Chinese Chemical Letters 35 (2024) 109400

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Progress and challenge of functional single-atom catalysts for the catalytic oxidation of volatile organic compounds

Zeyu Jiang[a,1], Yadi Wang[b,1], Changwei Chen[b], Chi He[a,b,c,*]

[a] Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] State Key Laboratory of Multiphase Flow in Power Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[c] National Engineering Laboratory for VOCs Pollution Control Material & Technology, University of Chinese Academy of Sciences, Beijing 101408, China

ARTICLE INFO

Article history:
Received 27 April 2023
Revised 4 December 2023
Accepted 18 December 2023
Available online 20 December 2023

Keywords:
Single-atom catalysts
VOCs catalytic oxidation
Hydrocarbon activation
Oxygen species transformation
Surface chemistry
Intrinsic mechanism

ABSTRACT

The catalytic oxidation of volatile organic compounds (VOCs) is of considerable significance for the sustainable development of the chemical industry; thus, considerable efforts have been devoted to the exploration of efficient catalysts for use in this reaction. In this regard, the development and utilization of single-atom catalysts (SACs) in VOCs decomposition is a rapidly expanding research area. SACs can be employed as potential catalysts for oxidizing VOC molecules due to their optimal utilization efficiency, unique atomic bonding structures, and unsaturated orbits. Progress has been achieved, while the challenges surrounding precise regulation of the microstructures of SACs for improving their low-temperature efficiency, stability, and product selectivity under practical conditions are remaining. Therefore, elucidating structure-performance relationships and establishing intrinsic modulating mechanisms are urgently required for guiding researchers on how to synthesize effective and stable functional SACs proactively. Herein, recent advances in the design and synthesis of functional SACs for application in the catalytic oxidation of VOCs are summarized. The experimental and theoretical studies revealing higher efficiency, stability, and selectivity of as-prepared functional SACs are being highlighted. Accordingly, the future perspectives in terms of promising catalysts with multi-sized composite active sites and the illustration of intrinsic mechanism are proposed. The rapid intelligent screening of applicable SACs and their industrial applications are also discussed.

1. Introduction

Volatile organic compounds (VOCs) are known to adversely affect the environment and human health [1]. Hence, the elimination of VOCs is a considerable challenge in the development of industrial chemistry [2–4]. In this regard, the catalytic oxidation of VOCs to harmless products, such as CO_2 and H_2O, is a promising strategy for VOC decomposition [5], and the development of efficient catalysts is central to this strategy [6]. Typically, supported noble metal-based catalysts are efficient in the catalytic oxidation of VOCs; however, their high costs and low utilization efficiency impede their further industrial applications [7]. Accordingly, extensive efforts have been devoted to improve the atomic utilization by decreasing the particle size of the catalyst, which may considerably increase the specific activity per metal atom and reduce the associated cost [8]. Ideally, single-atom catalysts (SACs) have attracted considerable attention in the field of catalysis owing to their 100% atom efficiency and unique catalytic performance. The optimal utilization efficiencies, unique atomic bonding structures, and unsaturated orbitals of SACs are considered to bring new opportunities for environmental pollution remediation, which becomes a prevalent research frontier [9,10].

Indeed, several SACs have been designed for use in the oxidation of VOCs, which exhibit better performance than the corresponding supported-nanoparticles catalysts [11]. For instance, Pei *et al.* synthesized an Ru/m-γ-Al_2O_3 SAC, which exhibited an outstanding catalytic efficiency in the selective degradation of 1,2-dichloroethane ($T_{90}=270\,°C$) compared to Ru NP/m-γ-Al_2O_3 ($T_{90}=323\,°C$) and pristine m-γ-Al_2O_3 ($T_{90}=386\,°C$) [12]. Furthermore, the Ru/m-γ-Al_2O_3 SAC was also found to display an excellent anti-Cl poisoning effect and water resistance during the stability test [12]. Additionally, Hao and co-workers verified that the single-atom Pt_1/OMS-2 catalyst is significantly more efficient

* Corresponding author at: Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China.
E-mail address: chi_he@xjtu.edu.cn (C. He).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.cclet.2023.109400
1001-8417/

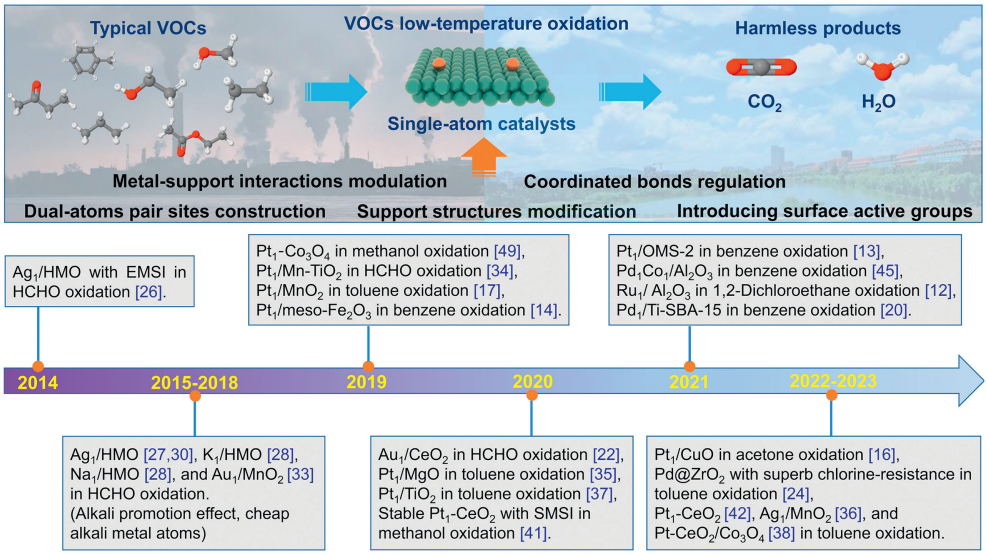

Fig. 1. Schematic illustration and overview of recent advances in the synthesis of functional single-atom catalysts for VOCs oxidation. Reprinted with permission [12]. Copyright 2021, American Chemical Society. Reprinted with permission [13]. Copyright 2021, American Chemical Society. Reprinted with permission [14]. Copyright 2019, Elsevier. Reprinted with permission [16]. Copyright 2022, Wiley-VCH. Reprinted with permission [17]. Copyright 2019, Elsevier. Reprinted with permission [20]. Copyright 2021, The Royal Society of Chemistry. Reprinted with permission [22]. Copyright 2020, Elsevier. Reprinted with permission [24]. Copyright 2022, Elsevier. Reprinted with permission [26]. Copyright 2014, Wiley-VCH. Reprinted with permission [27]. Copyright 2015, American Chemical Society. Reprinted with permission [28]. Copyright 2018, American Chemical Society. Reprinted with permission [30]. Copyright 2017, American Chemical Society. Reprinted with permission [33]. Copyright 2018, American Chemical Society. Reprinted with permission [34]. Copyright 2019, Elsevier. Reprinted with permission [35]. Copyright 2020, Springer. Reprinted with permission [36]. Copyright 2022, The Royal Society of Chemistry. Reprinted with permission [37]. Copyright 2020, Elsevier. Reprinted with permission [38]. Copyright 2023, Elsevier. Reprinted with permission [41]. Copyright 2020, Elsevier. Reprinted with permission [42]. Copyright 2022, Elsevier. Reprinted with permission [45]. Copyright 2021, Elsevier. Reprinted with permission [49]. Copyright 2019, Wiley-VCH.

than that of supported Pt_{NP}/OMS-2 sample in the low-temperature oxidation of benzene [13]. Meanwhile, Dai and co-workers identified that the TOF_{Pt} (2.69 s^{-1}) of a Pt_1/meso-Fe_2O_3 SAC at 160 °C was much higher than that of the Pt_{NP}/meso-Fe_2O_3 sample (1.16 s^{-1}) during benzene combustion [14]. Even though progress has been achieved, systematic SAC modification to enhance its low-temperature efficiency, stability, and product selectivity under practical conditions is still in its infancy. A detailed understanding of the relationship between structural regulation strategy and pollutant decomposition would help to further strengthen the performance of SACs and promote environmental sustainability.

