

Review

Single-Atom Catalysts: Preparation and Applications in Environmental Catalysis

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Abstract: Due to the expensive price and the low reserve of noble metals in nature, much attention has been paid to single-atom catalysts (SACs)—especially single-atom noble metal catalysts—owing to their maximum atomic utilization and dispersion. The emergence of SACs greatly decreases the amount of precious metals, improves the catalytic activity, and makes the catalytic process progressively economic and sustainable. However, the most remarkable challenge is the active sites and their stability against migration and aggregation under practical conditions. This review article summarizes the preparation strategies of SACs and their catalytic applications for the oxidation of methane, carbon monoxide, and volatile organic compounds (VOCs) and the reduction of nitrogen oxides. Furthermore, the perspectives and challenges of SACs in future research and practical applications are proposed. It is envisioned that the results summarized in this review will stimulate the interest of more researchers in developing SACs that are effective in catalyzing the reactions related to the environmental pollution control.

Keywords: single-atom catalysts; SACs; preparation strategy; maximum atomic utilization; catalytic activity; environmental catalysis



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1. Introduction

Heterogeneous catalysis is an important research hotspot in the global field. Due to its economic and energy-saving features, it is widely used in the transformation of various energy resources (e.g., petroleum, coal, natural gas, and solar energy) in nature [1–4], the synthesis of numerous industrial chemicals [5,6], the purification of vehicle exhaust, etc. [7]. It is estimated that catalysts are used in the production processes of about 80% of artificial chemicals at some stages, and about 35% of the world's gross domestic product (GDP) is accounted for by catalytic processes [8]. In the field of catalysis, exploring the efficient, stable, and economical catalyst formulations has promoted the rapid development of nano-materials synthesis methods. Traditional heterogeneous catalysts are metal nanoparticles (NPs) dispersed on supports [9]. Among them, noble metals are the most efficient catalysts. However, the reserve of noble metals in nature is only about 3%. Therefore, it is of practical economic value to maximize the utilization of noble metal atoms [10]. In 2011, Zhang et al. defined the concept of SACs: an isolated metal atom anchored by a support as a monatomic active site [11]. Since then, SACs have become a research hotspot in the past decade due to their 100% atomic utilization and maximum dispersion, which greatly improves the efficiency of different catalytic reactions. The alterations in surface and quantum size effects as well as metal–support interactions play important roles in boosting catalytic performance [12].

Currently, the research of SACs is mainly focused on synthesizing stable single atoms on suitable supports. The strategies are divided into “bottom-up” and “top-down” methods according to the difference in precursors. The former is to disperse metal precursors on

the support on the atomic scale, and the latter uses metal NPs or bulk metal as precursors to prepare the SACs [13]. Based on the two strategies, many preparation methods have been developed, such as atomic layer deposition (ALD), wet-chemistry, pyrolysis, electrochemical or photochemical methods, and other methods. Different types of supports (e.g., metal oxides, porous metal–organic framework (MOF) materials, two-dimensional layered materials, and so on) are used to form strong chemical bonds between metal atoms and support to improve the stability of SACs in various reactions. For instance, the Pt_1/FeO_x catalyst possessed a unique electronic structure of noble metal atoms and iron oxide [11]. The high specific surface area of $\text{Ru}_1/\text{N}-\text{C}$ [14] was beneficial for the occurrence of catalytic reactions, and the layered structures [15] were designed to embed single atoms into the support. Single-atom alloy catalysts were developed to further improve the catalytic performance, such as PdAu [16], PtPd [17], and CoNi-NC catalysts [18]. The as-prepared SACs are widely used in carbon monoxide oxidation, methane combustion, hydrogenation, water–gas shift reaction (WGS), hydrogen evolution reaction (HER), carbon dioxide reduction, nitrogen oxide reduction, etc.

In this review, we introduce the advanced strategies of SACs preparation and their applications in environmental catalysis, including methane combustion, carbon monoxide oxidation, volatile organic compound (VOCs) oxidation, and nitrogen oxide reduction (Figure 1). The most remarkable challenge is the active sites and their stability against migration and aggregation under practical conditions. The active component, calcination temperature, treatment atmosphere, support type, and defect site also play important roles in the synthesis process of SACs and directly influence the catalytic efficiency. Furthermore, the problems and perspectives in the scientific research and applications of SACs are presented in detail. The reasonable design of SACs with unique structures, a low cost, and high efficiencies is of great significance in future industrial applications.

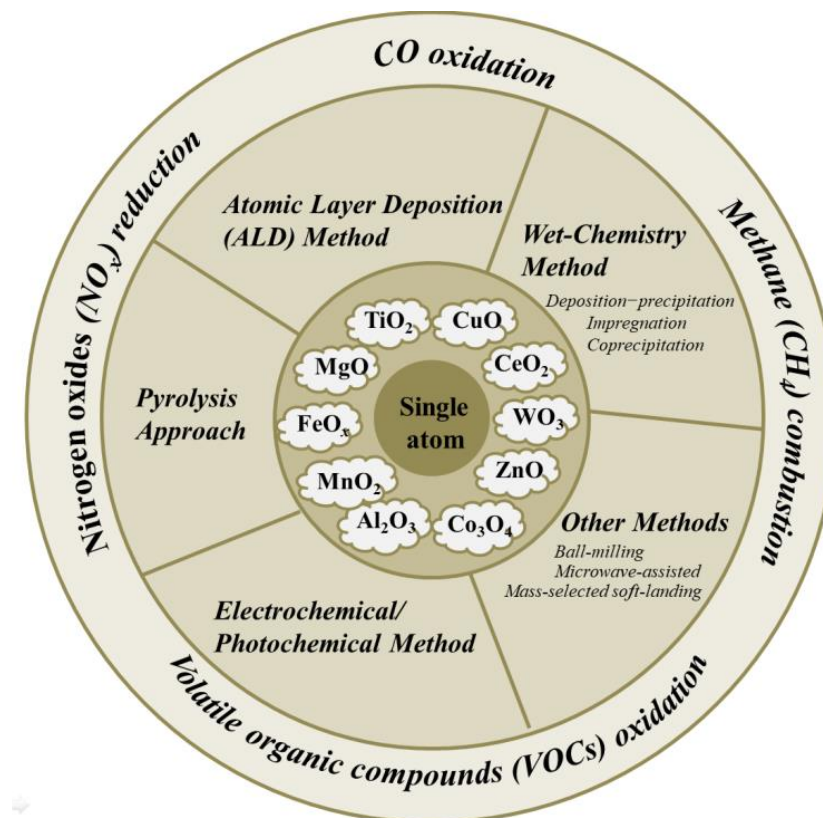


Figure 1. Supports, preparation strategies, and applications of SACs in environmental catalysis.

2. Synthesis of SACs

2.1. The Atomic Layer Deposition (ALD) Method

Earlier than the proposal of the SACs concept, the ALD technology has already been an optimal choice for coating various metals and metal oxides uniformly on the inner surface of porous nanostructures, such as ZnO, Al₂O₃, W, Cu, Pt, and Ru [19–24]. The ALD method usually includes the following two elementary steps: (i) exposure to a precursor vapor; and (ii) purging the residual precursors and by-products. In the former step, all of the active sites in the support interact with the precursors, and then extra reactants and by-products are swept with an inert gas. Next, another cycle starts, which can realize the required film thickness or design of specific materials by controlling the ALD cycle times and the deposition temperature [23,24]. This is also the unique advantage of the ALD method. In recent years, the selected metal deposition of graphene materials via the ALD route was rapidly developed [25–33]; the metal atoms could be precisely deposited into the defect of graphene, such as the crystalline phase interface [25]. CeO₂ [34], SiO₂ [35], and other metal oxides have also been developed as supports of the SACs. Figure 2a shows that the atomically dispersed Fe₁(OH)_x catalyst was fabricated on Pt NPs. Atom-level control was achieved by using the self-limiting and selective deposition. However, the ALD technology is generally only suitable for laboratory investigations and not for commercial purposes due to its high cost and low catalyst output, although a number of small-scale trials have been implemented [36,37].

