (HER) activity.[86] Density functional theory (DFT) calculations suggested that the in-plane S sites near the doped Pt atoms would be activated to promote HER activity and stability. By hydrothermally treating defect-rich single-layered MoS_2 with $Co(thiourea)_4^{2+}$, Co atoms were also nicely anchored to the S vacancies on MoS_2 (**Figure 9**a–c).[87] In this case, the Co sites were coordinately unsaturated.[88] The as-prepared Co_1/MoS_x catalysts exhibited ultrahigh activity in hydro-deoxygenation of 4-methylphenol to toluene with 89 times higher activity than commercial $CoMoS_x/Al_2O_3$. Theoretical calculations revealed that the existence of interfacial sulfur vacancies between Co and Mo made a significant contribution to the ultrahigh activity.

Creating atomically dispersed metal catalysts with high thermal stability is important for many high-temperature catalytic processes, such as conversion of natural gas. By fusing ferrous metasilicate with SiO_2 at 1973 K, the Fe ions were transferred and confined into the lattice of quartz (Figure 9d,e). Only the Fe−O coordination was observed for the as-prepared catalysts.[89] When applying this catalyst in CH_4 nonoxidative coupling at 1173 K, an astonishing selectivity to ethylene and aromatics was observed. As revealed by EXAFS, the Fe−Si and Fe−C bonds that were formed during the reaction resulted in an

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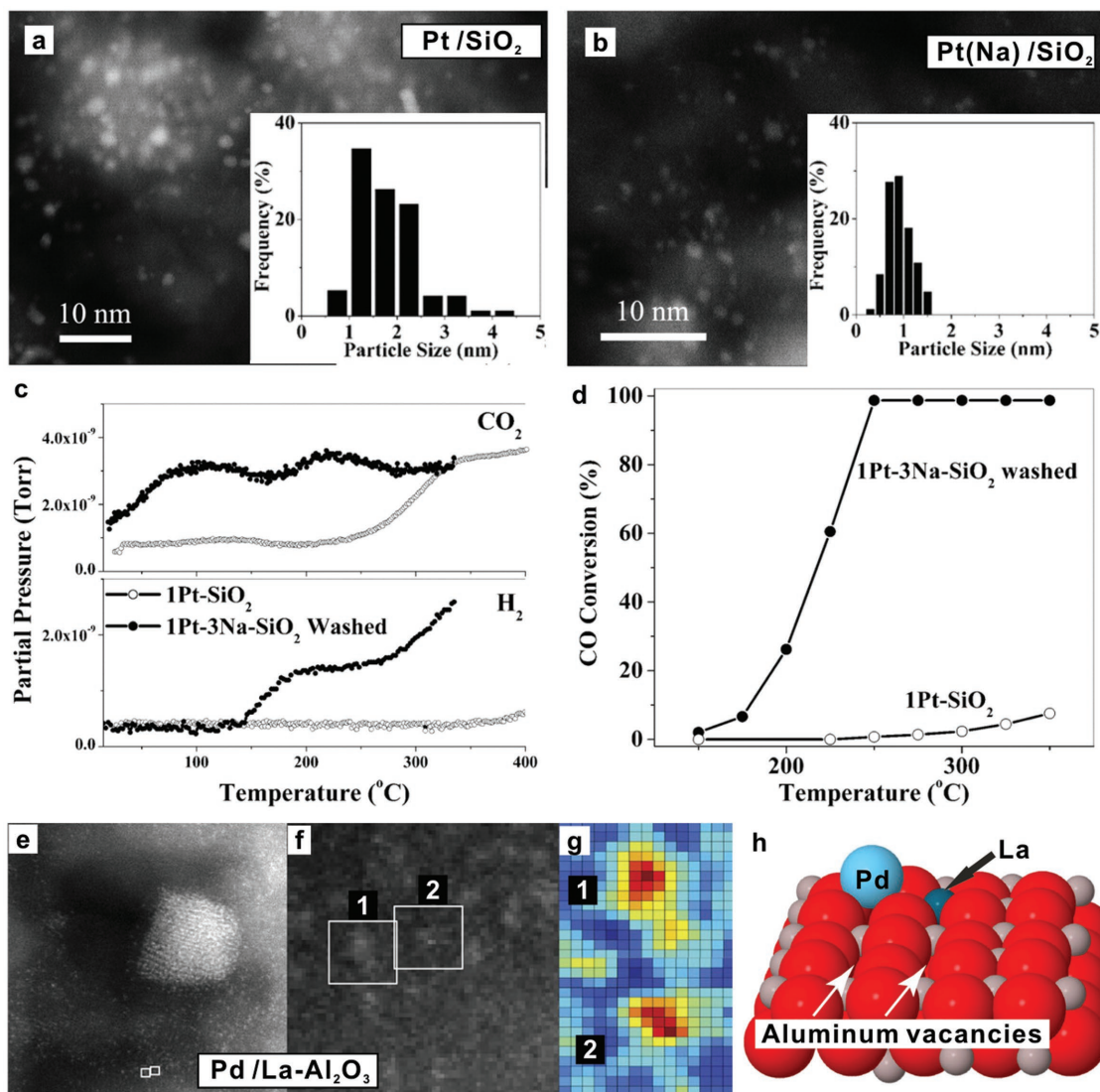
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Figure 8. Introducing additives/dopants to enhance interactions between supports and metal atoms. a,b) HAADF/STEM images and particle size distributions (insets) of a) 1Pt-SiO$_2$ and b) 1Pt-3Na-SiO$_2$. c) CO-TPR and d) steady-state WGS performance of Na$^+$-promoted and Na$^+$-free Pt/SiO$_2$. a–d) Reproduced with permission.[79] Copyright 2010, American Association for the Advancement of Science. e) A typical region of the La-stabilized γ-alumina support sample with a 2.5 wt% Pd loading. f) An enlarged region from panel (e), showing atomically dispersed species. g) Colorized intensity maps from region 1 in panel (f). h) Space-filling γ-alumina (100) surface model (spinel basis) with La and Pd. Color legends: oxygen: red; aluminum: gray; palladium: dark blue; and lanthanum: light blue. e–h) Reproduced with permission.[82] Copyright 2014, Macmillan Publishers Limited.