Notably, the performance of SACs for VOCs oxidation are highly dependent on the structural characteristic and micro-environment of supported metal active sites [15]. The homogeneity and unsaturated coordination of single-atom sites may facilitate facile modulation of their electronic structures to promote the activity and stability during the oxidation process of VOCs. In particular, the metal-support interactions (MSIs), resulting from the difference in chemical potentials of metals and supports, will induce the charge redistribution of the whole SAC systems, thus modulating the adsorption and activation behaviours towards reactants (oxygen species and VOC molecules) and enhancing their catalytic performances. Meanwhile, the coordination bonding between metal atoms and supports can stabilize the isolated metal atoms with high surface energy to prevent their migration and aggregation. As demonstrated, the rational design of SACs with distinct structures, low cost, and high efficiencies is of great significance in future industrial applications. Therefore, considerable effort has been devoted to the design and synthesis of promising SACs for application in VOCs oxidation by precisely regulating their structures and properties; such as optimizing electronic and coordinated structures for boosting VOC molecule activation, modifying surface characteristics for promoting active oxygen species activation, modulating MSIs and constructing dual-atom sites for improving their stability under practical conditions (Fig. 1).

Subtle difference of coordination and electron structure could cause distinct catalytic behaviour for identical single sites. So, the precise control of the local environment of SACs has been a hard task. The coordination structures and interactions between atomic metals and supports were discovered to pose a significant influence on the physicochemical characteristics and catalytic performances of SACs. However, there is still a lack of clarity on the structure-catalytic correlation. Consequently, it is of great importance to explore the structural composition and interaction between different types of supports and various loaded metals to promote the catalytic activity of SACs. Unfortunately, contemporary evaluations have repeatedly focused on the categorization of SAC structures and contaminant compounds. A comprehensive report specifically focusing on the catalytic oxidation of VOCs over metal SACs is lacking. Herein, we proposed that a summary and discussion of recent progresses, by detailing the functional SACs in different ways, is urgently required for guiding researchers on how to synthesize effective and stable SACs proactively.

With this background, in this review, we introduce the advanced strategies for creating functional SACs and how they may be used to oxidize VOCs. Previously reported experimental and theoretical studies revealing higher efficiency, stability, and selectivity of as-prepared functional SACs are being highlighted. More attentions have been paid to reveal the corresponding intrinsic catalysis mechanism for VOCs oxidation over these functional SACs. The structure-function relationship of functional SACs is also emphatically discussed to give a hand for the rational design of SACs. Moreover, perspectives related to further challenges, directions, and design strategies of SACs for use in VOCs oxidation are also provided. The synthesis strategies and modulating methods summarized in this review will provide a generalizable platform for the

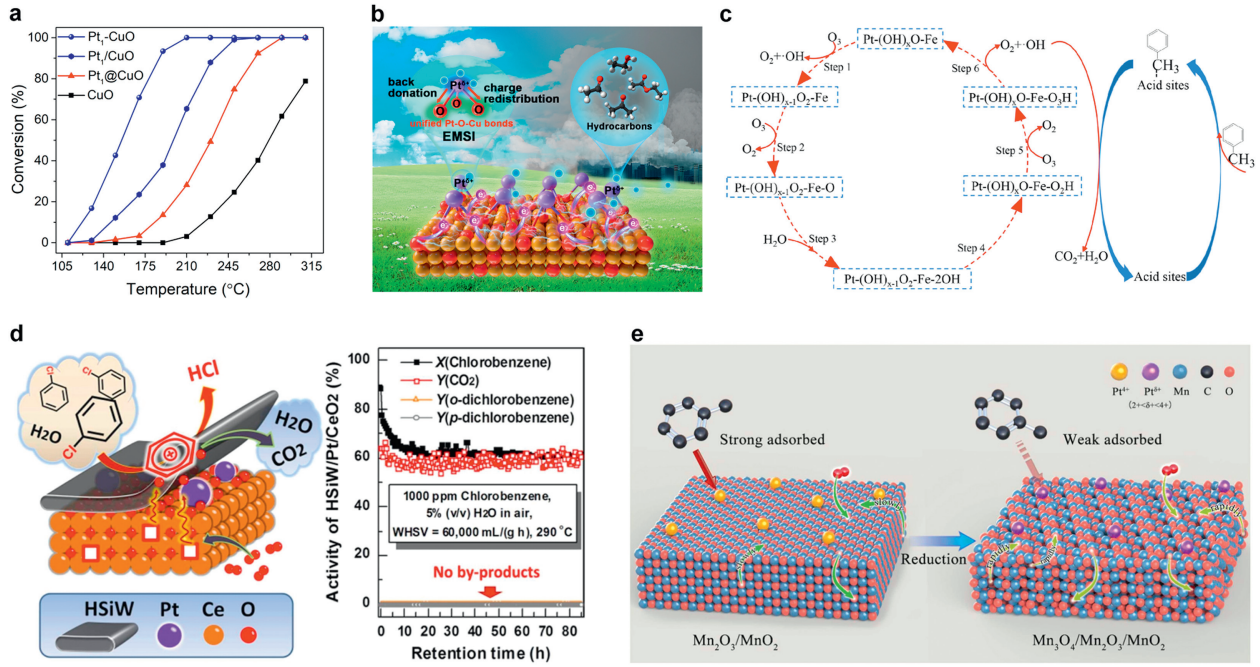

Fig. 2. (a) Catalytic performance of single-atom catalysts with diverse electronic metal-support interactions for the catalytic oxidation of acetone. Reprinted with permission [16]. Copyright 2022, Wiley-VCH. (b) Schematic presentation of acetone oxidation over the single-atom Pt_1-CuO catalyst. Reprinted with permission [16]. Copyright 2022, Wiley-VCH. (c) Reaction mechanisms of toluene oxidation over the atomically dispersed Pt−$(OH)_x$(O)−Fe species. Reprinted with permission [18]. Copyright 2021, American Chemical Society. (d) Schematic illustration and stability test of HSiW chainmail coated Pt/CeO_2 single-atom catalysts for chlorobenzene oxidation. Reprinted with permission [23]. Copyright 2023, Elsevier. (e) Schematic illustration of the hydrogen reduction treatment for Pt_1/MnO_x catalyst. Reprinted with permission [24]. Copyright 2022, Elsevier.

future design of well-defined functional SACs for efficient thermocatalytic oxidation reactions.

2. Synthesis of functional SACs for the catalytic oxidation of VOCs

2.1. Improving the activation of hydrocarbon molecules

The VOCs oxidation is typically initiated by hydrocarbon molecules adsorption and activation over active sites, and then proceeding by the cleavage of C–H/C–C/C=O/C–N/C–Cl bonds in collaboration with active oxygen species. As a result, the activation of reactants across a catalyst surface is the rate-determining step, which typically correlates positively with the catalytic efficiency of VOC oxidation. The intrinsic mechanism of this action has been discovered as the electron/charge transition from active sites to VOC molecules. Modulating the electronic structures of atomic metal species can dramatically improve VOC molecule adsorption and activation. For instance, metal species with lower charge density are favoured to adsorb and activate the low-polar ethane/propane molecules. While polarized metal species predominate in this mechanism for activating ketone/ester VOCs *via* C=O bonding. Furthermore, when oxidizing aromatic hydrocarbons, a mixture of metallic and positively charged metal species is required. Due to electron transfer and orbital hybridization that occur during metal-support interactions, single-atom active sites might potentially be used as the efficient active sites for the activation of different hydrocarbon molecules since their valence state and chemical bonding are readily regulated.