2.2. The Wet-Chemistry Method

The wet-chemistry method includes the impregnation, co-precipitation, deposition-precipitation, and so on. Using the precursors containing metal atoms can effectually prevent monatomic aggregation, which is thanks to the metal-support interaction.

2.2.1. The Impregnation Method

The impregnation method is the most promising method for the industrial production of SACs due to its simple operation and cheap raw reagents, but the uniform dispersion of single atoms is still a challenge. It was found that the dispersity and loading content of the metal depends on the ability of a support to adsorb precursors containing the metal atoms during the impregnation process. It is worth mentioning that a support rich in oxygen vacancies is more favorable for stabilizing single atoms, such as TiO₂ [38,39], an amorphous MoO_x phase with abundant defects [40], MnO_x with an Ru–O–MnO_x interface [41], CeO₂ nanorods rich in Ce³⁺ [42–44], and SnO₂ [45]. For example, specific surface functional groups (e.g., –OH) facilitate the electrostatic adsorption of the metal precursors, hence favoring the anchoring of the individual Pt atoms (Figure 2b). Furthermore, numerous investigations have found that supports with high surface areas are also beneficial for stabilizing the single atoms [15,46–48].

2.2.2. The Co-Precipitation Method

Many parameters in the process of preparing SACs by the co-precipitation method can influence the dispersion of the metal atoms, such as the order and speed of adding precursors, the temperature and pH value of the solution, the ageing time, and so on. A variety of SACs were successfully prepared using the co-precipitation strategy, and their catalytic performance was usually better than their NPs [49–53]. Except for the support with abundant oxygen vacancies, the obvious electron transfer between the metal atoms and support facilitates the regeneration of oxygen vacancies, which plays an important role in catalytic reactions. For example, the Pt sites occupy the higher electronic state and show a strong affinity for the orbitals of neighboring Co atoms, thus promoting the electron transfer between Pt and Co atoms and ultimately increasing the number of oxygen vacancies on the catalyst surface [54]. The interaction between Pt atoms and the support can be adjusted by doping the reducible Fe₂O₃ to the irreducible Al₂O₃ by means of the co-precipitation approach [55]. However, the shortcoming of such a method is that the

partial atoms would be restricted to the inside of the support, and the atomic utilization does not reach 100%.

2.2.3. The Deposition–Precipitation (DP) Method

The operation sequence of the deposition–precipitation method is as follows: The target metal solution is added to the support suspension, and a mixed uniform suspension is formed after the reaction, thus depositing metal hydroxide or carbonate on the support. Generally speaking, this method easily obtains small-sized NPs or clusters; the SACs with a high dispersion are also synthesized via precisely controlling the reaction temperature and pH value of the precursor solutions. Although the loading content of the metal atoms obtained by this strategy is relatively low, the as-obtained samples exhibit excellent properties; therefore, this method is also widely used [56–60]. The active sites efficaciously inhibit carbon deposition [58,59], and the strong metal–support interactions make metal single atoms more strongly bound to the lattice oxygen of the support [60]. For the successful preparation of the SACs by the DP method, it is hence very important to accurately regulate the anchoring sites on the support surface and the metal–support interaction.

2.3. The Pyrolysis Approach

The pyrolysis approach usually employs the coordination-assisted strategy to achieve the preparation of SACs, especially for preparing the carbon-based SACs. Metal–organic frames (MOFs), as ideal precursors, possess a coordination environment with the well-defined atomically dispersed metal sites and an adjustable structure. For example, as shown in Figure 2c, the existence of $-\text{NH}_2$ prevents Ru in the precursors from aggregating to Ru clusters in the nitrogen-doped porous carbon-supported ruthenium catalyst (Ru SAs/N–C), which takes advantage of the strong coordination of Ru^{3+} with $-\text{NH}_2$ on the metal–organic skeleton [14]. Various single noble metal (Ru, Au, Pd, Ir, or Pt) atoms have been successfully immobilized at anchoring sites of the MOF-like hollow nanotubes [61], which further demonstrates that the SACs have a maximum atomic efficiency, unique hollow structure, and excellent mass transfer efficiency [62–64]. Such a structurally tunable synthesis strategy shows great potential in improving the catalytic performance of the SACs.

2.4. The Electrochemical/Photochemical Method

The electrochemical/photochemical method refers to adsorbing a mononuclear metal precursor on the surface of a support by means of the electrochemical or photochemical process. Using ultraviolet light irradiation [65–67] or electrochemical potential deposition [68–70] could prepare high loadings of SACs [65,71]. The atoms are inserted into the lattice of the support via transferring the photoelectrons in a photochemical liquid-phase reaction. For instance, high-energy deep-ultraviolet photons induced photochemical cleavage and activated the metal and oxygen atoms to promote the generation of the $\text{M}-\text{O}-\text{M}$ bond [68]. Constant potentials and special treatments are used to activate the catalyst for the optimum performance and steady state, such as in situ anchoring Ni atoms to the carbon support via carbonizing the as-synthesized Ni-MOF at 700 °C in the nitrogen atmosphere and then activating it by the electrochemical approach (Figure 2d). However, the shortcoming is that the atoms will be aggregated if the rates of nucleus formation and growth cannot be reasonably adjusted [72]. Thus, the photochemical reduction-freezing strategy was developed to successfully stabilize noble metal atoms [73]. At present, this method has been extended to other oxide supports, except for carbon materials and TiO_2 .

2.5. Other Synthesis Methods

Other synthesis methods for the efficient preparation of SACs include mass-selected soft-landing [74–76], the microwave-assisted method [77–79], ball-milling [80,81], laser ablation [82], and so on. A variety of SACs have been fabricated via these advanced synthesis routes. As shown in Figure 2e, the solid amine-functionalized graphene oxide (AGO) containing Co^{2+} was irradiated at 1000 W for 2 s; then, the Co-NG-MW catalyst was obtained, and the irradiation created a high-energy environment which was favorable for the simultaneous reduction and N-doping of GO, thus producing the defects or vacancies to anchor the metal atoms. Table 1 summarizes the supports, active components, loadings, and catalytic applications of some typical SACs in recent years. However, the commercial application of SACs has been hindered, so it is necessary to further develop SACs with distinct structures, good stability, and high loadings.

Table 1. The SACs are prepared by the ALD, wet-chemistry, pyrolysis, electrochemical/photochemical, and other synthesis methods.