SiFeC$_2$ active center. The strong confinement by the lattice made the single Fe atoms ultrastable under the harsh catalytic conditions. Moreover, the absence of Fe—Fe bonds prevented the deposition of coke, resulting in nondetectable deactivation during a 60 h test. The introduction of nonoxygen binding sites plays a crucial role in stabilizing single Fe atoms against their sintering into nanoparticles and, thus, enhancing the catalytic selectivity.

4.5. Stabilizing Single Metal Atoms through Strong Metal—Metal Bonds

Due to strong metal—metal bonds, atomically dispersing catalytic metal atoms on metal surfaces is another important

strategy to prepare stable isolated metal catalysts. When the size and bond-formation energy of guest atoms are similar to those of the host metal atoms, the guest atoms tend to be homogeneously dispersed in alloys. Single-atom alloys (SAAs) can be formed when the loading amount of the guest metal is relatively small. In comparison to the tendency of phase separation for the metal species on other kinds of supports, single atoms in SAAs are more robust, and geometrically and electronically regulated by the host metals. Different from the partially charged single atoms stabilized by the covalent bonds, the mediated electron transfer makes SAAs distinct from other kinds of single-atom catalysts.[90]

As demonstrated in surface science studies, Pd atoms can be evaporated and deposited onto the single-crystal Cu surface as
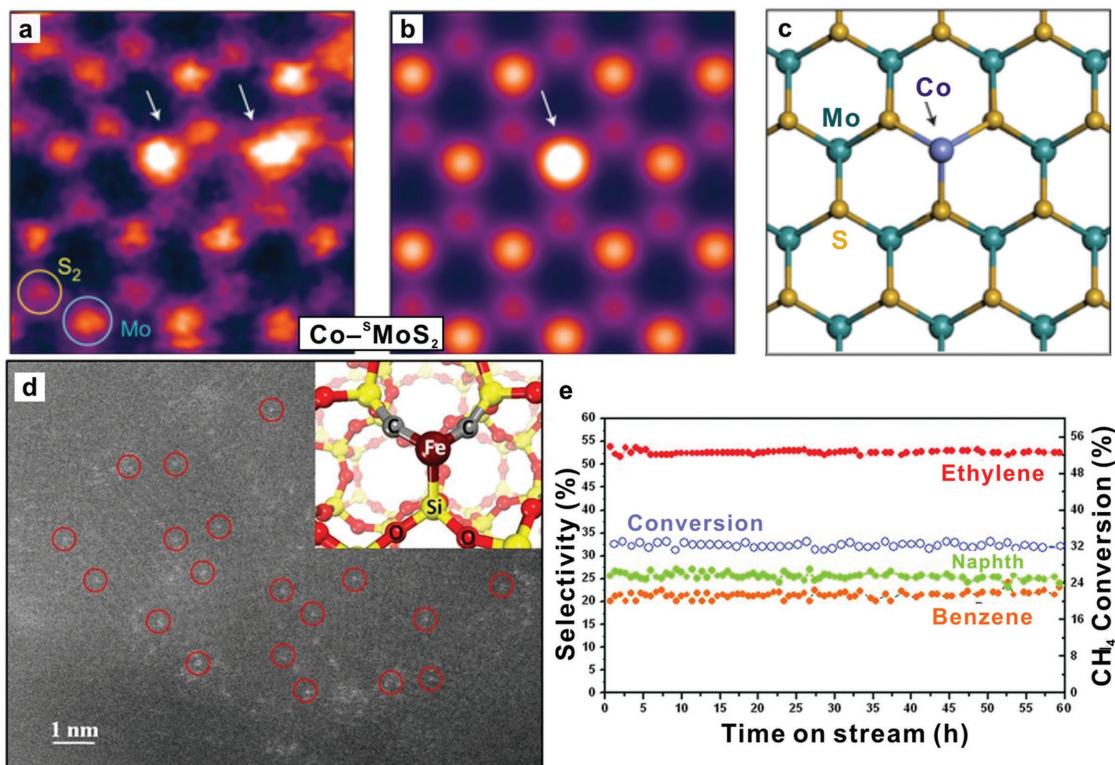
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Figure 9. Introducing strong binding elements to enhance interactions between supports and metal atoms. a) HAADF–STEM image of Co–$^SMoS_2$, showing two bright-contrast sites in the MoS_2 monolayer (arrows). b) An HAADF image simulation and c) the corresponding atomic model of Co–MoS_2. a–c) Reproduced with permission.[87] Copyright 2017, Nature Publishing Group. d) STEM–HAADF image of the catalyst after reaction, with the inset showing the computational model of the single iron atom bonded to two C atoms and one Si within silica matrix. e) Methane nonoxidative coupling long-term stability test of 0.5% Fe©SiO_2 at 1293 K and 14.5 L g_{cat}^{-1} h^{-1}. d,e) Reproduced with permission.[89] Copyright 2014, American Association for the Advancement of Science.

isolated atoms. After diffusion over terraces by random walking, Pd atoms are trapped at step-edge sites (**Figure 10**a).[91] These atomically dispersed Pd sites substantially facilitate hydrogen dissociation. The dissociated H atoms are then spilled over into Cu, which plays an important role in the selective hydrogenation of acetylene to ethylene.