To that purpose, scientists have made significant attempts to increase the catalytic efficiency of SACs by modulating the coordinated and electronic structures of their atomic sites. For instance, in a recent study, Jiang and co-workers proposed that modulating the electronic metal-support interactions (EMSIs) of a Pt_1–CuO SAC significantly promoted its activity in acetone oxidation (Fig. 2a) [16]. This is attributed that the EMSIs are determined to promote charge redistribution *via* the Pt−O−Cu moieties, modulating the d-band structures of the atomic Pt sites and strengthening the adsorption and activation of reactants. Here, positively charged Pt atoms are superior in activating acetone at low temperatures, and the stretched Cu−O bonds facilitate the activation of lattice oxygen atoms to participate in the subsequent oxidation (Fig. 2b) [16].

Furthermore, introducing several surface-active groups, such as acid sites and hydroxyl groups, may significantly increase the ability of SACs for VOCs activation [17]. Accordingly, Liu *et al.* reported a facial method for introducing sufficient hydroxyl groups into a single-atom Pt/FeO_x catalyst [18]. Based on a comprehensive experimental study, the active sites in the catalytic ozonation of toluene were identified as atomically dispersed Pt-$(OH)_x$(O)-Fe. The surface hydroxyl groups greatly promoted the adsorption and activation of toluene molecules (Fig. 2c) [18]. Cui *et al.* also demonstrated that sodium ion doping (Na-Pt/TiO_2 SAC) facilitates the formation of ·OH around atomically dispersed Pt and dramatically enhances the catalytic performance with 100% of isopropanol conversion and 91.34% of CO_2 selectivity [19]. Additionally, Wen *et al.* successfully demonstrated a synergy relation between Pd atoms and surrounding acid sites in promoting cyclohexane adsorption and decomposition [20]. Notably, Brønsted acid sites, in the form of proton-donating hydroxyl groups, can stabilize cyclohexane molecules, which would be further oxidized over atomic Pd sites (Fig. 2d). The Pd/Ti-SBA-15 SAC, with an extremely low Pd loading (0.04 wt%), has been found to demonstrate an excellent catalytic activity ($T_{90} = 270$ °C) in cyclohexane combustion, exceeding those of Pd nanoparticles supported on Ti-SBA-15 with a high Pd loading (0.5 wt%, $T_{90} = 370$ °C) and Pd/SBA-15 without Ti substitution ($T_{90} = 420$ °C) [20]. Wang *et al.* increased the Lewis acid sites over Pt_1Pd_1/Al_2O_3 catalyst by introducing rare earth ions (La^{3+} and Ce^{3+}), which greatly promote the adsorption and activation of toluene molecules [21].

Regulation of support structure and property was chosen as an effective technique to increase SAC performance. For instance, Chen

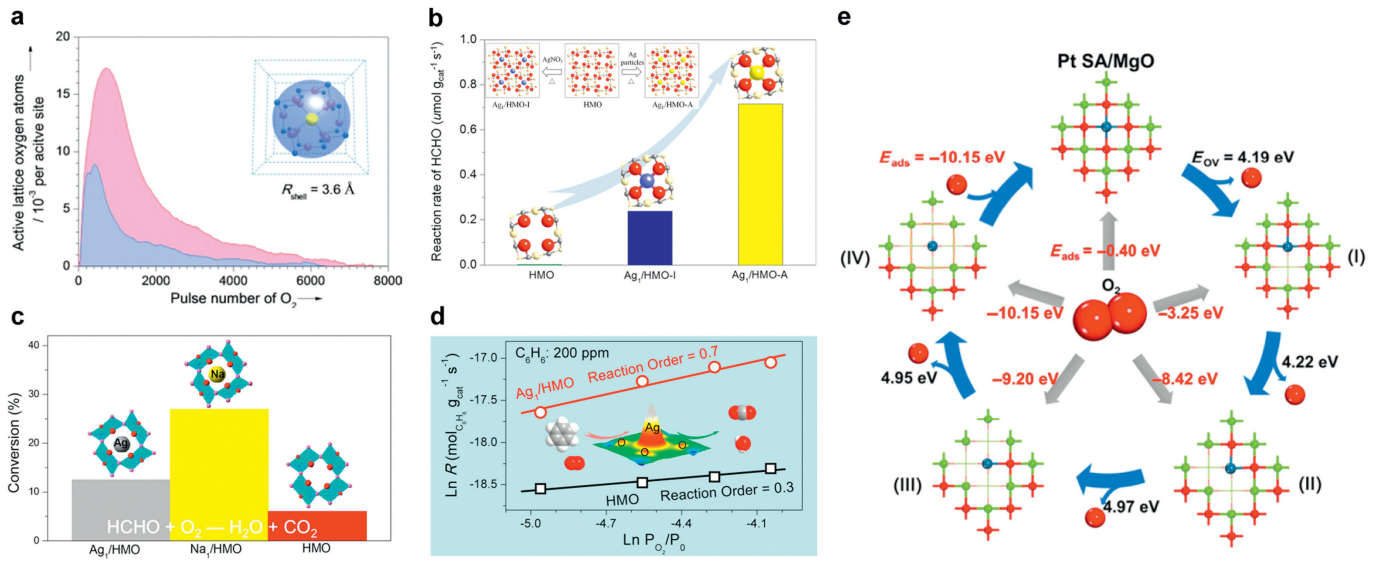

Fig. 3. (a) Temporal analysis of products results of Ag-HMO at 70 °C (blue shade) and 100 °C (red and blue shades) using a CO probe. The inset model shows twelve lattice oxygen atoms (pink) within a shell with a radius of approximately 3.6 Å (R-shell) of the CAS (yellow) at 70 °C. Mn atoms are depicted as blue balls. Reprinted with permission [26]. Copyright 2014, Wiley-VCH. (b) The structure and performance of Ag-HMO SAC. Reprinted with permission [27]. Copyright 2015, American Chemical Society. (c) The comparison efficiency and structure of hollandite manganese oxide (HMO) and supported single-atom catalysts in formaldehyde oxidation. Reprinted with permission [30]. Copyright 2017, American Chemical Society. (d) The catalytic performance of HMO and single-atom Ag_1/HMO catalyst for benzene abatement. Reprinted with permission [32]. Copyright 2017, American Chemical Society. (e) Theoretical calculations of the most stable structures of MgO and Pt SA/MgO and their effects on the formation of oxygen vacancy and subsequently O_2 adsorption. Reprinted with permission [35]. Copyright 2020, Springer.

et al. claimed that regulating the exposed facet of CeO_2 supports in Au_1/CeO_2 SACs can considerably improve their HCHO removal ability [22]. Jia and co-workers reported a HSiW chainmail coated Pt/CeO_2 SACs. They further proved that the outside layer of HSiW coating facilitated the activation and hydrolysis of chlorobenzene as well as provided a buffer between Pt and HCl, as a result, substrate activation was promoted and excessive oxidation of HCl was prohibited [23]. By using a hydrogen reduction procedure, Feng *et al.* increased the performance of the single-atom Pt_1/MnO_x catalyst. The researchers demonstrated that the hydrogen-treated SACs possessed weaker Mn-O bonds and a lower Pt-O coordination number, which results in balanced lattice oxygen mobility and volatile organic compound adsorption, both of which are necessary for the oxidation of toluene and isohexane. (Fig. 2e) [24]. As demonstrated above, optimizing electronic and coordinated structures are determined to be effective methods for boosting VOC molecule activation, which significantly improve the utilization efficiency of supported metal atoms. Combining the reaction characteristics of different VOCs, further selection of suitable supports and metals can be achieved accordingly.

2.2. Promoting the activation of oxygen species

The activation of molecular oxygen (O_2) is another critical step in oxidation reactions. The activation of oxygen species (generally containing one of or both lattice and/or adsorbed oxygen) significantly affects the mechanism and reaction pathways of VOCs oxidation [25]. Notably, SACs with highly dispersed metals are known to be efficient in VOCs activation; nevertheless, the size and structure effects are projected to simultaneously inhibit the capacities of such SACs for oxygen species activation. Therefore, considerable attention has been paid to explore potential strategies for activating oxygen species at low temperatures. Generally, introducing reducible metal oxides, modifying support structures, and strengthening the MSIs are crucial methods of improving oxygen species activation.