Method	Catalyst	Loaded Metal	Support	Catalytic Reaction	Ref.
The ALD method	$\text{Co}_1/\text{graphene}$	Co (2.50 wt%)	Graphene	Hydrogenation of nitroarenes	[26]
	$\text{Pd}_1/\text{Graphene}$	Pd (0.25 wt%)	Graphene	Selective hydrogenation of 1,3-butadiene	[28]
	$\text{Co}_1\text{-N}_4/\text{g-C}_3\text{N}_4$	Co (1.00 wt%)	$\text{g-C}_3\text{N}_4$	Photocatalytic hydrogen production	[30]
	$\text{Pt}/\text{C}_3\text{N}_4$	Pt (0.14–0.32 wt%)	C_3N_4	photocatalytic hydrogen production	[32]
	Pt_1/CeO_2	Pt (0.22 wt%)	CeO_2	CO oxidation	[34]
The impregnation method	$\text{Fe-Pt}/\text{SiO}_2$	Fe (0–0.75 wt%)	SiO_2	Preferential oxidation of CO in hydrogen (PROX)	[35]
	Ru/TiO_2	Ru (1.00 wt%)	TiO_2	Photocatalytic fixation of nitrogen to ammonia	[38]
	$\text{Au-SA}/\text{TiO}_2$	Au (0.25 wt%)	TiO_2	CO oxidation	[39]
	$\text{Pt-SA}/\alpha\text{-MoO}_3$	Pt (0.28 wt%)	$\alpha\text{-MoO}_3$	Hydrogen evolution reaction (HER)	[40]
	$\text{Ru}/\text{MnO}_2\text{-r}$	Ru (0.10 wt%)	$\text{MnO}_2\text{-r}$	Oxidative cyanation of alcohols	[41]
	Pt/CeO_2	Pt (1.00 wt%)	CeO_2	CO oxidation	[42]
	Ru/CeO_2	Ru (0.89 wt%)	CeO_2	CO_2 methanation	[43]
	$\text{Pt}_1/\text{CuO-CeO}_2$	Pt (0.39 wt%)	CuO-CeO_2	Photothermal catalytic oxidation of toluene	[44]
	Pt_1/ATO	Pt (1.0, 4.0, 8.0 wt%)	SnO_2	Formic acid oxidation reaction	[45]
	$\text{Pd}/\text{Al}_2\text{O}_3$	-	Al_2O_3	Selective aerobic oxidation of allylic alcohols	[46]
The co-precipitation method	$\text{Pt}_1/\text{meso-Fe}_2\text{O}_3$	Pt (0.15 wt%)	Fe_2O_3	Benzene combustion	[47]
	$\text{Ru}/\text{CoFe-LDHs}$	Ru (0.45 wt%)	CoFe-LDHs	Oxygen evolution reaction.	[15]
	$\text{Ru}/\text{Al}_2\text{O}_3$	Ru (0.1–5.0 wt%)	Al_2O_3	CO_2 reduction	[48]
	CuCe	Cu (1.00 wt%)	CeO_2	CO oxidation	[49]
	Ni/MgO	Ni (0–18.7 wt%)	MgO	Reverse water–gas shift (rWGS)	[51]
The deposition–precipitation method	Ir_1/FeO_x	Ir (0.01 wt%)	FeO_x	Water–gas shift reaction (WGS)	[52]
	Pt_1/FeO_x	Ir (0.08 wt%)	FeO_x	Chemoselective hydrogenation	[53]
	$\text{Pt}_1\text{-Co}_3\text{O}_4$	Pt (0.02–0.30 wt%)	Co_3O_4	Methanol oxidation	[54]
	$\text{Pt}/\text{Fe}_2\text{O}_3$	Pt (0.30 wt%)	Fe_2O_3	Methane oxidation	[55]
The pyrolysis approach	Au_1/CeO_2	Au (0.05, 0.30 wt%)	CeO_2	Preferential oxidation of CO (PROX)	[56]
	$\text{Au}_1/\text{Co}_3\text{O}_4$	Au (0.05 wt%)	Co_3O_4	CO oxidation	[59]
	Pt_1/ZnO	Pt (0.0125 wt%)	ZnO	Methanol steam reforming	[60]
	Au_1/ZnO	Au (0.0125 wt%)			
The electrochemical/photochemical method	$\text{Ru SAs}/\text{N-C}$	Ru (0.30 wt%)	N-C	Chemoselective hydrogenation	[14]
	HNTM-Ir/Pt	Ir (1.05 wt%), Pt (2.54 wt%)	MOF (HNTM)	Photocatalytic H_2 evolution	[61]
	Co-N-graphene	Co (0.57 wt%)	N-graphene	Hydrogen generation	[63]
	$\text{RGO@AC}/\text{Pd}$	Pd (0.43–0.87 wt%)	RGO@AC (carbon)	4-Nitrophenol (4-NP) reduction	[64]
	$\text{Au-(OH)}_x/\text{TiO}_2$	Au (~1.0 wt%)	TiO_2	WGS	[65]
Other synthesis methods	$\text{Pd SA}/\text{TiO}_2$	Pd (0.53 wt%)	TiO_2	HER	[66]
	Pd_1/TiO_2	Pd (1.50 wt%)	TiO_2	Hydrogenation of aldehydes	[67]
	$\text{Ir}_1/\text{Co(OH)}_2$	Ir (1.2, 2.0 wt%)	Co(OH)_2	HER	[69]
	Ni-Carbon	Ni (1.50 wt%)	Carbon	HER	[70]
	Pd_1/TiO_2	Pd (1.20 wt%)	TiO_2	Toluene and methane oxidation	[71]
	Pt/RuCeO_x	Pt (0.49 wt%)	RuCeO_x	HER	[72]
	Pt_1/MC	Pt (2.60 wt%)	Carbon	HER	[73]
	Microwave-assisted	Co-NG-MW	N-graphene	HER	[78]
	Shock-heating	Pt-CA-CNF	Carbon	CO oxidation, direct methane conversion	[79]
	Ball milling	CoN_4/GN	Graphene	Interconversion of the redox couple I^-/I^{3-}	[80]
Mass-selected	FeN_4/GN	Fe (1.50 wt%)	Graphene	Benzene oxidation	[81]
	$\text{Au}_x(\text{TiO}_2)_y\text{O}_z^-$	-	TiO_2	CO oxidation	[76]
Laser ablation	$\text{PtAl}_x\text{O}_y^-$	-	Pt/Al mixed metal	Thermal methane conversion to formaldehyde	[82]