Although using single-crystal surfaces as model catalysts is a nice approach to fabricate catalysts for understanding catalytic mechanism, the approach does not create SAAs for practical applications. For this reason, much research effort has been devoted to the development of SAA catalysts through wet-chemical methods.[92] One method for preparing SAAs is to deposit guest metal atoms on premade ultrathin host metal materials through IMP and galvanic replacement reactions.[93] A catalyst with Ru atomically dispersed on Pd was obtained by simply injecting a $RuCl_3$ solution into as-synthesized Pd nanoribbons. The Ru loading was as high as 5.9%. The as-obtained catalyst remarkably prohibited the hydrolysis reaction of allyl benzyl ether during the hydrogenation of C=C.[94]

In addition to the postdeposition method, the controlled synthesis of bimetallic nanocrystals with a specific composition, exposed facets, and crystalline structure provides an alternative effective method to prepare SAA catalysts. For example, as demonstrated by Li and co-workers,[95] *Pm-3m* PdIn alloy nanocrystals enclosed by (110) facets offer catalytic surfaces with atomically dispersed Pd sites (Figure 10b). The surface

makes the nanocrystals highly selective for the hydrogenation of acetylene to ethylene (92%). In comparison, nanocrystal P_4/mmm Pd_3In enclosed by (111) facets with Pd trimer sites gave a much lower selectivity toward ethylene (21%).

In addition to metal supports, metal-like materials with metal centers exposed on their surface can also serve as supreme supports to stabilize atomically dispersed catalysts through strong metal–metal interactions. For instance, atomically dispersed Pt atoms were stabilized on α-MoC by forming Pt—Mo bonds.[96] The as-prepared $Pt_1/α$-MoC showed unprecedented catalytic activity and stability in the low-temperature aqueous-phase reforming of methanol. Similarly, WC_x,[97] TiN and TiC,[98] and MXenes[99] have been demonstrated or predicted as promising supports to stabilize single catalytic metal atoms.

5. Atomically Dispersed Metal Catalysts on Metal-Free Supports

By taking advantage of the rapid development of material science in the past two decades, abundant materials with high surface area, controllable composition, and fine structure have been fabricated, such as carbon-based materials. Different coordinating sites (e.g., C, O, N, and S) are easily introduced into these materials. The chemical bonds that are formed between the metal atoms and supports will definitely enhance the
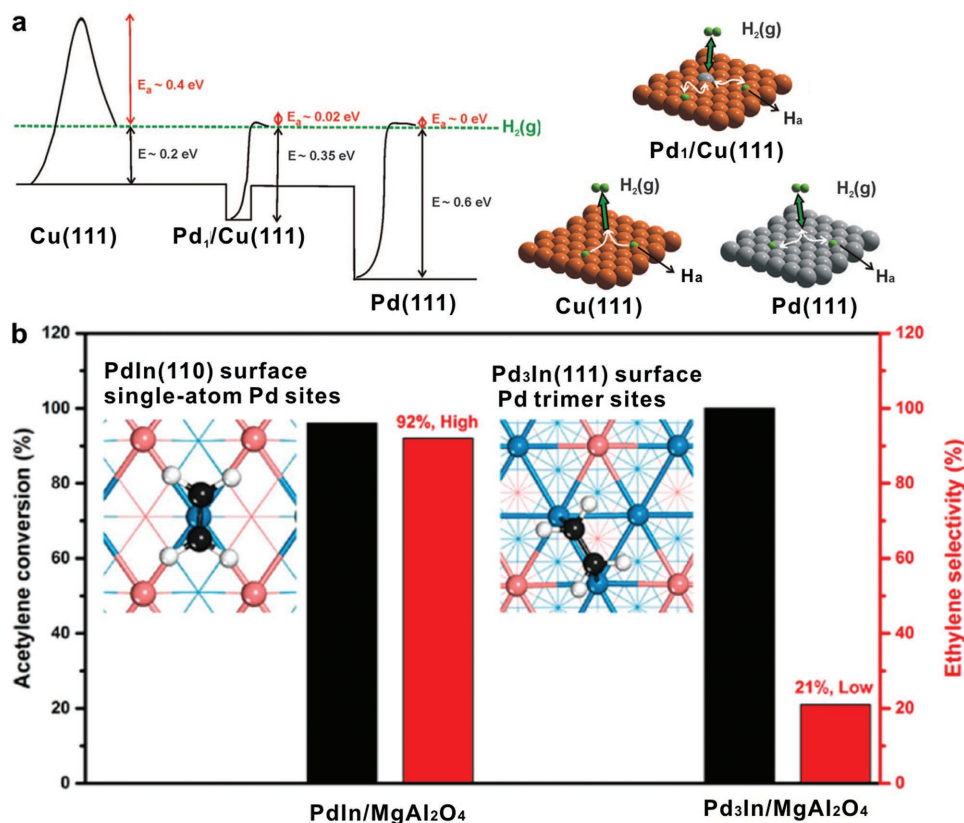
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Figure 10. Stabilizing single metal atoms through strong metal–metal bonds. a) Potential energy diagram depicting the mode of action of single-atom Pd on the Cu(111) surface compared with those of pure Cu(111) and Pd(111). The regulated energy for H$_2$ activation resulted in the promoted performance in selective hydrogenation of alkyne. Reproduced with permission.[91a] Copyright 2012, American Association for the Advancement of Science. b) Schematic illustration of the isolated Pd$_1$ on PdIn(110) and Pd$_3$ on Pd$_3$In(111) of intermetallic nanostructures, and their catalytic performance in selective hydrogenation of acetylene. Reproduced with permission.[95] Copyright 2017, American Chemical Society.

