



# Engineering metal oxide catalyst for volatile organic compounds oxidation

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## Abstract

Volatile organic compounds (VOCs) are atmospheric pollutants that are considered the concerns for researchers as they can damage the human health by irritating the eyes and respiratory tract, causing skin allergies, headaches, sore throat, and fatigue. Therefore, the removal of indoor VOCs is urgently sought. Catalytic oxidation of VOCs over cost-effective metal oxides has been reported to be a promising strategy for the removal of VOCs because of the advantages of high efficiency, low cost, and less secondary pollution. In this review, we summarize the recent advances of metal oxide engineering for VOC oxidation, with the special attention to the categories and features of each VOC and the engineering strategies of metal oxides. Moreover, the applications of various metal oxides for catalytic VOC oxidation and the underlying structure-activity relationship are also illustrated. We hope this review will bring researchers new ideas for the design and fabrication of more efficient metal oxide catalysts.

**Keywords** Volatile organic compounds · Metal oxide · Catalytic oxidation · Structure

## Introduction

Volatile organic compounds (VOCs) refer to organic compounds that have high saturated vapor pressure, low melting point, and low content, and are prone to volatilization under normal conditions at room temperature [1, 2]. In general, VOCs are a class of organic compounds with cheerful physical properties, volatility, and potential harm [3, 4]. The key components of VOCs include carbon compounds (commonly known as carbon oxides, which are chemical substances composed of carbon and hydrogen atoms, including ethane, cycloalkanes, cyclohexanols, alkynes, and aliphatic hydrocarbons), homologues of benzene (chemical substances in which hydrogen atoms in hydrocarbon molecular structures are replaced by halogen atoms), oxygen containing organic compounds, and nitrogen containing organic compounds [5–7].

VOCs have a pungent and irritating taste, which can damage the respiratory system. In addition, VOCs contain compounds with carcinogenic and teratogenic, such as benzene and volatile phenols [8, 9]. Moreover, it is also demonstrated that VOCs can cause serious harm to the natural environment and induce haze pollution, which will thus damage the atmosphere and lead to global warming. As a unique type of pollutant, VOCs have unique pollution characteristics that distinguish them from other pollutants. Due to their diverse composition and adverse effects, they are listed as potentially hazardous pollutants in the natural environment and should be prioritized for manipulation [10]. Therefore, how to effectively and reasonably handle and repair volatile organic chemical pollution has become an urgent problem to be solved.

Many effective strategies have been proposed for the removal of VOCs, which can be divided into two types: recycling technology and destruction technology. Generally, the recycling technology includes the condensation technology, adsorption technology, membrane separation technology, and so on, whereas the destruction technologies are consisted of plasma degradation, biological oxidation, catalytic oxidation, and so on [11]. In the last decades, the adsorption and membrane separation technologies have been widely used for the removal of VOCs. However, the use of