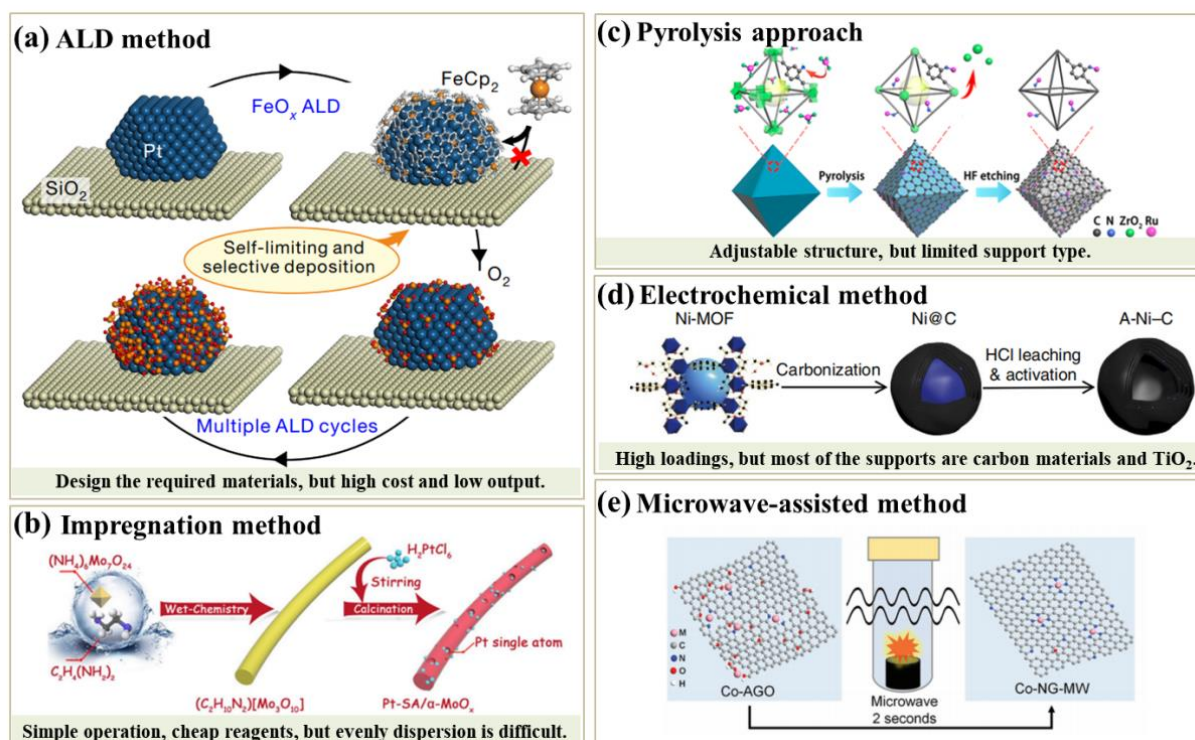


Figure 2. Schematic illustrations of preparing (a) $\text{FeO}_x\text{-Pt/SiO}_2$ by the ALD method. Reprinted/adapted with permission from Ref. [35]. Copyright 2019, copyright Springer Nature Limited, (b) $\text{Pt-SA}/\alpha\text{-MoO}_3$ by the impregnation method. Reprinted/adapted with permission from Ref. [40]. Copyright 2020, copyright Elsevier Ltd, (c) Ru SAs/N-C by the pyrolysis approach. Reprinted/adapted with permission from Ref. [14]. Copyright 2017, copyright American Chemical Society, (d) Ni-C catalysts by the electrochemical method. Reprinted/adapted with permission from Ref. [72]. Copyright 2020, copyright Willy-VCH GmbH, and (e) Co-NG-MW by the microwave-assisted method. Reprinted/adapted with permission from Ref. [78]. Copyright 2018, copyright Willy-VCH Verlag GmbH & Co. KGaA, Weinheim.

3. Catalytic Applications of SACs

A great number of studies on SACs have rapidly emerged in recent decades. In general, the detailed surface structure of a single atom can be obtained by a scanning tunneling microscope (STM) and aberration-corrected scanning transmission electron microscopy (STEM). X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure spectra (EXAFS) can provide the valence states of the metal atoms and the properties and oxidation states of the neighbor species, which are the most effective ways to determine metal coordination numbers and judge whether SACs have been successfully prepared. Nuclear magnetic resonance spectroscopy (NMR) is used to provide coordinate information of metal species and ligands during in situ reactions. Density functional theory (DFT) calculations can reveal the geometrical configuration and strong interaction of the SACs according to the bond lengths, bond energies, electron transfer, binding energies, orbital hybridization, and density of the states. SACs exhibit excellent catalytic activity and high stability in heterogeneous catalytic reactions owing to their specific geometries, unique electronic structures, and strong interactions. The properties and development potential of SACs in the aforementioned reactions are listed in Table 2 and described below in detail.

Table 2. Summary of the SACs for applications in environmental catalysis.

Reaction	SACs Catalyst	Catalytic Activity	Stability	Ref.
Photothermocatalytic oxidation of toluene	Pt ₁ /CuO-CeO ₂	Toluene conversion at 160–180 °C was increased by 48% after light illumination.	No obvious change in activity within 25 h of on-stream toluene oxidation at 185 °C.	[44]
Formic acid oxidation	Pt ₁ /ATO	The Pt ₁ /ATO catalyst showed activity and durability superior to those of the commercial Pt/C catalyst.	The structure was retained after a test of 1800 cycles.	[45]
Crotyl alcohol, cinnamyl alcohol, benzyl alcohol oxidation	Pd/meso-Al ₂ O ₃	TOF = 7080 h ^{−1} at 60 °C in crotyl alcohol oxidation; the most active catalyst reported at present for cinnamyl alcohol oxidation (TOF = 4400 h ^{−1}); TOF = 4096 h ^{−1} and more than 99% selectivity of benzaldehyde for benzyl alcohol oxidation.	—	[46]
Benzene oxidation	Pt ₁ /meso-Fe ₂ O ₃	The TOF _{Pt} (2.69 s ^{−1}) over Pt ₁ /meso-Fe ₂ O ₃ was much higher than that (1.16 s ^{−1}) over 0.25 Pt NP/meso-Fe ₂ O ₃ at 160 °C.	No significant change in activity after 40 h of on-stream reaction.	[47]
Methanol oxidation	Pt ₁ -Co ₃ O ₄	The reaction rate at 70 °C (0.013 mol/(g _{Pt} s)) over Pt ₁ -Co ₃ O ₄ was over four times higher than that (0.03 mol/(g _{Pt} s)) over Pt/Co ₃ O ₄ .	After water-resistant tests, notable losses were observed; the Pt ₁ -Co ₃ O ₄ catalyst possessed a better CO ₂ (5 vol%) resistance.	[54]
Toluene oxidation	Pd ₁ /TiO ₂	Complete toluene removal was achieved at 190 °C (Pd/TiO ₂ required a much higher temperature at 250 °C).	—	[69]
Oxidation of benzene to phenol	FeN ₄ /GN	The conversion was 23.4% and the yield was 18.7% at room temperature.	Benzene oxidation took place efficiently at 0 °C, with a phenol yield of 8.3% after 24 h of reaction.	[80]
Methanol oxidation	Pt ₁ -CeO ₂ {100}	The TOF _{Pt} was 0.68 s ^{−1} at 50 °C (T _{50%} = 33.7 °C, T _{90%} = 51.9 °C).	Negligible deactivation can be observed for an extended 800 min at 52 °C in a mixture airflow.	[83]
Toluene oxidation	Pt/MnO ₂	100% conversions of 0.42 ppm and 10 ppm toluene were achieved at 28 and 80 °C, respectively. The complete oxidation of toluene into CO ₂ took place at 220 °C.	Kept stable at 220 °C within 10 h of reaction.	[84]
HCHO oxidation	Ag-HMO	The TOF at 80 °C (0.035 s ^{−1}) over Ag-HMO was about seven times higher than that (ca. 0.005 s ^{−1}) over Ag/HMO.	—	[85]
	Alkali-Metal- Pt/TiO ₂	A 100% conversion of HCHO was achieved at 40 °C over the 1% Na-Pt/TiO ₂ catalyst.	—	[86]
	Pt/Mn-TiO ₂	The complete oxidation of 100 ppm HCHO was achieved at room temperature under the conditions of WHSV = 60,000 mL/(g h) and RH = 50%.	During the long-term activity test (>75 h), Pt/Mn-TiO ₂ displayed good stability, even at a WHSV of 120,000 mL/(g h).	[87]
CO oxidation	0.22Pt ₁ /CeO ₂	100% CO conversion was obtained at 160 °C, and the temperature was remarkably decreased to 98 °C in the presence of water.	The activity was virtually preserved at 92 °C after 96 h.	[34]
	0.25Au/TiO ₂	The full conversion temperature was 120 °C, which was significantly lower than that over Au/Per-TiO ₂ .	Without an obvious decrease in catalytic activity after 600 min of reaction.	[39]
	CeO ₂ -AA-Pt	The temperature of the CO complete conversion was 60 °C.	No activity losses in five cycle tests.	[42]
	CuCe	A CO consumption rate of 6100 μmol _{CO} /(g _{Cu} s) was achieved at 120 °C, which was much higher than that over the other reported copper catalysts.	Possessed remarkable cyclic stability at 600 and 200 °C (5 mg of catalyst, GHSV = 240,000 mL/(g h)).	[49]
	Pt-HT-SAs	—	Kept the excellent stability in CO or methane conversion at 220 °C for 50 h.	[78]
	Pt/ <i>m</i> -Al ₂ O ₃	TOF was 0.023 s ^{−1} at 200 °C and steadily increased to 0.175 s ^{−1} at 250 °C (GHSV = 4.8 × 10 ⁷ mL/(g h)).	Kept the stable activity after 60 cycles within a month.	[88]
	Au ₁ /Co ₃ O ₄	TOF was 3.1 s ^{−1} at −75 °C, which was one of the most active Au catalysts for CO oxidation (T _{90%} = −100 °C).	Kept stable after 10 cycle tests.	[89]
	CoO _x /Pt/CeO ₂	TOF was 0.88 s ^{−1} at 25 °C, with a GHSV of 75,000 mL/(g h) (T _{50%} = 6 °C, T _{90%} = 20 °C).	Kept stable during 36 h of on-stream reaction.	[90]
	Pt/Fe ₂ O ₃	The specific activity (2.01 mol _{CH₄} /(g _{Pt} h)) over Pt/Fe ₂ O ₃ was 4 times higher than that (0.47 mol _{CH₄} /(g _{Pt} h)) over Pt/Fe ₂ O ₃ -NP and 20 times higher than that over Pt/Al ₂ O ₃ .	Maintained a similar activity for over 16 h of on-stream reaction.	[55]
CH ₄ oxidation	Pd ₁ /TiO ₂	The temperature (380 °C) for the complete oxidation of methane was substantially decreased.	—	[71]
	1Pd/2Pt@CeO ₂	At 300 °C, the reaction rate (3.27 mmol _{CH₄} /(mol _{Pd} s)) was three times higher than that (0.91 mmol _{CH₄} /(mol _{Pd} s)) of (1Pd + 2Pt)/CeO ₂ .	A loss of 3.8% in reactivity in the presence of 4 v/v% water vapor and a loss of 15.7% in reactivity in the presence of 10 v/v% water.	[91]
	PdW ₁ /Al ₂ O ₃	The TOF at 260 °C over PdW ₁ /Al ₂ O ₃ was much higher than that over Pd/Al ₂ O ₃ .	No deactivation during the 30 h reaction process.	[92]
	Cu ₁ /ZSM-5	The Cu ₁ /ZSM-5 catalyst was highly active (C ₁ oxygenates productivity of 4800 μmol/g _{cat} at 50 °C and 12,000 μmol/g _{cat} at 70 °C within 30 min) and selective (C ₁ oxygenates selectivity of 99% at 50 °C). C ₁ oxygenate productivity of 4800 and 12,000 μmol/g _{cat} was achieved at 50 and 70 °C, respectively. A C ₁ oxygenate selectivity of 99% was achieved at 50 °C.	—	[82]
	Au ₁ /BP	The mass activity reached 113.5 μmol/g _{cat} in the presence of water with 33 bar of mixed gas (CH ₄ :O ₂ = 10:1) at 90 °C under light irradiation (1.2 W).	After 10 in situ cycles (20 h), about 205.2 μmol of methanol was generated.	[93]