stability of single metal atoms thereon. Moreover, due to good electronic conductivity and high surface area of many carbon-based materials, the use of these materials as supports expands the scope of catalytic reactions, such as electrocatalysis.[7a,100]

When metal-free materials are used as supports for the synthesis of atomically dispersed metal catalysts, preparation protocols have been developed far beyond those for oxide-dispersed single metal atoms. For example, various carbon-supported atomically dispersed metal catalysts have recently been synthesized by decomposing metal–organic or metal (hydr)oxide–organic precursors.[101] Due to the lightweight of supports with no metal species, the metal loading of atomically dispersed metal catalysts thereon can be much higher than those on metal-containing supports. For example, 5 wt% Pt atoms were dispersed on a sulfur-doped carbon framework prepared from a zeolite template.[102] It is impossible to obtain such a high noble-metal loading on metal-containing supports. Moreover, the use of supports based on doped carbon provides versatile binding sites to anchor catalytically active metal species, resulting in diverse coordinative environments. Coordinative species around the metal atoms have been demonstrated to participate in the activation/stabilization of substrates or intermediates in some reactions.[103] While the Mars–Van Krevelen mechanism was often proposed for CO oxidation on oxide-supported atomically dispersed metal catalysts,[63]

the Langmuir–Hinshelwood mechanism and the Eley–Rideal mechanism were more plausible for single-metal-atom catalysts on supports without metals, such as BN.[104] In some reactions, the distinct coordinative environment and electronic structure of atomically dispersed metal atoms on these supports make them superior to their oxide-supported counterparts.

5.1. Dispersed Metal Atoms by Carbon Species

Carbon-based nanomaterials, especially graphene and graphene-like materials,[105] are extensively used as supports for preparing supported metal catalysts, especially for electrochemical reactions, due to their high electronic conductivity. Fe species are often used as catalysts in the synthesis of graphene. It was observed that atomically dispersed Fe atoms were bound with the carbon atoms at the edge site,[106] indicating that unsaturated C atoms are capable of forming strong metal–carbon σ-bonds. The incorporation of atomically dispersed Nb into the graphitic layers redistributed the d-band electrons of the Nb species, making the as-prepared catalyst much more active for O$_2$ adsorption and dissociation in the oxygen reduction reaction (ORR) (**Figure 11**a,b).[107]

In addition to forming σ-bonds, metal atoms can interact with carbon-based materials through M–π interactions. Similar

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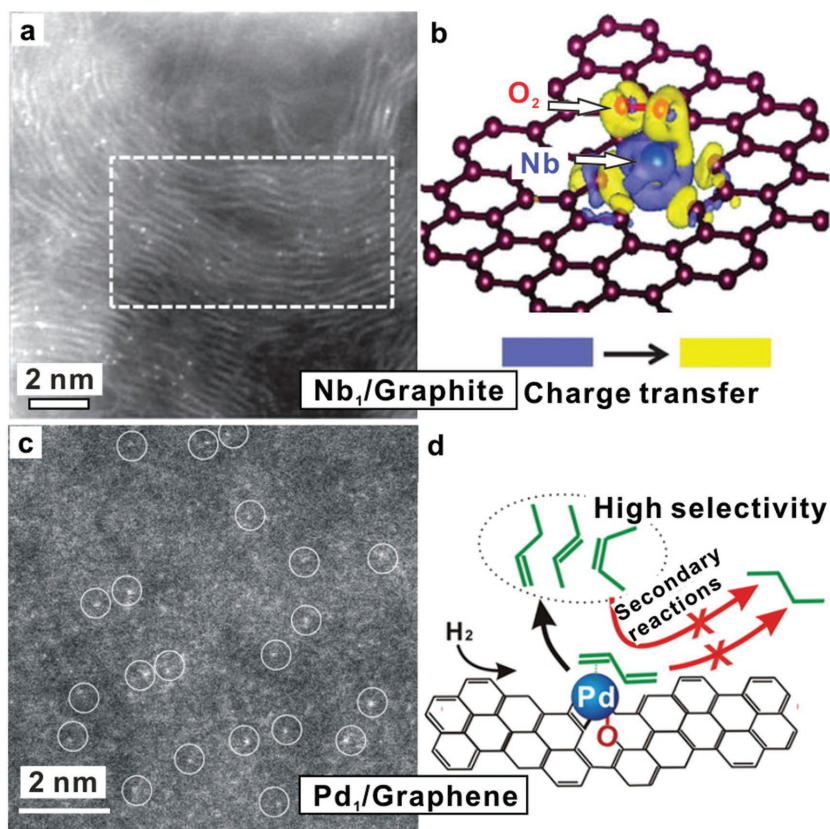
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Figure 11. Dispersed metal atoms by carbon and oxygen species on carbon-based materials. a) Direct observation of single niobium atoms in graphitic layers. b) Isosurface of the difference in electron density before and after O_2 adsorption. Charge flows from the niobium atom (blue) into the O atoms (yellow). a,b) Reproduced with permission.[107] Copyright 2013, Macmillan Publishers Limited. c) Representative HAADF–STEM images of Pd_1/graphene synthesized by ALD. d) Schematic illustration of improvement of butene selectivity on Pd_1/graphene catalyst. c,d) Reproduced with permission.[111] Copyright 2015, American Chemical Society.