In this regard, Hu *et al.* reported the promotion of oxygen species activation over an SAC [26]. They discovered that the single silver atoms (converted from Ag particles under thermal driving force) were confined at 4-fold O_4-terminated surface hollow sites of a hollandite manganese oxide (HMO) and trapped by the tunnel of MnO_2 at its openings (Fig. 3a) [26]. Correspondingly, the so-called single-atom Ag chains could activate both the lattice and molecular oxygen species, leading to enhance its low temperature HCHO oxidation activity (Fig. 3b) [27]. Accordingly, this method was developed for designing other SACs using low-cost alkali metal catalysts, which also exhibited outstanding efficiencies in activating oxygen species [28–30]. For instance, Chen *et al.* determined that the surface lattice oxygen atoms could be easily activated at low temperatures using the Na_1/HMO SAC, which was attributed to the high electronic densities of the Na atoms [30]. Hence, the surface lattice oxygen species of Na_1/HMO, which displayed higher negative charges, exhibited stronger nucleophilic properties. The catalytically active centres included the surface single Na, vicinal lattice oxygen atoms, and the electronic states of the surface lattice oxygen species were critical in determining the catalytic performance in HCHO oxidation (Fig. 3c) [30]. Wang *et al.* also demonstrated that the strong electron transfer from Pt single-atoms to MnO_2 can improve the activity of surface lattice oxygen to boost the mineralization of toluene [31].

Notably, the capacities of SACs in oxygen species activation are essentially attributed to the electronic states or the d-band centroids of the metal atoms. Therefore, modulating the d-band structures of atomic active sites *via* interactions with reducible supports is a possible approach for promoting the activations and transformations of active oxygens. In this regard, a method of improving the activation of the lattice and adsorbed oxygen species over a single-atom Ag/HMO catalyst has been reported by Chen and co-workers [32]. Here, the upshifted d-band centroids of the atomic Ag sites favoured the dissociation of O_2 *via* charge transfer from the Ag 4d orbitals to the antibonding π^* orbitals of O_2, significantly promoting the circulation of diverse oxygen species and oxygen vacancies (Fig. 3d) [32]. A similar study conducted by Jia and co-workers demonstrated that the synergy between Au atoms and metal oxide supports in the Au_1/MnO_2 SAC could liberate more surface oxygen vacancies, promoting the activation of oxy-

gen species and improving the low-temperature catalytic oxidation activity toward HCHO [33].

For lattice oxygen activation, Chen *et al*. reported the Pt/MnO_x-TiO_2 SAC with high-valence Mn cations as "anchors" in TiO_2 [34]. The introducing of Mn species significantly promoted the transformation of lattice oxygens on the catalyst surface, which improved the performance of low-temperature HCHO oxidation. Similarly, another example of the oxygen species activation was reported by Zhao *et al*. [35]. In this work, the introducing of Pt atoms promoted the activation of lattice oxygens, and the oxygen vacancies could be easily generated on the Pt SA/MgO surface, which facilitated the activation of O_2 for participation in the oxidation reaction [35]. Crucially, the activated O_2 molecules generally dissociated to $^*O$ atoms at the Pt sites and then reacted with the adsorbed H_2O to generate $^\bullet OH$ *via* the following reactions: $O_2 \rightarrow {}^*O + {}^*O$ and $^*O + H_2O \rightarrow {}^\bullet OH + {}^\bullet OH$ (Fig. 3e). The high coverage of OH species was conducive to further oxidation processes, thereby improving the low-temperature activity [35]. Additionally, the atomic dispersion of Ag on MnO_2 was achieved by the redox reaction of H_2O_2 by Li and co-workers [36]. They demonstrated that the *in situ* generated Mn vacancies on $[MnO_6]^{\delta-}$ layers during H_2O_2 corrosion are beneficial for the trapping sites of Ag^+. The Mn vacancy-trapped Ag improves the reducibility and active lattice oxygen storage capacity of MnO_2 [36]. Combined with DFT calculations, Ag single atoms in Ag–O–Mn units show remarkable promotion for the adjacent oxygen vacancies and lattice oxygen activation compared to Ag nanoparticle counterparts.

In general, the in-depth decomposition of VOCs to harmless products such as H_2O and CO_2 at low temperatures coincides with the activation of oxygen species. It is well acknowledged that the surface properties of the catalysts, especially for surface imperfections, are connected to the activation process of O_2 and the kinds of active oxygen species. Surface imperfections, particularly oxygen vacancies in catalysts, can promote O_2 activation and the production of active oxygen species. They can react rapidly with the pre-adsorbed reactants, and then readily converted to oxygenates or non-toxic products, thus greatly increasing catalytic efficiency. Generally, introducing reducible metal oxides, modifying support structures, and strengthening the MSIs are crucial methods for improving oxygen species activation.

2.3. Improving the stability of single-atom catalysts

As industrial emissions often comprise H_2O, CO_2, and SO_2, the tolerance and stability of SACs are critical in their practical applications [37]. The most remarkable challenge is the stability of active sites against migration and aggregation under practical conditions. Therefore, the development of thermally robust and stable SACs that can sustain complicated oxidative processes at high temperatures has attracted considerable interest; however, the discovery of such SACs presents several challenges. Reducible metal oxides, such as CeO_2, Co_3O_4, MnO_x, FeO_x, and TiO_2, possessing strong redox properties and relatively low O_2 vaporization enthalpies, are prospective for interaction with atomic metal species, which can significantly facilitate the stabilization process of supported SACs. For instance, the Pt-CeO_2/Co_3O_4 and Ag/CeO_2-Mn_2O_3 single-atom catalysts exhibit the superb long durability for toluene oxidation due to the strong interactions between Pt/Ag atoms and supports [38,39]. A proper H_2 reduction treatment of Pt_1/MnO_x at 200 °C benefits the generation of Pt–O with low coordination number and the weak Mn–O bonds, resulting in the excellent catalytic stability (Fig. 4a) [24]. Wang *et al*. reported that the MSIs of Au-loaded WO_3/TiO_2 SACs greatly improve the thermodynamic stability of Au atoms, resulting in the durability of VOCs degradation [40]. Jiang *et al*. developed a universal strategy to stabilize Pt atoms at the mono-oxygen vacancies of CeO_2 with diverse exposed facets [41]. The proposed stabilization mechanism was as follows: the formed Pt–O–Ce interface had to be spontaneously distorted *via* strong MSIs to maintain its thermodynamic stability. The obtained Pt-CeO_2 SAC exhibited an exceptional efficiency and thermal stability, even when calcined at 800 °C (Fig. 4b) [41]. Similarly, a recent study conducted by Yang *et al*. confirmed that the MSIs of an as-synthesized Pt/CeO_2 SAC could facilitate the formation of oxygen vacancies, further promoting its thermal stability, even during extended calcination at 400 °C [42].

The development of dual-atom sites is a beneficial strategy for the widespread application of SACs in complex oxidation reactions [43]. Notably, adjacent metal atoms in bimetallic SACs may provide a synergistic effect for improving the anti-poisoning performance of SACs operating in complex conditions. Recently, the meso–Fe_2O_3-supported bimetallic Au-Pt single-atom catalyst was successfully prepared by Deng and co-workers, which possessed the best resistance to SO_2 due to the unique bimetallic atomic active sites that promote its strong sulfate decomposition ability and prevent it from being poisoned [44]. As illustrated in Fig. 4c, for Pt_{np}/meso–Fe_2O_3, Pt active sites were easily poisoned by SO_2, resulting in severe deactivation of the key step (the first C–H bond activation in methoxy species assisted by SMSI) during the reaction. However, SO_2 prone to adsorb on Fe_2O_3 to form iron sulfate over the Au_1Pt_1/meso–Fe_2O_3 catalyst, preventing the irreversible bonding of SO_2 with the active sites of Au_1Pt_1 [44]. In addition, Hou *et al*. adopted a novel strategy to prepare the bimetal Pd_1Co_1/Al_2O_3 SAC with dual active sites and good dispersions of Pd and Co single atoms [45]. Notably, the bimetallic Pd_1Co_1/Al_2O_3 SAC exhibited a superior SO_2 resistance compared to Pd_1/Al_2O_3, and the catalytic efficiency of Pd_1Co_1/Al_2O_3 gradually recovered in the presence of SO_2 (Fig. 4d) [45]. This excellent stability can be ascribed to the stronger circulation of Pd^0-$Pd^{\delta+}$ from the Pd_1Co_1 bimetal sites to potentially prevent the formation of the PdO-SO_3 complex and promote sulfate decomposition at low temperatures. Consequently, recoveries of the active sites after SO_2 poisoning were promoted (Fig. 4e) [44].