Table 2. Cont.

Reaction	SACs Catalyst	Catalytic Activity	Stability	Ref.
NO _x reduction	Pd/TiO ₂	The presence of Pd led to a drastic increase (4–5 times) in NO _x removal efficiency after 5 h of reaction.	—	[94]
	NbCuCe	80% NO _x conversion was achieved at 150 °C, and a high N ₂ selectivity was detected during the activity testing process.	Under the conditions of 5 vol% H ₂ O, 5 vol% CO ₂ , and 200 ppm C ₃ H ₆ , NbCuCe still exhibited a better catalytic performance than Cu-CHA and NbCe.	[95]
	Mo ₁ /Fe ₂ O ₃	TOF at 270 °C over Mo ₁ /Fe ₂ O ₃ was ca. $1.7 \times 10^{-3} \text{ s}^{-1}$, comparable to TOF at 277 °C ($1.3 \times 10^{-3} \text{ s}^{-1}$) and TOF at 323 °C ($2.4 \times 10^{-3} \text{ s}^{-1}$) over V ₂ O ₅ /TiO ₂ .	—	[96]

3.1. CO Oxidation

CO oxidation is the most widely studied field of SACs. As early as 1999, researchers studied CO oxidation over the Pt/MgO catalyst and put forward the correlation between monodisperse Pt cluster size and catalytic activity [74]. The concept of SACs was first proposed by Zhang and colleagues when they concluded that partially vacant orbitals of high-valence Pt atoms contributed to reducing the adsorption energy of CO and the activation energy barrier of CO oxidation, thereby increasing the catalytic activity [11]. At present, the most commonly studied catalysts in SACs take Pd and Au as the active sites; FeO_x [11], CeO₂ [34,57,97], TiO₂ [98], Co₃O₄ [59], and Al₂O₃ [88] are used as the supports for CO oxidation. Generally speaking, the catalytic performance of CO oxidation over SACs is better than that of its corresponding NPs, such as Pt₁/FeO_x [11], Pt/*m*-Al₂O₃ [88], and Au₁/Co₃O₄ [89]. The activity of CO oxidation over the Pt/*m*-Al₂O₃ SAC was still maintained after 60 circles of testing in a month, while the temperature went up dramatically after 10 testing circles of the NPs catalyst [88]. The excellent activity and high stability of CO oxidation over the Au₁/Co₃O₄ SAC depend upon the interaction between Au₁ atoms and neighboring Co or O atoms (or oxygen vacancies), not only the individual Au₁ atoms [89]. Nevertheless, SACs do not always exhibit a better performance than NPs catalysts—for example, the catalytic activity of Pt SAC/SiO₂ is lower than that of Pt NPs/SiO₂ [99]. The Pt SACs prepared by electrostatic adsorption and high-temperature atomic capture were not active for CO oxidation at low temperatures, but the CO oxidation activities of both catalysts were improved after the catalysts were treated in a CO atmosphere at 275 °C, which was mainly attributed to the reduction in lattice oxygen in the CeO₂ support [100]. Another study reported that the active sites were the Pt–O–Pt sites, rather than the Pt–O–Ce interface. The Pt–O–Pt sites were more likely to activate oxygen molecules, and its CO oxidation activity was 100–1000 times higher than that of Pt₁/CeO₂ [101]. At the same time, the oxidation activity of CO was related to the migration of Pt sites to the position of clusters containing a small number of Pt atoms [102]. The reduced Au sites (Au⁰), which are the pivotal active sites in CO oxidation, demonstrate a higher CO adsorption capacity compared with the completely oxidized Au species [103]. In conclusion, the advantages of SACs in CO oxidation depend upon the interaction between metal atoms and support, but they cannot be simply generalized.

The activities of CO oxidation can also be further improved by doping other components to modified SACs. First, 1 wt% Ce was introduced to modify the TiO₂ support particles, which could stabilize Pt single atoms through the strong electronic interaction. The as-formed CeO_x–TiO₂ mixed oxide interface could stabilize Pt single atoms through the strong electronic interaction. Compared with the Pt/TiO₂ catalyst, the mass activity of the compact Pt SAC formed on CeO_x/TiO₂ mixed oxide increased by about 15 times [98]. Fe atoms, displaying a similar oxygen affinity to Pt, were inserted in nitrogen-doped graphene to prevent CO poisoning [90]. On the atomic scale, Luo et al. visualized the evolution of the AuCu alloy NPs supported on CeO₂ during the CO oxidation process and found that CO exposure led to the formation of the metal–CO bonds, while O₂ exposure resulted in the formation of the Cu₂O–AuCu interface, thereby promoting CO–O interaction [97].

3.2. Methane Combustion

Methane is abundant in natural reserve, and it is also the main component of natural gas and biogas. It is used as low-value fuel at all times, and its emission leads to increased methane concentration in the atmosphere, not only causing a waste of resources but also aggravating the greenhouse effect and bringing great environmental pressure. Therefore, it is desirable to study the complete oxidation of methane and convert methane to high-value chemicals for air pollution control and the utilization of low-carbon alkanes, respectively. In view of the highly symmetric tetrahedral stability and strong C–H bond energy of CH₄, the activation and directional transformation of CH₄ molecules have been hot topics in the field of catalysis.