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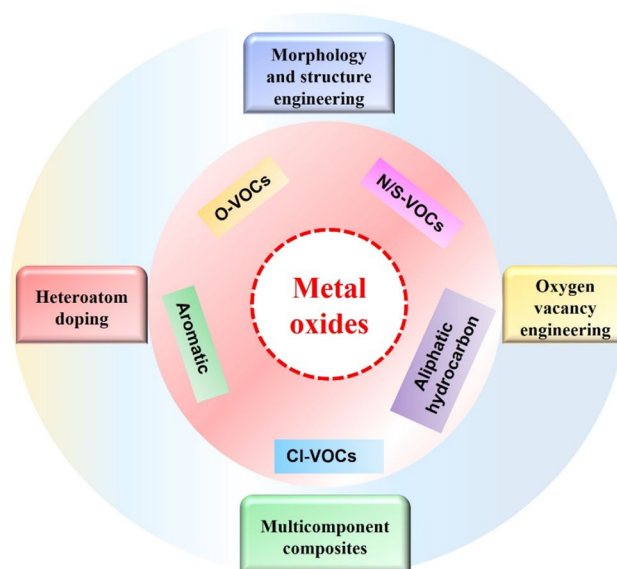
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highly effective adsorbents and membranes will inevitably lead to a high cost and the problems of secondary pollution [12]. In recent years, the catalytic oxidation technologies are standing out among various methods, which are demonstrated to be promising VOC elimination technologies with few byproducts under relatively low operation temperatures [8, 13]. However, the catalytic oxidation efficiency and rate are strongly correlated with the properties of catalyst. Noble metals, such as Pt, Pd, Ru, Rh, and their alloys are well documented to be highly active for VOC oxidation. However, the high cost of these noble metals and unsatisfactory performance have seriously hampered their widespread applications [14, 15]. To this end, exploring low-cost catalysts to substitute noble metals is an attractive topic. Upon the enormous endeavors devoted, it is found that transition metal oxide catalysts also possess high catalytic activity. The mostly used transition metal oxides are often composed of oxides of elements in the fourth period of the periodic table, such as  $\text{CuO}_x$ ,  $\text{TiO}_2$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{Fe}_2\text{O}_3$ . [16]. These metal oxides have the merits of good electronic mobility, strong oxidation, and outstanding catalytic activity [17]. Therefore, these oxides can function as the promising substitute of noble metals. Benefitting from these merits, transition metal oxides are emerging as promising catalysts for the removal of VOCs, and enormous endeavors have been dedicated to the design and fabrication of more effective metal oxide catalysts. Therefore, many effective strategies for further promoting the catalytic performance of metal oxides toward VOC oxidation have been proposed. However, a systematic review in terms of the engineering strategies and their influences on catalytic oxidation performance has been rarely reported.

Herein, we summarize the recent progress of the effective strategies for further enhancing the catalytic performance of metal oxides for VOC oxidation (Scheme 1). In this review, we have firstly illustrated the five main VOCs in atmosphere. Subsequently, four effective strategies proposed for enhancing the catalytic VOC performance of metal oxides are also systematically discussed, which include the morphology design, vacancy engineering, heteroatom doping, and constructing multicomponent composites. Finally, the challenges and prospects of this interesting field are also briefly discussed. Expectedly, this review will appeal widespread attention toward metal oxide catalysts for VOC elimination.

### Main VOCs and their catalytic oxidation

VOCs are harmful for human health. As well known, VOCs released into the atmosphere are made up of more than 300 groups, which can be primarily divided into five types: aromatic, aliphatic hydrocarbon, oxygen-containing VOCs (OVOCs), halogenated VOCs, and N/S-containing VOCs [18–20]. Due to the complexity and large emissions



**Scheme 1** Schematic diagram of the categories of VOCs and effective strategies for optimizing the catalytic performance of metal oxides

of VOCs, the VOC treatment technology still has huge challenges. The widely known VOCs are aromatics, such as toluene, xylene, benzene, acetaldehyde, butyl acetate. These compounds may be released into indoor air through volatilization, thereby polluting indoor air. According to previous research, long-term inhalation of these compounds can affect human health, including causing headaches, eye discomfort, impaired smell and memory, and damage to the immune system [21]. Aliphatic hydrocarbon, such as ethylene, butane, hexane, and octane, is also an important type of VOCs that can cause damage to human health [22]. Besides, the OVOCs are the second largest VOCs in industrial emissions that can cause photochemical destruction of ozone layer secondary aerosols and ozone generation. HCHO is a typical representative of the OVOCs with carcinogenicity and teratogenicity. HCHO can react with  $\text{NO}_x$  and thus poses an adverse effect on the air quality [23–25]. Therefore, removing HCHO is meaningful for achieving green atmosphere. Halogenated VOCs are common industrial pollutants and an important cause of greenhouse gases. Among various halogenated VOCs, Cl-VOCs have become the key pollutants to be removed due to their high emission, high toxicity, and low biodegradability [26]. In regard to N/S-VOCs, it is well known that the N/S-VOCs are released into air by natural and man-made sources [27]. To remove the N-VOCs, it should carefully consider the selectivity of  $\text{N}_2$  and the control of  $\text{NO}_x$  formation to avoid secondary pollution [28]. For S-VOCs, it should be noted that the S atoms or their intermediates may preferentially adsorb on the active site of catalyst, resulting in the low catalytic activity.