Exploration of SACs with superb anti-poisoning performance is also critical for their use in catalytic oxidation of VOCs. Generally, inhibiting the adsorption of poisonous molecules on active sites is an efficient approach to increase the anti-poisoning performance of functional SACs. Recently, ZrO_2-supported Cl-coordinated Pd single atoms with exceptional Cl resistances were reported, which exhibited satisfactory water resistance, long-term stability, and sufficient resistance to CO and dichloromethane (DCM) during VOC elimination [46]. Here, the residual Cl species from the Zr-metal–organic framework coordinated to Pd facilitated the formation of Pd_1-Cl species during pyrolysis, suppressing the adsorption of DCM and freeing more active sites for the adsorption of toluene and its intermediate (Fig. 4f). Therefore, the anti-poisoning performance of the Pd@ZrO_2 SAC was considerably improved [46].

Therefore, strengthening the metal-support interactions (MSIs) and optimizing the coordinated bonds have been identified as crucial methods for improving the thermal stability and anti-poisoning performance of synthesized SACs. The electron transfer between oxide supports and noble metal atoms is promoted for MSIs attributing to their orbital hybridization. The interface contact is also more favourable for the mutual effect of noble single atom and support, thereby enhancing the Cl-/S-/H_2O-resistance and long durability of the catalyst.

3. Intrinsic mechanism of VOCs oxidation over functional SACs

Notably, the rational design of effective SACs for use in VOCs oxidation requires a comprehensive understanding of the underlying reaction mechanism. With the size of metal species decreasing, the changes of VOCs adsorption and activation capacity of prepared

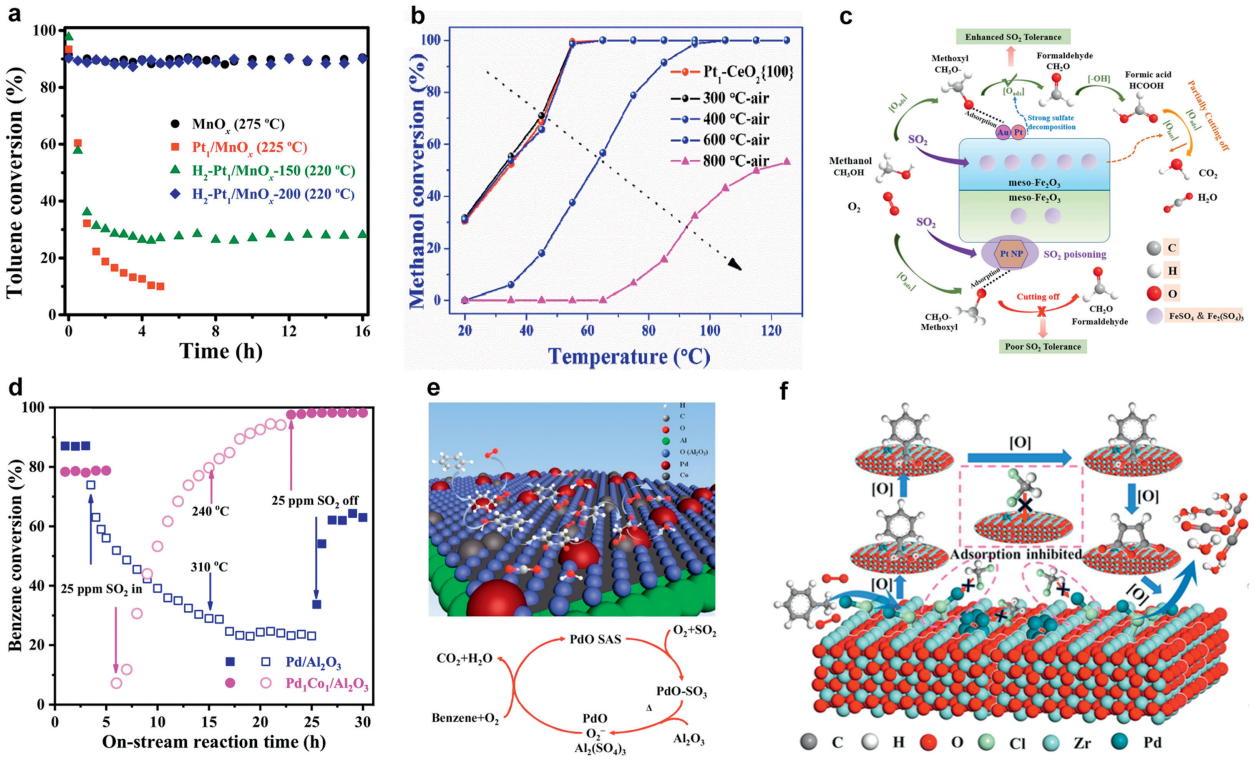

Fig. 4. (a) Stability test of single-atom Pt/MnO_x catalyst during toluene oxidation within 16 h of on-stream reaction. Reprinted with permission [24]. Copyright 2022, Elsevier. (b) The catalytic performance for methanol oxidation over prepared Pt_1-CeO_2 material after annealing at different temperatures. Reprinted with permission [41]. Copyright 2020, Elsevier. (c) Proposed mechanism of methanol oxidation over the Au_1Pt_1/meso–Fe_2O_3 and Pt_{np}/meso–Fe_2O_3 catalysts in the presence of SO_2. Reprinted with permission [44]. Copyright 2023, Elsevier. (d) Benzene conversion as a function of on-stream reaction time in the presence or absence of SO_2 over the Pd_1Co_1/Al_2O_3 and Pd_1/Al_2O_3 catalysts. Reprinted with permission [45]. Copyright 2021, Elsevier. (e) Schematic illustration of the recovery process after SO_2 poisoning on Pd_1Co_1/Al_2O_3 surface. Reprinted with permission [45]. Copyright 2021, Elsevier. (f) Stability test of single-atom Pd@ZrO_2 catalyst and its stabilization mechanism. Reprinted with permission [46]. Copyright 2022, American Chemical Society.

catalysts significantly influence their catalytic mechanism [47]. Determining the kinetic model and mechanism of VOCs oxidation on the catalyst surface is of great importance for designing the functional SACs. In general, three mechanism models for VOCs oxidation over supported SACs have been proposed, including Langmuir-Hinshelwood (L-H) mechanism, Eley-Rideal (E-R) mechanism, and Mars-van Krevelen (MvK) mechanism [9]. The L-H model begins with the adsorption of oxygen species and VOC molecules on the surface of the catalyst. Then the redox reaction proceeds between the adsorbed oxygen species and the adsorbed reactant, which is the rate-controlling step. Comparatively, for E-R model, the oxygen species are adsorbed on the catalyst surface, and VOC molecules are oxidized in the gas phase. The MvK mechanism is also known as redox mechanism, because the catalyst is reduced in the first step and then re-oxidized in the second step [48]. First, the VOC molecules are adsorbed on the catalyst and interact with the lattice oxygen on the catalyst surface, resulting in the reduction of metal oxides and the formation of oxygen vacancies. Then the reduced site is regenerated rapidly by the compensation of gaseous oxygen or the transfer of oxygen atoms.