On the one hand, the present literature concentrates on the high-temperature tolerance [56] and water resistance [91,92] of SACs on CH₄ combustion. The activity and stability were improved several times when Pt NPs were converted into Pt atoms in situ [56]. By combining the experiments with the DFT calculations, the volatilization of Pt at less than 600 °C is found to be thermally neutral or slightly endothermic, indicating that temperature plays a critical role in the dispersion of Pt NPs, that is, monoatomic dispersion can only be achieved at a temperature higher than 600 °C. Doping Fe₂O₃ into Al₂O₃ is beneficial to the dispersion of Pt atoms, because the reducible Fe₂O₃ displays a stronger interaction with Pt atoms than the irreducible Al₂O₃ displays with Pt atoms. In fact, a large amount of water vapor in the exhaust gas of methane combustion in actual situations will influence the performance of the Pd catalyst, even inducing deactivation. As shown in Figure 3a, two-dimensional Pt rafts were formed on the surface of cerium oxide (2Pt/1Pt@CeO₂), which showed a higher reactivity in CH₄ oxidation because of the weak interaction between the Pt atoms and support. However, deactivation after introducing water gas is inevitable (Figure 3b). The deactivation was mainly attributed to the generation and migration of the Pd–OH species strongly adsorbed on the PdO surface, and the surface active sites were poisoned due to the binding of water vapor to PdO, which was substantiated by the fact that the surface coverage of CH₄ on PdO (101) in the presence of water vapor is only 3% of the CH₄ saturation coverage [91]. In view of such a phenomenon, 1Pd/2Pt@CeO₂ derived from the atomic trapping route exhibited higher CH₄ combustion reactivity and better water resistance than 1Pd/CeO₂, 2Pt@CeO₂ and (1Pd + 2Pt)/CeO₂. Hence, the addition of Pt atoms is favorable for forming the PtPd bimetallic atoms and can stabilize the Pd species in a metallic state, thus improving the water vapor resistance. The W single atoms-modified PdO (PdW₁/Al₂O₃) catalyst [92] exhibited better water resistance than the traditional catalysts. When 3–10 vol% water vapor was first added to the reaction system and then cut off, the catalytic activity of PdW₁/Al₂O₃ first decreased and then recovered (Figure 3c). Interestingly, as the testing time got longer, the CH₄ conversion even exceeded the initial conversion, which was completely different from the activity of the traditional Pd catalyst (Figure 3d), which is due to the fact that water molecules participate in methane combustion in the form of the peroxy hydroxyl group, and W atoms change the electronic state of the PdO particles, thus regulating the adsorption energy and mobility of oxygen or water molecules. In general, the development of stable and efficient catalysts for CH₄ catalytic combustion still needs further exploration—from the perspective of either catalyst preparation strategies or reaction mechanisms.

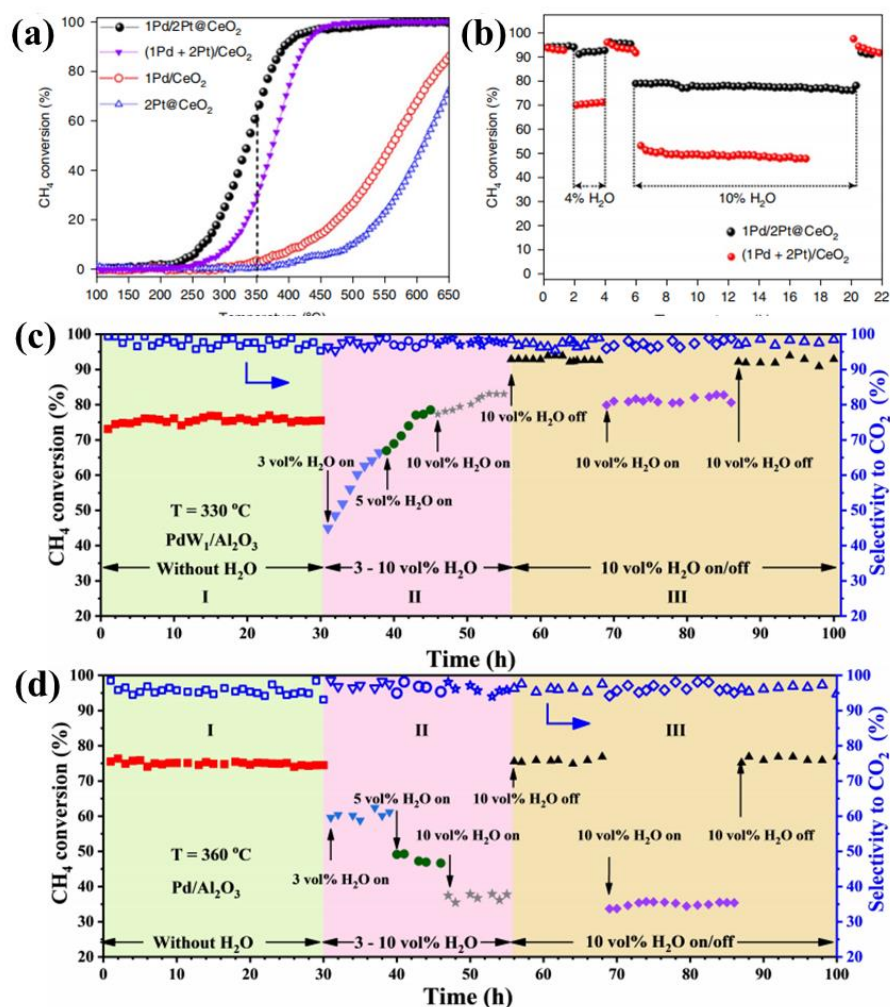


Figure 3. (a) Light-off curves of CH₄ combustion under dry conditions. (b) Time-on-stream measurements for CH₄ combustion at 500 °C under different steam concentrations over 1Pd/2Pt@CeO₂. Reprinted/adapted with permission from Ref. [91]. Copyright 2021, copyright Springer Nature Limited. The effect of water vapor concentration on the catalytic activity and selectivity of (c) PdW₁/Al₂O₃ and (d) Pd/Al₂O₃ for methane combustion. Reprinted/adapted with permission from Ref. [92]. Copyright 2022, copyright Willy-VCH Verlag GmbH. On the other hand, SACs are also used to convert CH₄ into high-value chemicals, such as methanol [93,104], ethylene, and aromatic hydrocarbons [58]. The general strategy in industry is to first convert CH₄ into syngas (CO and H₂) and then into higher-value products, but this process is energy-intensive and tends to produce by-products, such as CO₂. So, how should methane be directly oxidized to higher-value chemicals under mild conditions? How can we ensure the high methane conversion and high selectivity of higher-value products? These are worldwide problems that attract much attention in chemistry. From the perspective of active sites, Cu₁/ZSM-5 SAC can realize high CH₄ conversion and high methanol selectivity (99%) because the active sites preferentially activate CH₄ over methanol [104]. The Au₁/BP (black phosphorus) catalyst showed excellent activity and selectivity in the photocatalytic oxidation of CH₄ to methanol, and water plays an important role [93]. In addition to oxidizing methane to another chemical, Guo et al. proposed a non-oxidative pathway by which to convert methane to ethylene and aromatic hydrocarbons over Fe/SiO₂ SAC. At 1090 °C, the methane conversion, ethylene selectivity, and total hydrocarbon selectivity were 48.1, 48.4, and more than 99%, respectively. This catalyst also showed good stability, and no deactivation took place within 60 h of continuous reaction, since the absence of the adjacent Fe sites suppressed the catalytic C–C coupling and ensured that the methyl radical was to be formed without the deposition of solid carbon [58]. As mentioned above, studies on the active sites and catalytic performance for CH₄ combustion and selective oxidation are still being explored, which are of great significance for the world to control air pollution problems and resource utilization.