In recent years, the government has limited the emissions of VOCs. However, due to the high demand for industrial products, it is still challenging for society to decrease the production and emissions of VOCs. Accordingly, developing effective strategies to degrade VOCs is now becoming a hotspot.

Generally, the catalytic oxidation technology has been widely regarded as an effective and promising strategy for the removal of VOCs. For catalytic oxidation technology, the use of catalysts is highly important [29–31]. For instance, noble-metal-based catalysts are demonstrated to display low catalytic activity for the degradation of S/N-VOCs or VOCs containing Cl because of the toxicity of catalysts. The Cl, S, or N atom will react with the active ingredients of the catalyst, resulting in permanent deactivation of the catalyst. To address this issue, introducing appropriate supports to load noble metals can effectively alleviate the toxicity of catalysts. Besides, support can also well disperse the noble metal nanoparticles to expose a great deal of active sites. Furthermore, the strong metal-support interaction of supported catalysts can also significantly improve the intrinsic activity of catalyst by unique electronic effect [32, 33]. In addition to introducing appropriate supports, synthesizing other cost-effective catalysts to substitute noble metals is also another effective method for achieving high catalytic VOC oxidation performance. For example, metal oxides are widely investigated and considered to be a good choice for catalytic VOCs because of their low cost and superb reducibility and toxicity resistance. In recent years, enormous endeavors have been dedicated to the design and fabrication of high-performing metal oxide catalysts.

### Types of metal oxide catalyst for VOC oxidation

Non-noble metal oxide catalysts, including oxides of Cu, Mn, Co, Fe, etc., although the activity maybe not as good as that of noble metal catalysts, their inexpensiveness and long-term thermal stability have drawn increasing attention and have the potential to be dominant in the future. These metal oxides have the merits of good electronic mobility, strong oxidation, and outstanding catalytic activity [17]. Owing to these advantageous merits, metal oxide catalysts are now attracting great interest in recent years for catalytic VOC oxidation reactions. In general, the mostly used metal oxide catalysts are titanium dioxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), manganese oxide ( $\text{MnO}_x$ ), and mixed metal oxides such as cerium-based oxides, copper-based oxides, and vanadium-based oxides. Although the great advantages, the performance of these metal oxide catalysts still cannot meet the standards, which require further modifications.