nearly 100% selectivity in the selective hydrogenation of 1,3-butadiene into butenes in the presence of excess propene. The catalyst also showed excellent durability in a 100 h test, suggesting that the oxygen functional groups significantly stabilized the oxophile Pd. Inspired by this, it is reasonable to assume that materials based on natural macromolecules (e.g., cellulose, lignin, and chitin),[112] with abundant oxygen (and other) groups, can serve as promising supports for preparing atomically dispersed metal catalysts.

5.3. Dispersed Metal Atoms by Nitrogen Species

Nitrogen-doped carbon materials are rapidly rising star supports for creating catalysts for photo-electrochemical applications,[113] such as the ORR for proton-exchange-membrane fuel cells,[114] the HER, and the oxygen-evolution reaction for water electrolysis.[115] In the N-doped carbon materials, a variety of N functional groups, such as pyridinic N, pyrrolic N, graphitic N, quaternary N, and nitrilic N,[116] provide rich coordination sites for binding metal atoms. Using N-doped graphene as the support, stable single-atom Pt catalysts were successfully prepared through ALD (**Figure 12**a,b).[114] The Pt atoms were bound to the graphene C edge sites because of the dangling bonds and pyridinic-type dopants thereon. A CN_x-supported atomically dispersed Pt catalyst was demonstrated to exhibit greatly enhanced HER performance than nanoparticles.[117]

N-doped carbon materials are easily fabricated on a large scale by decomposing N-bearing organic precursors, which can be polymers,[118] dendrimers,[119] or MOFs.[120] Among these precursors, MOFs have recently been extensively used for the fabrication of N-doped carbon-supported atomically dispersed metal catalysts.[121] In MOFs, metal atoms are uniformly spatially separated by organic linkages. Such a unique feature allows metal atoms to be well isolated and trapped by N atoms on carbon during the pyrolysis of MOFs. As shown in Figure 12c,d, by the pyrolysis of Co/Zn bimetallic MOF precursor (ZIF-67) under an inert atmosphere, a catalyst with about 4 wt% Co atomically dispersed on N-doped porous carbon was prepared. In the bimetallic MOF precursor, Co^{2+} ions were spatially separated by the 2-methylimidazole and also by Zn^{2+}. During the high-temperature pyrolysis, Zn^{2+} was reduced and evaporated, leaving the Co atoms nicely dispersed on the obtained N-doped carbon matrix. The Co_1 catalyst not only surpassed Pt/C in ORR activity in 0.1 M KOH, but also exhibited outstanding chemical stability during electrocatalysis.[122]

While graphitic carbon nitride (g-C_3N_4) with well-defined arrangement of structures of both C and N atoms has been

to the binding in ferrocene, atomically dispersed Fe atoms are also present in bucky ferrocenes[108] and confined in single-wall carbon nanotubes (SWCNTs).[109] The atomically dispersed Fe atoms effectively catalyze C—C bond reorganization and fabricated new C—C networks. The M–π interaction and the tight packing mode in the limited space inside SWCNTs prevented the Fe species from forming metallic clusters.[109] Moreover, the carbon–carbon triple bonds in graphdyne networks also provide π orbitals for binding single metal atoms.[110]

5.2. Dispersed Metal Atoms by Oxygen Species on Carbon

Besides C atoms, oxygen atoms on functional carbon materials offer excellent binding sites for dispersing metal atoms. As demonstrated in Figure 11c,d, partially deoxygenated graphene oxide was used as the support for the atomic-layer deposition Pd atoms using palladium hexafluoroacetylacetate, [Pd(hfac)$_2$], as the metal precursor.[111] Oxygen atoms on the surface not only facilitated the removal of hfac ligands for the Pd deposition, but also stabilized the deposited Pd atoms against sintering into nanoclusters or nanoparticles. The as-synthesized Pd_1/graphene showed