3.3. Volatile Organic Compounds (VOCs) Oxidation

Given that noble metal catalysts are of high cost, SACs show great potential in many oxidation reactions, such as the oxidation of alcohol [46,54,83], formaldehyde [85–87], and benzene/toluene [47,80,84]. These studies were mainly focused on Pt, Pd, Ag, and other SACs. The extensive applications of metal SACs in VOCs oxidation will be introduced in detail.

First of all, a proper reducible support is critical to successfully preparing SACs. Except for the excellent pollutant removal efficiency, maintaining stability for a long time is also important to the catalytic performance of SACs. As is well known, the metal–support interaction helps to maintain the thermodynamic stable state of SACs. For the supports with more oxygen vacancies, the oxygen vacancies strongly combine with the metal atoms and are difficult to replenish in time, resulting in a drop in catalytic activity. For the supports with a low number of oxygen vacancies, the binding force to the noble metal atoms is too weak to stabilize single atoms, so supports such as CeO_2 [83], MnO_x [84,85], and Co_3O_4 [54] were rapidly developed for the thermocatalytic oxidation of VOCs. For instance, Pt atoms are attached to the Co_3O_4 (111) crystal plane and occupy part of the Co^{2+} atomic sites. The electrons are transferred from Pt to Co sites, thus increasing the proportion of oxygen vacancies on the $\text{Pt}_1\text{-Co}_3\text{O}_4$ surface. The regeneration of these oxygen vacancies reduces the adsorption energy of methanol and significantly promotes the dissociation of the C–H bond in methanol oxidation [54]. Furthermore, the majority SACs showed a better performance than their NPs counterparts in many VOCs oxidation reactions. For example, the reaction rate of $0.25\text{Pt}_1/\text{meso-Fe}_2\text{O}_3$ for benzene oxidation was seven times higher than that of the NPs sample, which was undoubtedly related to the good utilization of Pt atoms [47]. The 0.03 wt% Pd/ Al_2O_3 SAC was the most active cinnamyl alcohol oxidation catalyst reported so far; the activity of each Pd atom increased by 30 times if the 4.7 wt% Pd cluster catalyst was prepared to the 0.03 wt% Pd SAC catalyst [46]. The above-mentioned cases indicate that the metal–support interaction in SACs highlights the advantages in the oxidation reaction. Interestingly, Jiang et al. further discovered that the Pt–O–Ce interface in Pt_1/CeO_2 SAC could spontaneously deform to balance the Fermi energy and charge density between Pt and the support, and the changes in the valence state and electronic structure increased the adsorption of oxygen and methanol, which was the essential reason for the excellent catalytic activity and thermal stability of the Pt_1/CeO_2 catalyst in the oxidation of oxygenated hydrocarbons [83].

Secondly, modifying the catalyst to form hydroxyl radicals can promote the oxidative activity for pollutant removal. Over the Pt/ MnO_2 SAC, a 100% conversion of toluene (0.42 ppm) was obtained at room temperature, and the oxygen vacancies and strong oxidizing hydroxyl radicals were considered to be the main reasons for its outstanding stability and excellent activity [84]. Moreover, introducing alkali metal ions (e.g., Li^+ , Na^+ , and K^+) to Pt/ TiO_2 SAC promoted the highly efficient removal of formaldehyde. The formed PtO(OH)_x -alkali metal species, as a promoter for the dispersion of Pt atoms, remarkably promoted the activity of formaldehyde oxidation by activating the simple reaction between hydroxyl and formate species on the surface [86].

In addition, the loading of metal or metal oxides, the addition of water vapor, and the special structure of the catalyst also seriously affect the performance of the catalyst. Pt/Mn–TiO₂, with excellent activity and an acceptable cost, was screened as the best catalyst for formaldehyde oxidation. The loading of Pt enhanced the reactivity of surface lattice oxygen [87]. However, it is worth noting that only 0.5 wt% Pt loading can completely oxidize formaldehyde at low temperatures and achieve long-term stability under simulated conditions. The addition of water vapor can suppress the side reaction and favor the deep oxidation of formaldehyde. The MnO_x nanorods-supported monoatomic Ag chain catalyst possessed a good activation ability for molecular and lattice oxygen at low temperatures [85], in which the Ag atoms were initially uniformly dispersed and then thermally migrated to the end of the support to generate a single-atom Ag chain. In general, SACs have shown promising application prospects in many fields. A number of targeted strategies have been developed to improve the efficiency of SACs, especially those aiming at multicomponent VOCs, which are still under development.

3.4. NO_x Reduction

Nitrogen oxides (NO_x, $x = 1$ or 2), derived from the exhaust emissions of diesel vehicles, are one of the important precursors of the atmospheric pollutants PM_{2.5} and the ozone. Their large amount of emissions lead to environmental pollution (e.g., haze, acid rain, and photochemical smog). The most effective NO_x removal technology is using NH₃ for the selective catalytic reduction of NO_x (NH₃-SCR) to generate environmentally friendly N₂ and H₂O. The key issue is the successful preparation of high-performance SCR catalysts with a high N₂ selectivity.

The Pt group catalysts have a great potential for NO_x emission control [94,105]. The 0.06 wt% Pt single-atom catalyst (Pt-SAC) could efficiently eliminate NO in a wide temperature range and showed a high N₂ selectivity. Compared with the NPs catalyst, Pt-SAC possessed more oxygen vacancies for NO adsorption and the breaking ability of the N–O bond [105]. Pd SACs exhibited a high selectivity for converting NO into nitrate and an excellent resistance to nitrate poisoning [94]. However, when the Pd loading increased to more than 0.055 wt%, Pd atom clusters or particles will form and significantly decrease the activity. This indicates that the catalytic performance of SACs is governed by the content of noble metals.

Transition-metal SACs have also received much attention [95,106] in NO_x reduction. Acidic metal oxides (e.g., Nb₂O₅, WO₃, and MoO₃)-modified CeO₂ catalysts show excellent NH₃-SCR performance at medium and high temperatures, especially the Nb₂O₅–CeO₂ catalyst. Ulteriorly, Xie et al. prepared a Cu atom-promoted Nb₂O₅/CeO₂ catalyst (NbCuCe), and the formed strong interaction of Nb–O–Cu and Cu–O–Ce effectively promoted the activation of reactant molecules [95]. After aging under actual reaction conditions, the NbCuCe catalyst showed better activity than the commercial Cu-CHA catalyst. Such a catalyst shows good application prospects in diesel vehicle exhaust low-temperature denitrification.

The Mo₁/Fe₂O₃ catalyst has been used to study the active sites and reaction mechanisms of NO_x reduction [96,106]. The formation of acidic-redox double active sites was caused by the Mo atoms and the surrounding Fe atoms (Figure 4a,b). The SCR performance was linearly related to the number of active catalytic sites (ACS) (Figure 4c–g). The redox ability of the binuclear W₁–Fe₁ site in Fe₁/WO₃ was much weaker than that in W₁/Fe₂O₃, which mainly led to an SCR performance of Fe₁/WO₃ that was inferior to that of W₁/Fe₂O₃ (Figure 4g). Thus, modulating the acidity or redox properties of W₁/Fe₂O₃ and Fe₁/WO₃ SACs can improve the SCR activity [106]. In addition, commercial catalysts are often inactivated due to the occupation of the active sites by the formed NH₄HSO₄ in the presence of SO₂. The acidic (Mo) sites and basic (Ti) sites in the Mo₁/TiO₂ catalyst adsorbed NH₄⁺ and HSO₄^{2−} in NH₄HSO₄, respectively, thus decomposing NH₄HSO₄ at 225 °C and releasing SO₂ at low temperatures without causing the poisoning of the catalyst [96]. The exploration

of the active sites for NO_x reduction and the reaction mechanisms under complex industrial conditions will help to develop high-performance catalysts.