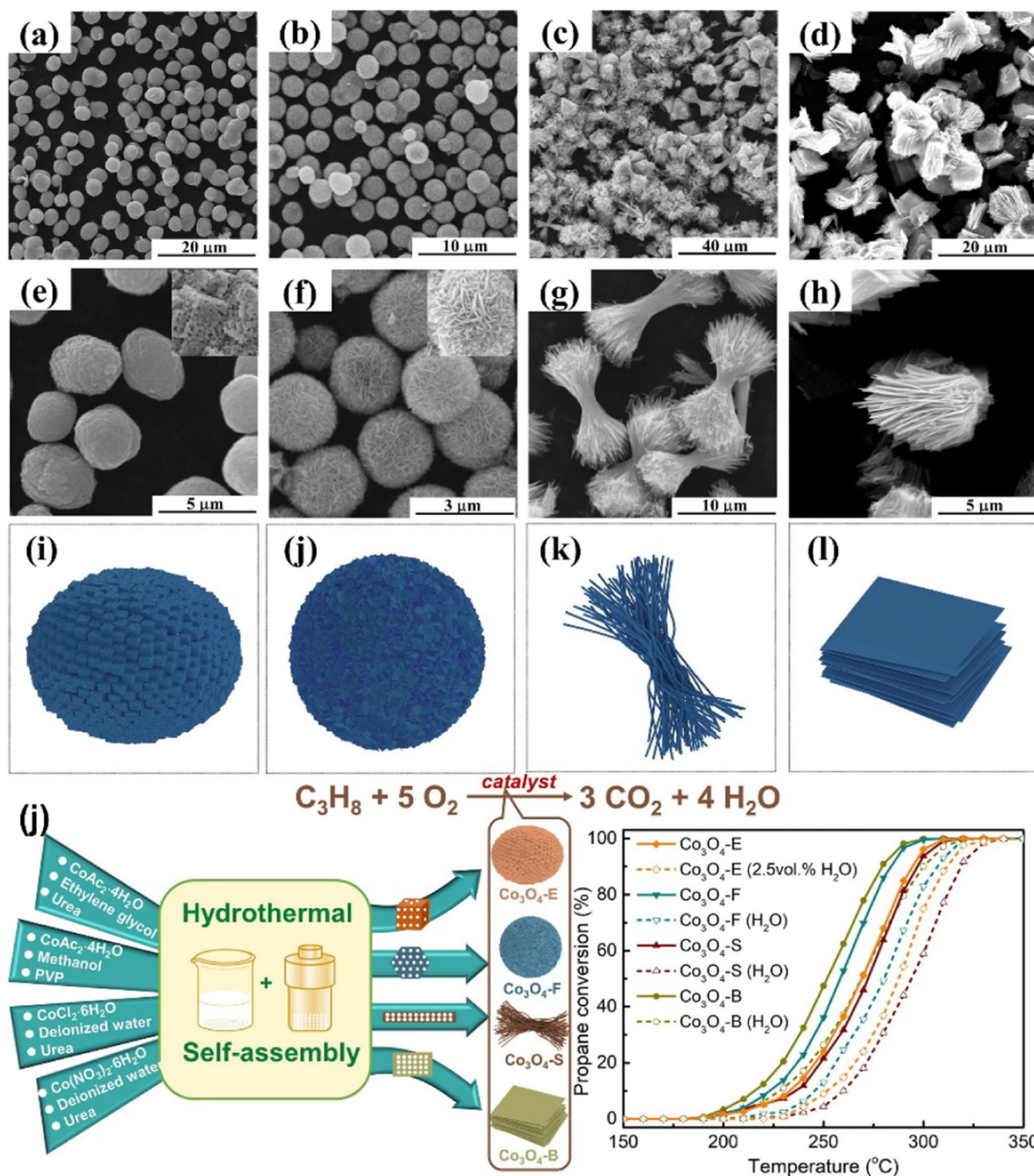
## Strategies for improving catalytic oxidation performance of metal oxide catalysts

### Morphology design

The surface morphology of catalysts refers to the morphological structure, crystal surface morphology, pore distribution, and surface species of the catalyst surface, which directly affects the reaction activity, selectivity, and stability of the catalyst [34–36]. Research has shown that surface morphology poses an important impact on the catalytic performance of catalysts [37–39]. Generally, the effects of surface morphology on the catalytic performance can be divided into three categories.