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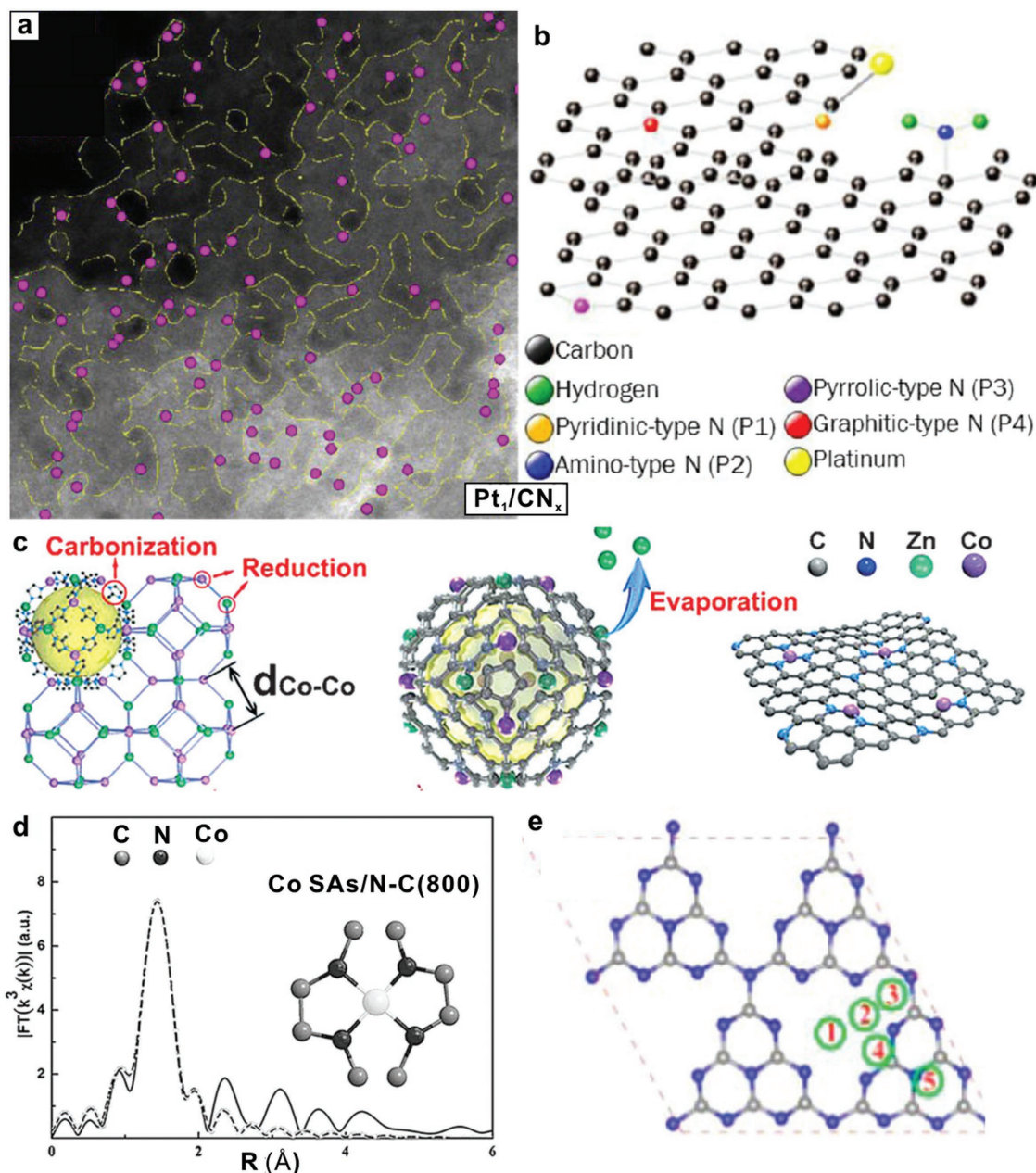small
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Figure 12. Dispersed metal atoms by nitrogen species. a,b) Processed HAADF images of a) atomically dispersed Pt on N-doped graphene edge (a), and b) schematic diagram of Pt atom. Reproduced with permission.[114] Copyright 2014, American Chemical Society. c) Schematic illustration of the formation of a single atom from an MOF. d) The k^3-weighted $\chi(k)$ function and the corresponding EXAFS fitting curves for Co SAs/N-C(800). The insets are the proposed Co–N$_x$ architectures. c,d) Reproduced with permission.[122] Copyright 2016, Wiley-VCH. e) Schematic illustration of the g-C$_3$N$_4$ and the proposed binding sites for the single atoms. Reproduced with permission.[124c] Copyright 2016, American Chemical Society.

demonstrated as a supreme metal-free catalyst for several reactions,[123] g-C$_3$N$_4$ is also emerging as an important support for preparing atomically dispersed metal catalysts.[124] As illustrated in Figure 12e, single metal atoms on g-C$_3$N$_4$ were predicted to be located either on top of the ring[124d] or at the center/corner/edge of the sixfold cavity.[124c] The charge transfer between metal atoms and pyridinic-N helps to enhance their binding strength and also perturbs the electronic structure of single atoms. g-C$_3$N$_4$ supported atomically dispersed Pd and Pt catalysts have been successfully prepared and show enhanced catalytic performances

in different kinds of reactions, such as hydrogenation,[125] photo-catalytic HER,[124d] and visible-light-driven CO$_2$ reduction.[124e]

Similar to g-C$_3$N$_4$, heterogeneous materials derived from porphyrins and phthalocyanines are attractive supports for atomically dispersed metal catalysts.[126] Single metal atoms can be coordinated into the pyrrole rings of porphyrins and phthalocyanines,[127] serving as molecule-like precursors. Benefiting from the conjugated π bonds of these molecules, the precursors can be easily loaded onto the surface of carbon-based materials, such as CNTs[128] and graphene,[129] through π–π interactions.

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For example, the incorporation of hemin on graphene, followed by introducing glucose oxidase to the carboxyl groups at the edge sites of graphene,[129] resulted in the formation of a molecule and enzyme tandem catalyst with the graphene–hemin–glucose oxidase hybrid structure. It should be noted that the π–π interaction can also take place on peripheral substitution groups on porphyrins and phthalocyanines. For example, iron porphyrins with pyrene groups were successfully bound to CNTs through the π–π interaction between the CNTs and the pyrene units in porphyrins.[130] The resulting composite catalyst exhibited high electrocatalytic activity for the reduction of CO_2 to CO at low overpotential.