Initially, a typical L-H mechanism with the representative oxidation routes for the low-temperature oxidation of HCHO over the Au/α-MnO_2 SAC was revealed by Chen and co-workers [33]. As displayed in Fig. 5a, HCHO was initially adsorbed, activated by the catalyst, and then oxidized by O_2 to CO_2 *via* several intermediates (H_2CO_2, HCOO, and CO) [33]. During the reaction, a gaseous O_2 molecule was adsorbed and dissociated by Au to form adsorbed oxygen species, which were then transferred by surface oxygen vacancies to the oxygen lattice to supplement consumption (Fig. 5a) [33]. Note that an outstanding capacity for oxygen activation-desorption is crucial in realizing the complete oxidation of HCHO at a lower temperature [33]. For another situation, HCHO oxidation over a Pt/Mn-TiO_2 SAC was determined to obey the Mars-van Krevelen (MvK) mechanism, according to the correlation between the structure and performance, with lattice oxygen species on the catalyst surface playing a critical role [34]. Based on the results of *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and H-D exchange, it can be inferred that O_{Latt} coordinated to the Pt atoms may be consumed *via* the oxidation of HCHO and the intermediates. This would result in unsaturated Pt coordination, further activating O_2 and providing active O_{Latt} for the reaction, thereby inducing enclosed oxygen circulation (Fig. 5b). The foregoing study further analysed the MSI effect (from a redox-driven hydrolysis-precipitation process) in facilitating the activation and mobility of O_{Latt} of this Pt-based SAC, which was the crucial factor influencing its remarkable performance in the low-temperature oxidation of HCHO [34].

Additionally, to understand the influences of the MSIs on the surface mechanism, subsequent studies were conducted by Jiang *et al.* [49]. Further, experimental and theoretical investigations indicated that this catalyst consisted of Pt sites with a large proportion of occupied high electronic states. These sites were found to present strong affinities for inactive Co^{2+} sites and functioned as anchors on the surface of the (111) crystal plane, increasing the MSIs of the Pt_1-Co_3O_4 material and accelerating the rate of oxygen vacancy regeneration. This promoted the co-adsorption of the probe methanol and O_2 molecules [49]. Density functional theory (DFT) calculations confirmed that electron transfer over the oxygen vacancies reduced the methanol adsorption energy and activation barriers to methanol oxidation. This theoretical investigation serves

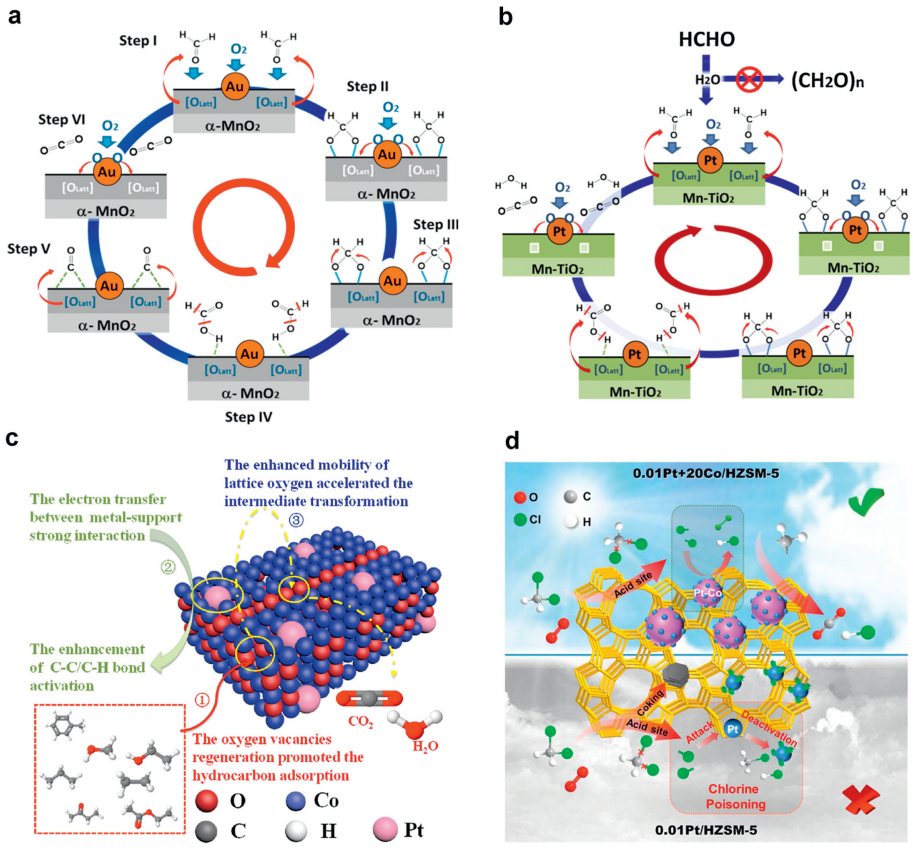

Fig. 5. (a) Representative oxidation routes for low-temperature oxidation of formaldehyde over a single-atom Au/α-MnO_2 catalyst. Reprinted with permission [33]. Copyright 2018, American Chemical Society. (b) The mechanism of formaldehyde oxidation over a single-atom Pt/Mn-TiO_2 catalyst. Reprinted with permission [34]. Copyright 2019, Elsevier. (c) The schematic diagram of promoted efficiency of Pt_1-Co_3O_4 material for typical VOCs oxidation. Reprinted with permission [49]. Copyright 2019, Wiley-VCH. (d) Schematic diagram of dichloromethane oxidation over Pt-Co/HZSM-5 catalyst. Reprinted with permission [50]. Copyright 2021, Elsevier.

as a solid foundation for characterizing and understanding single-atom catalysts for the enhancement of the C–H bonds dissociation during methanol decomposition (Fig. 5c) [49].

Subsequently, Su *et al.* revealed the DCM degradation mechanism on Pt-Co/HZSM-5 ternary catalyst [50]. As given in Fig. 5d, the DCM molecule was initially adsorbed on HZSM-5 with abundant acid sites and completely oxidized under the joint action of Pt and Co. Co can effectively anchor Pt atoms to realize the monoatomic dispersion of Pt, and the formed single-atom Pt, in turn, can increase the proportion of oxygen vacancies on the Co_3O_4 surface, thereby enhancing the redox performance of Co_3O_4 [50]. The synergistic effect among the Pt, Co, and HZSM-5 promoted the dissociation and deep oxidation of DCM and protected the catalyst from poisoning [50].

The clear structure of SACs makes them potential to be taken as the promising platforms to explore how the reaction proceed. Generally, the mechanism of VOCs oxidation is associated with the processes of pollutants and oxygen species activation. The MvK and L-H mechanism models are preferable for this reaction. The SACs with reducible transition metal oxides supports (such as CoO_x and FeO_x) can operate *via* MvK mechanism, where the lattice oxygen species are activated and the dissolved O* will participate to the intermediate transformation. The metal-support interactions are crucial in this process. When a metal is loaded on the support, the loaded metal disrupts the structure of the support, weakening the metal-O bonds, which in-turn promote the activation of lattice oxygen at low-temperatures. The generated oxygen vacancies can be re-filled by the O_2 gaseous. Correspondingly, the L-H mechanism occurs over the SACs with oxides support that containing abundant oxygen vacancies (such as CeO_2 and HMO). The sufficient surface oxygen vacancies promote the activation of adsorbed oxygen species, which can boost the mineralization of hydrocarbons. Therefore, we can select the proper supports and modulate the MSI to optimize the oxidation mechanism based on the molecular structure characteristics. In some cases, the combination of L-H and MvK models can significantly improve the low-temperature efficiency of VOCs decomposition.

4. Summary and outlook

Interestingly, owing to their unique coordination structures, SACs with the highest utilization efficiency are promising for use in the low-temperature catalytic oxidation of VOCs. Thus, substantial effort has been devoted to discovering SACs with characteristic structures that can be used for VOCs oxidation. In this concept, we summarized recent advances in the design and synthesis of efficient SACs for use in the catalytic oxidation of VOCs. Particularly, recent studies in the field were found to focus on the construction of efficient SACs and modulation of their structures and properties to improve their catalytic performance, stability, and selectivity. These considerable efforts have yielded extremely good prospects in terms of VOCs decomposition. Correspondingly, the field has witnessed progress, but certain challenges prevail; including the fabrication of multi-sized composite active sites, improvement of the selectivity towards specific product, determination of the intrinsic mechanism and active site evolution, industrial production and application, and rapid intelligent screening of applicable SACs.