First, the effect of surface morphology on reaction activity. Surface morphology can affect the quality of the catalyst surface and the rate of chemical reactions, changing the position of active centers, binding energy, structure, electron distribution, and charge transfer properties [40–42]. For example, pore structure and particle size can affect chemical adsorption and diffusion, thereby affecting the reaction rate constant. In addition, the surface crystal planes can affect surface structure and electrical properties, alter surface characteristics, and play an important role in redox catalysts [43–45]. Moreover, the surface oxide content, crystal surface configuration, and defects can effectively affect the electronic state and energy of the active centers on the catalyst surface, significantly affecting the catalytic reaction activity [36, 46, 47]. For example, Liang et al. selectively synthesized a series of  $\text{Co}_3\text{O}_4$  nanomaterials with different morphologies ranging from hierarchical ellipsoidal (Fig. 1a, e, i) to hierarchical flowerlike (Fig. 1b, f, j), hierarchical spindle-like (Fig. 1c, g, k), and hierarchical book-shaped structure (Fig. 1d, h, l) [48]. After a thorough study, they found that the catalytic oxidation performance of propane was strongly correlated with the morphology of  $\text{Co}_3\text{O}_4$  nanomaterials, where the book-shaped  $\text{Co}_3\text{O}_4$ -B catalyst can exhibit the highest catalytic activity toward propanol oxidation (Fig. 1j). More importantly,  $\text{Co}_3\text{O}_4$ -B catalyst shows the highest propane oxidation rate ( $0.86 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$ ) and the highest turnover frequency ( $\text{TOF} = 11.49 \times 10^{-3} \text{ s}^{-1}$ ) at 220 °C. Detailed mechanisms revealed that the superb catalytic performance was stemmed from the large specific surface area, small crystal size, and a highly exposed (110) facet, which facilitated the low-temperature reducibility and oxygen mobility and thereby accounted for the promoted adsorption and activation of propane on the surface of catalyst.

Second, the surface morphology of catalyst also poses a significant impact on the selectivity [49]. As well known, surface morphology not only affects the activity of the reaction, but also determines the selectivity of the reaction [50]. For example, the crystal morphology of Au surface



**Fig. 1** SEM images of the  $Co_3O_4$  samples with different morphologies. **a, e, i**  $Co_3O_4-E$ ; **b, f, j**  $Co_3O_4-F$ ; **c, g, k**  $Co_3O_4-S$ ; and **d, h, l**  $Co_3O_4-B$ . **j** Schematic images of the controlled synthesis of  $Co_3O_4$

nanomaterials with different shapes and their applications for catalytic propane oxidation at different temperatures. Reproduced with the permission from ref. [48] Copyright 2021, Elsevier

can affect the oxidation selectivity of redox reactions. The Ag surface has excellent selectivity, which can promote the reaction to be dominated by heterogeneous reactions

[51, 52]. The surface structure of Ni can regulate the reaction route of carbonyl gas phase reactions [53]. Similar to the metal nanocatalysts, the surface morphology of metal

oxides also significantly affects the catalytic selectivity of VOC oxidation. For instance, Wu and coworkers synthesized the  $\text{CeO}_2$  with different morphologies (rod, particle, and cube) and combined with non-thermal plasma to catalytic methanol oxidation [54]. After a systematic test, they found that the optimal  $\text{CeO}_2$  rods could display the highest methanol conversion (94.1%),  $\text{CO}_2$  selectivity (90.1%),  $\text{CO}_x$  selectivity (96.3%), and ozone suppression, followed by the  $\text{CeO}_2$  particle and  $\text{CeO}_2$  cube. Detailed mechanism study demonstrated the great significance of oxygen vacancies on the catalytic selectivity, where the  $\text{CeO}_2$  rods possessed the highest concentration of oxygen vacancies, which could exhibit better ozone decomposition performance and create more reactive oxygen species (Fig. 2).