Recent studies also revealed that cyano-bridged coordination polymer,[131] triazine framework,[132] graphene-like C_2N,[133] and BN[134] are promising materials to stabilize atomically dispersed metal catalysts by $M_1–N_x$ interactions.

5.4. Dispersed Metal Atoms by Sulfur Species

Different from oxygen and nitrogen species, sulfur species are usually considered deleterious to metal catalysts and thus are avoided for use as supports for the design of metal catalysts.

However, while the strong binding of thiols on metal allows the synthesis of a large number of stable protected metal clusters,[135] studies have also demonstrated that thiolated metal nanoclusters with the surface thiols partially removed turn out be catalytically active,[136] suggesting that the strong M–S interactions would not totally switch off the catalytic activity of thiolated metals. Another interesting finding is that the carbon nanotube surface exposing S serves as coordinative site to stabilize undercoordinated Pt species.[137]

More spectacularly, as shown in **Figure 13**, an atomically dispersed Pt catalyst with a loading of up to 5 wt% was successfully prepared by a conventional impregnation–reduction method where S-doped graphene nanoribbons prepared from zeolite templates were used as the support.[102] In this case, the support was made of highly curved 3D networks prepared by the chemical vapor deposition method, providing plenty of surface-confined S sites (17%). The as-prepared Pt_1 catalyst exhibited an onset potential of 0.71 V versus reversible hydrogen electrode (RHE) for the ORR, close to the thermodynamic potential of H_2O_2 production ($E°_{O_2/H_2O_2}$ = 0.69 V versus standard hydrogen electrode (SHE)), resulting in up to 96% selectivity for H_2O_2. Theoretical calculations revealed that the production of H_2O_2 on an atomically dispersed Pt catalyst was controlled by kinetics.
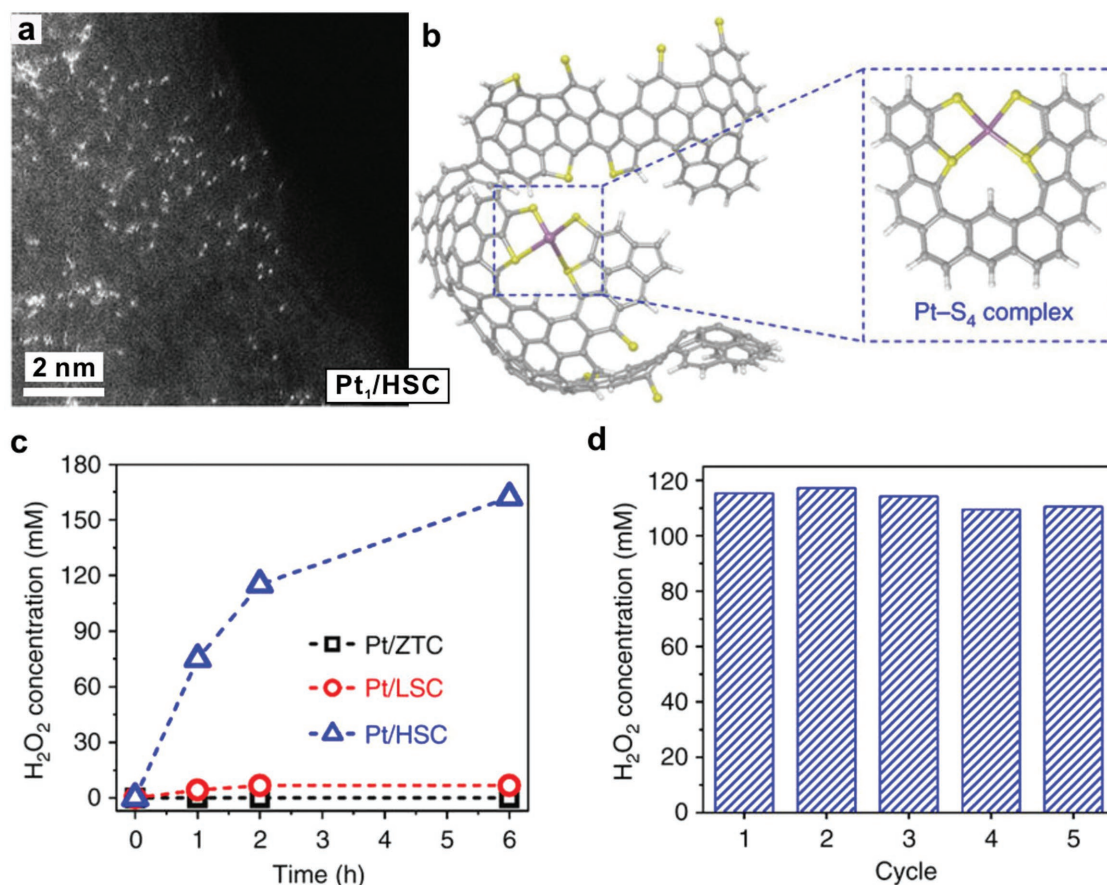

Figure 13. Dispersed metal atoms by sulfur species. a) TEM images of the atomical Pt species on high-S-content doped carbon made from a zeolite template. b) Proposed atomistic structure of the Pt/HSC (carbon: gray; hydrogen: white; sulfur: yellow; and platinum: purple). c) Accumulated H_2O_2 concentrations in an H-cell with a 1 M $HClO_4$ electrolyte and a Nafion 115 membrane. The H-cell was operated in short-circuit condition (V = 0) at 278 K. d) Concentrations of H_2O_2 produced on the Pt/HSC in an electrochemical H-cell during repeated 2 h operation cycles. Reproduced with permission (under the terms of the CC-BY Creative Commons Attribution 4.0 International License).[102] Copyright 2016, Nature Publishing Group.