(1) Fabrication of multi-sized composite active sites. Notably, the typical SACs only comprise individual metal atoms with size of approximately 0.25–0.45 nm. These metal atoms may not adsorb VOCs (with a size of 0.50–0.75 nm) and O_2 molecules (0.33 nm in size) simultaneously. The charged metal atoms are highly effective in activating organic hydrocarbons, but they may not co-activate the adsorbed oxygen species owing to the size effect, resulting in a lower selectivity toward harmless total oxidation products. By contrast, the nanoclusters active sites exhibit outstanding capacities for the adsorption and activation of surface O_2 molecules, attributing to their metallic properties. Therefore, through careful optimization of the distributions and relative proportions of these species (atoms and nanoparticles), a highly effective catalyst for total oxidation reactions can be synthesized.

(2) The selective catalytic conversion of hydrocarbons into high-value products is a promising technique in VOCs controlling. However, Improving the desirable product selectivity meanwhile restraining deep oxidation still mains a great challenge [51]. The unique structure and uniform coordination environment of SACs make them easier to be modulated for improving the specific product selectivity. Geometric changes relative to the parent metal, such as variations in metal bond lengths and strain effects due to lattice distortions, can affect the electrical structure of atomic species. Furthermore, ensemble effects, by means of the replacement of adjacent atoms, can markedly affect the type of surface intermediates and the adsorbed layers stably formed during the reaction process. Additionally, the construction of bifunctional active sites is determined as the efficient method to facilitate the selectivity of harmless products during heteroatoms-containing VOCs decomposition. For instance, the synergy between redox sites and acid sites can greatly enhance the selectivity of HCl selectivity (restraining harmless Cl_2) for chlorinated VOCs oxidation. Moreover, the combination of weak oxidation sites (noble metal atoms) and suitable reducible sites (transition metal oxides clusters) will promote the N_2 selectivity and inhibit the NO_x production during the oxidation of nitrogen-containing VOCs.

(3) Determination of the intrinsic mechanism and active site evolution. The intrinsic mechanism of VOCs catalytic oxidation over an SAC needs to be clarified, as the rational design of effective SACs for use in VOCs oxidation requires a comprehensive understanding of the underlying reaction mechanism. Accordingly, determining the intrinsic mechanism of VOC decomposition at the atomic scale is expected to promote the widespread use of promising SACs. Notably, dynamic catalytic reactions generally occur at the atomic level in active catalyst structures. Therefore, novel insights into the complex catalytic reactions at the atomic level are crucial in understanding the mechanisms and structure/property relationships. In this regard, *in-situ* characterisation methods, including *in-situ* DRIFTS, proton-transfer-reaction mass spectrometry, *operando* near-ambient pressure X-ray photoelectron spectroscopy, *in-situ* transmis-

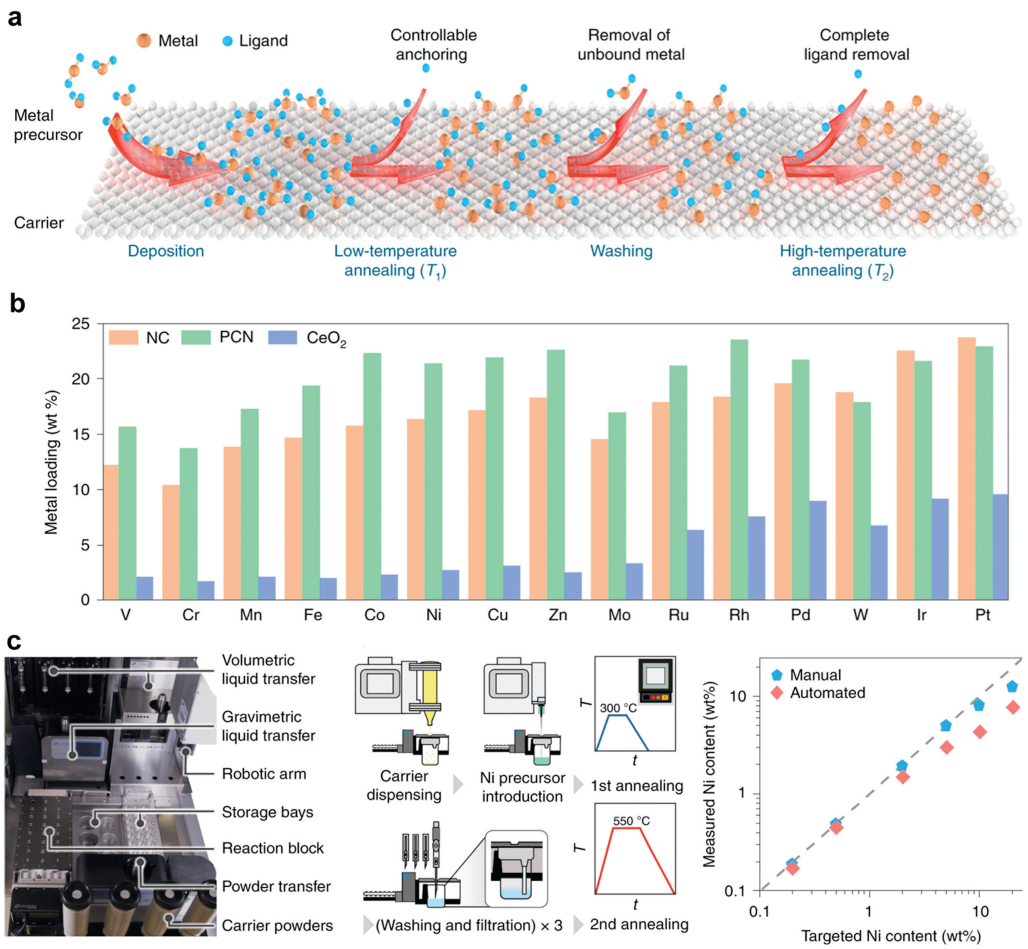

Fig. 6. (a) Strategy illustration for the preparation of ultra-high-density single-atom catalyst libraries. (b) The universal of achieved metal loadings on NC, PCN and CeO_2 supports. (c) Automated synthesis protocol for the synthesis of single-atom catalysts. Reprinted with permission [52]. Copyright 2022, Nature Publishing Group.

sion electron microscopy, and *in-situ* X-ray absorption spectroscopy, should be developed and employed to determine the changes of metal species. Moreover, in-depth observations of the VOCs oxidation processes would aid in providing reasons for the effectiveness of these SACs and thus guide the synthesis of promising SACs.

(4) Industrial production and application. Although numerous studies on the synthesis of efficient SACs have been reported, the practical applications of such materials in industrial production are yet to be realized. This is attributed that the industrial VOCs emissions are usually accompanied by multicomponent pollutants, such as H_2O, SO_2, NO_x, and halogenated or sulfur-containing VOCs, which will react with metal atoms to cause their deactivation. In addition, the long-term operation and transient high temperature may induce migration of isolated atoms, then inhibit the catalytic activity of SACs. Owing to the inevitable complexities of such industrial emissions, effective strategies for use in synthesizing stable, efficient SACs must be explored. How to maintain atomic dispersion of metals on SACs under working conditions is worth careful considerations. Moreover, currently reported methods of preparing SACs are generally restricted to specific supports or metals; thus, a universal preparation method is necessary. Large-scale production (above the kilogram level) is essential for the industrial application of SACs. Notably, a recent study conducted by Hai *et al.* contributed to overcoming this challenge. The authors introduced a versatile approach combining impregnation and two-step annealing to synthesise ultrahigh-density SACs with metal contents of up to 23 wt%, with 15 metals on chemically distinct carriers (Fig. 6) [52]. Finally, in available literatures, in most cases SACs work in powder form; but industrial catalysis requires monolithic catalysts and set reaction devices. it can be predicted that the integration of SACs into set reactors will be a top priority for their large-scale applications.