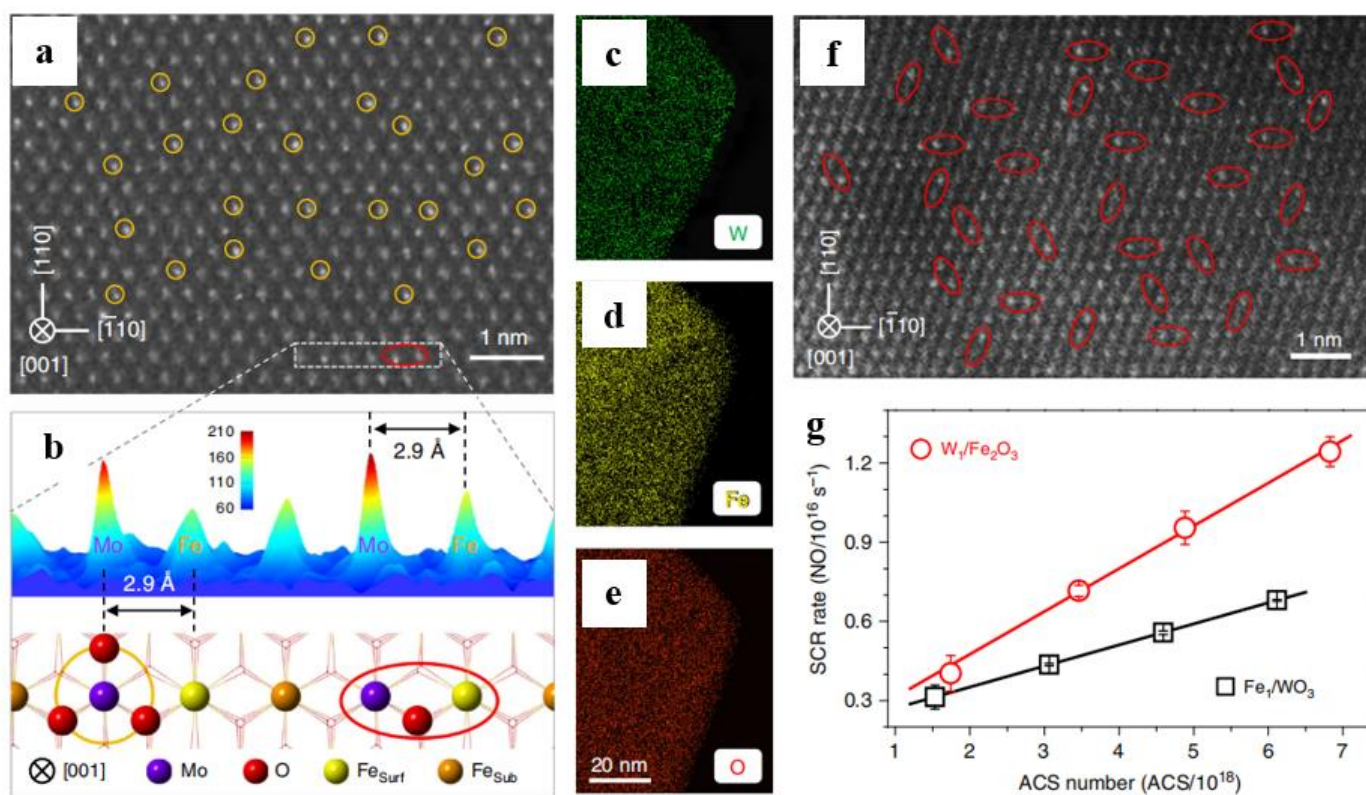


Figure 4. (a) AC-STEM image of $\text{Mo}_1/\text{Fe}_2\text{O}_3$, (b) intensity surface plot and the corresponding structural model of the selected area, (c–e) EDX mappings and (f) AC-STEM image of $\text{W}_1/\text{Fe}_2\text{O}_3$, (g) SCR rates of $\text{W}_1/\text{Fe}_2\text{O}_3$ and Fe_1/WO_3 with different ACS numbers at 270 °C [96].

4. Conclusive Remarks and Perspectives

Recent studies have shown that SACs have been rapidly developed in heterogeneous catalysis. The preparation methods of SACs and their applications in different reactions were briefly reviewed in this paper. The importance of support selection, catalytic performance, active sites, and reaction mechanisms was discussed. Due to their unique electronic structures, unsaturated coordination states, quantum size effects, and metal–support interactions, SACs have the following advantages over their nanocluster or nanoparticle counterparts:

- (i) **Efficiency:** SACs have achieved the maximum atomic utilization efficiency and have made great progress in CO oxidation, methane oxidation, VOCs oxidation, and NO_x reduction. In general, SACs are usually more active than their NPs catalysts, mainly due to the reducibility of the support (i.e., the number of oxygen vacancies, which is critical for anchoring single atoms) and the presence of OH groups on the support surface.
- (ii) **Economy:** The high atomic utilization reduces the amount of precious metal used in the catalyst and effectively reduces the cost.
- (iii) **Uniqueness:** The single active sites of SACs are helpful for further studying the active sites and catalytic mechanisms of various reactions.

However, there are the following challenges:

- (i) At present, there are many strategies to synthesize SACs, such as the ALD, wet chemical, and pyrolysis methods. However, the loading of monatomic metals is limited, so it is necessary to explore a common strategy to achieve the scale-up

production of SACs with high metal loadings, a satisfactory catalyst output, and good activity.

- (ii) The agglomeration of single atoms is still a common phenomenon, and the influence of inorganic molecules in the reaction atmosphere under actual industrial conditions should also be considered, such as the presence of H₂O, CO₂, SO₂, and HCl. Selecting a suitable metal to dope into a support or form an alloy structure can effectively modify the electronic structure of SACs and enhance the single atoms–support interaction, which is a good pathway to maintain the stability of SACs.
- (iii) SACs are currently limited to traditional pollutants (e.g., VOCs) in the atmosphere and need to be further expanded to other fields, such as the synthesis of high-value chemicals, the dehydrogenation of VOCs, the resource utilization of CO₂, the purification of water, and so on.
- (iv) Optimizing the catalyst structures to improve catalytic performance: Since the atomic structure has a direct effect on reactivity, it is highly desirable to use in situ characterization techniques to study the catalyst structures so as to design the catalysts rationally. The catalyst support with a high surface area has a complex nanostructure and abundant surface active sites, which is beneficial for improving the catalytic performance.
- (v) In addition to the development of in situ STM, STEM, and XAFS as well as the DFT theoretical calculations, more techniques need to be developed to recognize single atoms and further identify controversial active sites and mechanisms. The understanding of catalyst structures has a guiding role for the design of highly efficient catalysts. In addition, the current DFT calculations can only provide theoretical models of simple pollutant molecules, and more computational methods need to be explored to evaluate the reaction mechanisms of complex molecules.

In conclusion, SACs show great potential in the environmental remediation field. Although certain advancements have been achieved in fabrication strategies, performance evaluation, characterization techniques, and mechanism research, there are still some challenges, which are mentioned above. The reasonable design of SACs with a clear structure, a high efficiency, economy, and simple and controllable preparation methods is of great significance in future potential industrial applications. It is envisioned that this review article can draw more researchers' attention to achieving the goal of controlling single atoms.

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