6. Perspective

Structurally, supported atomically dispersed metal catalysts contain catalytic metal centers with structures that are much better defined than those on supported metal nanoparticle catalysts, helping us to bridge the traditional gap between homogeneous catalysts and heterogeneous catalysts. In atomically dispersed metal catalysts, all the catalytic metal atoms interact directly with the supports. In other words, supports serve as ligands to metal centers just like the situation in homogeneous organometallic catalysts. Therefore, compared with supported metal nanocatalysts, the nature of the support must play a very important role in determining the overall catalytic performances of atomically dispersed metal catalysts. Here, we have summarized strategies to prepare atomically dispersed metal catalysts on supports with various binding sites for anchoring metal atoms. The local coordination environments of metal in different atomically dispersed catalysts can be completely different. It is thus not surprising that the same metal atoms dispersed on different supports exhibit different catalytic properties, and sometimes even contradictory performances. For example, the FeO_x-supported single-atom Pt was active for CO oxidation, but SiO_2- or Al_2O_3-supported atomically dispersed Pt exhibited low activity.[138] Single-atom Pt catalysts supported on TiC and TiN were also demonstrated to exhibit quite different properties in electrochemical oxygen reduction.[139] From this perspective, investigating the vicinity of the metal atoms (e.g., the binding elements, metal coordination structures, and redox properties of adjacent metals) is crucial to understand their catalytic mechanisms.[140] These studies should be emphasized in the future research of atomically dispersed metal catalysts.

Currently, common techniques used for the structure characterization of atomically dispersed metal catalysts include HAADF–STEM, FTIR spectroscopy, XAS spectroscopy, nuclear magnetic resonance spectroscopy, and electron spin resonance spectroscopy. It is difficult to resolve the local coordination environments of metal atoms using any individual technique due to their own shortcomings. Taking XAS as an example, although the technique is powerful enough to detect the "single-atom" feature of atomically dispersed metal catalysts, it is difficult to apply the technique to identify the small difference in the coordination environment of metal atoms. XAS cannot effectively distinguish scattering atoms with a small difference in atomic number, for example, C, N, and O. The structure and thermodynamic disorder also affect the resolution, especially for samples with low metal loading and the structural information derived from a longer scattering distance.[141] Moreover, the fitting is not very sensitive to the coordination number, which, usually, has about 20% bias.[142] Researchers must be careful of any results obtained by any individual technique. It is particularly important to combine different characterization techniques to confirm the overall global and local structures of atomically dispersed metal catalysts.

The understanding of the molecular mechanisms of atomically dispersed metal catalysts is expected to shed light on the nature of the metal–support interfacial effects that have been widely observed in supported metal–nanocatalyst systems, which is important for the design of heterogeneous metal catalysts with optimized activity, selectivity, and also durability. Moreover, compared with homogeneous organometallic catalysts, atomically dispersed metal catalysts on supports usually exhibit much better stability.[143] Together with the well-defined metal coordination structure, the reasonable stability and dispersity of atomically dispersed metal catalysts in solution make them important systems for investigating some interesting phenomena that are difficult to achieve by both homogeneous and heterogeneous metal catalysts. For example, understanding the pH- and solvent-dependent catalysis of metal catalysts in a wide range of pH and solvents is often challenging.

While progress has been made in controlling the local coordination structure of metal centers, much work remains to be done to control the location and loading density of metal centers in atomically dispersed metal catalysts. Such a level of control requires the use of supports with controllable binding sites. MOFs, small nanoclusters, and 2D nanomaterials with well-defined structures are excellent support candidates for creating controllable binding sites. For example, MOFs with different loading of catalytic metals have recently been used as precursors to control the metal loading on N-doped carbon.[121a] In the case of atomically precise nanoclusters, the location of the loaded metal atoms should depend highly on their surface structure. Together with well-defined supports, the use of organometallic precursors with controllable bulkiness and reactivity should help to achieve the controlling goal. Bulky precursors with poor reactivity are expected to give a low loading density.

Moreover, although the variation of the metal and the support creates a high diversity of atomically dispersed metal catalysts, their catalysis is determined mainly by the nature of the metal atoms and their interaction with the supports. Besides these parameters, by contrast, the catalysis of supported metal nanoparticles is also influenced by the metal–metal interactions within the metal nanoparticles. However, in atomically dispersed catalysts on nonmetallic supports, there is lack of such an important factor for manipulating their catalysis. It is thus interesting to develop strategies for the fabrication of metal catalysts with well-defined multiple metal atoms, presented as small metal clusters, on supports. Recently, a catalyst with an RhCo bimetallic center was prepared by using CoO_x-supported atomically dispersed Rh as a precursor, which exhibited excellent catalytic performance in the reduction of NO by CO.[144] Dispersing premade dinuclear or trinuclear metal clusters on various supports might be another effective strategy for creating well-defined heterogeneous metal catalysts for investigating the contribution of metal–metal interactions to the overall catalysis of supported metal nanocatalysts.[145] By extending the research from single-atom dispersed metal catalysts to supported catalysts with nanoclusters of well-defined metal cores, more model catalyst systems will be created for understanding complicated phenomena in heterogeneous catalysis.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomically dispersed metal catalysts, heterogeneous catalysts, metal–support interactions, nanocatalysts, single-atom catalysts

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