(5) Rapid intelligent screening of applicable SACs. Typically, the design of catalysts to accelerate reactions is challenging, as catalyst exploration is currently conducted *via* blanket screening; however, the machine learning (ML) technology may resolve this problem. ML is a subfield of data science, playing a central role in the paradigm shift from the use of traditional approaches. Thus, ML is a powerful approach for identifying and designing novel catalysts *via* the establishment of deeper correlations between the structure/activity relationship and principles of catalysis. Correspondingly, ML has been exploited in predicting catalysis and chemical reactions. Hence, ML may be used to screen for similarities in SACs to identify useful pathways for designing and fabricating novel SACs for their rational application in the low-temperature catalytic oxidation of VOCs. This may emerge as the primary method of catalyst design in the future.

Owing to their unequalled advantages, SACs have shown conspicuously improved performance on VOCs catalytic oxidation. In this review, we particularly focus on the specific manner and structural regulation methods to enhance catalytic performance of functional SACs. More importantly, the structure-function relationship of SACs is discussed to give a hand for the rational design of SACs. We believe that such a comprehensive understanding can help researchers to synthesize the functional SACs in a target, and boost the industrial development and green development at the same time.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 22276145, 21876139, and 21922606), National Key R&D Program of China (No. 2022YFB4101500), and China Postdoctoral Science Foundation (No. 2023M732783).

References

[1] C. He, J. Cheng, X. Zhang, et al., Chem. Rev. 119 (2019) 4471–4568.
[2] W. Ling, Y. Feng, J. Wei, X. Tang, H. Yi, Chin. Chem. Lett. 33 (2022) 3087–3090.
[3] M. Qi, Z. Li, Z. Zhang, Y. Gao, Q. Wang, Chin. Chem. Lett. 34 (2023) 107437.
[4] M. Guo, P. Ma, J. Wang, et al., Angew. Chem. Int. Ed. 61 (2022) e202203827.
[5] Y. Sun, S. Xu, B. Bai, et al., Environ. Sci. Technol. 56 (2022) 5796–5807.
[6] L. Xiang, F. Lin, B. Cai, et al., Environ. Sci. Technol. 56 (2022) 13379–13390.
[7] L. Zhang, L. Xue, B. Lin, et al., ChemSusChem 15 (2022) e202102494.
[8] L. Liu, A. Corma, Chem. Rev. 118 (2018) 4981–5079.
[9] F. Jiang, Z. Zhou, C. Zhang, et al., Nano Res. 16 (2023) 1967–1983.
[10] Z. Li, S. Ji, Y. Liu, et al., Chem. Rev. 120 (2020) 623–682.
[11] Y. Wang, M. Wang, Front. Chem. 10 (2022) 1039874.
[12] J. Pei, B. Peng, H. Lin, et al., ACS Appl. Mater. Interfaces 13 (2021) 53683–53690.
[13] X. Hao, L. Dai, J. Deng, et al., J. Phys. Chem. C 125 (2021) 17696–17708.
[14] K. Yang, Y. Liu, J. Deng, et al., Appl. Catal. B: Environ. 244 (2019) 650–659.
[15] X. Yu, J. Deng, Y. Liu, et al., Catalysts 12 (2022) 1239.
[16] Z. Jiang, M. Tian, M. Jing, et al., Angew. Chem. Int. Ed. 61 (2022) e202200763.
[17] H. Zhang, S. Sui, X. Zheng, R. Cao, P. Zhang, Appl. Catal. B: Environ. 257 (2019) 117878.
[18] R. Liu, S. Liu, H. Ding, et al., Ind. Eng. Chem. Res. 60 (2021) 3881–3892.
[19] J. Cui, Z. Hao, Y. Wang, et al., Chem. Eng. J. 446 (2022) 136989.
[20] M. Wen, S. Song, W. Zhao, et al., Environ. Sci. Nano 8 (2021) 3735–3745.
[21] T. Wang, S. Li, S. Chen, et al., Catal. Lett. 153 (2022) 3534–3545.
[22] J. Chen, M. Jiang, J. Chen, W. Xu, H. Jia, J. Hazard. Mater. 392 (2020) 122511.
[23] J. Chen, C. Wang, X. Lv, et al., J. Hazard. Mater. 441 (2023) 129925.
[24] Y. Feng, C. Wang, C. Wang, et al., J. Hazard. Mater. 424 (2022) 127337.
[25] N. Zhang, C. Ye, H. Yan, et al., Nano Res. 13 (2020) 3165–3182.
[26] P. Hu, Z. Huang, Z. Amghouz, et al., Angew. Chem. Int. Ed. 53 (2014) 3418–3421.
[27] P. Hu, Z. Amghouz, Z. Huang, et al., Environ. Sci. Technol. 49 (2015) 2384–2390.
[28] J. Chen, J. Gao, Y. Chen, et al., Ind. Eng. Chem. Res. 57 (2018) 12352–12357.
[29] F. Xu, Z. Huang, P. Hu, et al., Chem. Commun. 51 (2015) 9888–9891.
[30] Y. Chen, J. Gao, Z. Huang, et al., Environ. Sci. Technol. 51 (2017) 7084–7090.
[31] Y. Wang, J. Dai, M. Wang, et al., J. Colloid Interf. Sci. 636 (2023) 577–587.
[32] Y. Chen, Z. Huang, M. Zhou, et al., Environ. Sci. Technol. 51 (2017) 2304–2311.
[33] J. Chen, D. Yan, Z. Xu, et al., Environ. Sci. Technol. 52 (2018) 4728–4737.
[34] J. Chen, M. Jiang, W. Xu, et al., Appl. Catal. B: Environ. 259 (2019) 118013.
[35] S. Zhao, Y. Wen, X. Liu, et al., Nano Res. 13 (2020) 1544–1551.
[36] W. Yang, X. Zhao, Y. Wang, et al., Catal. Sci. Technol. 12 (2022) 5932–5941.
[37] Z. Wang, H. Yang, R. Liu, et al., J. Hazard. Mater. 392 (2020) 122258.
[38] H. Shi, P. Yang, L. Huang, et al., J. Colloid Interf. Sci. 641 (2023) 972–980.
[39] Y. Zhang, Y. Liu, S. Xie, et al., Environ. Int. 128 (2019) 335–342.
[40] X. Wang, H. Pan, M. Sun, Y. Zhang, J. Mater. Chem. A 10 (2022) 6078–6085.
[41] Z. Jiang, M. Jing, X. Feng, et al., Appl. Catal. B: Environ. 278 (2020) 119304.
[42] Q. Yang, L. Li, X. Wang, Y. Ma, J. Hazard. Mater. 424 (2022) 127601.
[43] L. Tu, R. Liu, D. Zhao, et al., Cataly. Surv. Asia 25 (2021) 389–398.
[44] W. Pei, K. Yang, J. Deng, et al., Appl. Catal. B: Environ. 335 (2023) 122888.
[45] Z. Hou, L. Dai, Y. Liu, et al., Appl. Catal. B: Environ. 285 (2021) 119844.
[46] F. Bi, Z. Zhao, Y. Yang, et al., Environ. Sci. Technol. 56 (2022) 17321–17330.
[47] S. Peng, Z. Ma, J. Ma, et al., Processes 10 (2022) 1773.
[48] J. Li, J. Hu, Y. Shi, et al., Chem. Eng. J. 451 (2023) 138721.
[49] Z. Jiang, X. Feng, J. Deng, et al., Adv. Funct. Mater. 29 (2019) 1902041.
[50] Y. Su, K. Fu, Y. Zheng, et al., Appl. Catal. B: Environ. 288 (2021) 119980.
[51] M. Guo, P. Ma, L. Wei, et al., J. Am. Chem. Soc. 145 (2023) 11110–11120.
[52] X. Hai, S. Xi, S. Mitchell, et al., Nat. Nanotechnol. 17 (2022) 174–181.