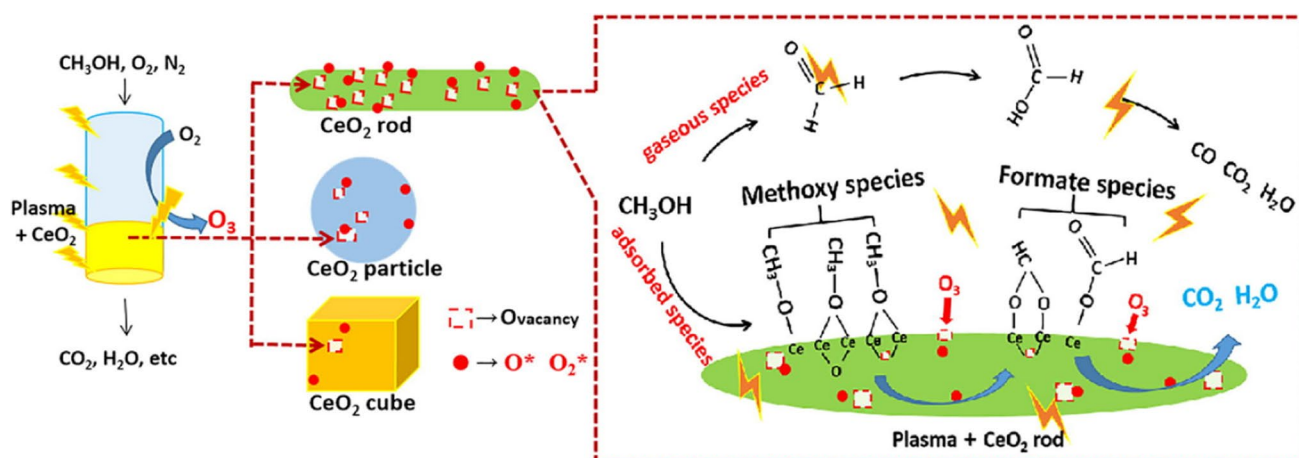
Third, before influencing the catalytic activity and selectivity, the morphology can also significantly affect the catalytic durability of catalysts. Previous works have demonstrated that the morphology can affect the stability of the catalyst. For example, in CO oxidation reactions, the Pt (111) surface is more stable than the Pt (100) surface and has a longer average lifespan [55]. In addition, the distribution of surface species also affects the stability of chemical reactions, and the Pt-CO bond length can be controlled to improve the stability of Pt catalysts. When turning the attention to the catalytic VOC oxidation over metal oxides, the similar phenomenon can also be clearly observed. As demonstrated by Zhang and coworkers, they realized the controllable synthesis of 3D hierarchical  $\text{Co}_3\text{O}_4$  catalysts with different morphologies and facets toward catalytic toluene combustion (Fig. 3a–f) [56]. According to a series of tests, it is demonstrated that the optimal samples with closely packed regular  $\text{Co}_3\text{O}_4$  plates are highly active toward toluene oxidation (Fig. 3g). More importantly, it can also display a stable activity during 100 h test (Fig. 3h), suggesting that the

morphology is also very significant for affecting the catalytic stability of catalyst.

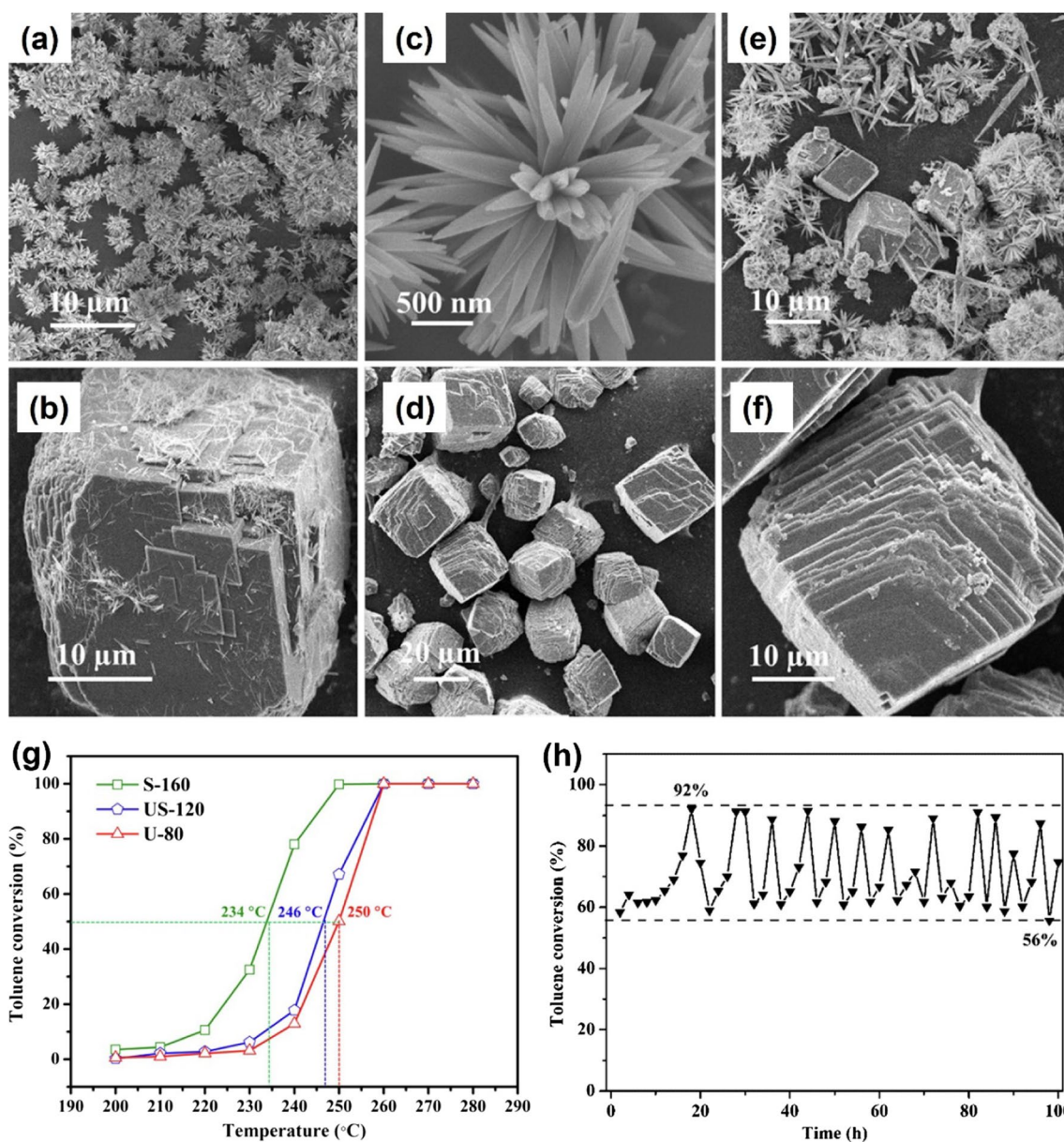
### Heteroatom doping

Transition metal oxides or complexes are gradually becoming the next-generation candidate catalysts in electrochemical equipment that can replace precious metals [57–60]. Under the induction effect, doping foreign metal ions with strong electronegativity will decrease the number of electrons in the anti-bonding state between the core metal ions and oxygen ions [61–63], leading to a downward shift in the Fermi surface and an increase in the corresponding redox potential of the core metal ions in the chemical reaction [64–66].

In addition, heteroatom doping can also modify the electronic properties of metal oxides because of their difference in electronegativity [67–69]. And the modified electronic structure will affect the adsorption of intermediates. Rationally tailoring the doped element and dopant amount will achieve the optimized binding strength with intermediates [70]. Moreover, the introduction of heteroatom may also function as new active sites for further elevating the catalytic performance. Furthermore, the strong synergistic effect between host metal ions and doped ion will greatly contribute to the further improvement in catalytic performance [71]. Taking these favorable terms into consideration, enormous endeavors have been dedicated to the design and fabrication of heteroatom-doped metal oxides to boost catalytic VOC oxidation. For instance, Sun et al. reported the synthesis of metal-doped  $\alpha\text{-MnO}_2$  and  $\beta\text{-MnO}_2$  and investigated their catalytic performance toward VOCs [19]. Compared with pure  $\alpha\text{-MnO}_2$  and  $\beta\text{-MnO}_2$ , it is reported Co and Ni doping can greatly enhance the catalytic activity toward toluene and HCHO. And the extraordinary catalytic performance is



**Fig. 2** Schematically illustrating the synthesis of  $\text{CeO}_2$  with different morphologies (rod, particle, and cube) and employed them as advanced catalysts for the selectively catalytic methanol oxidation. Reproduced with the permission from ref. [54] Copyright 2019, Elsevier



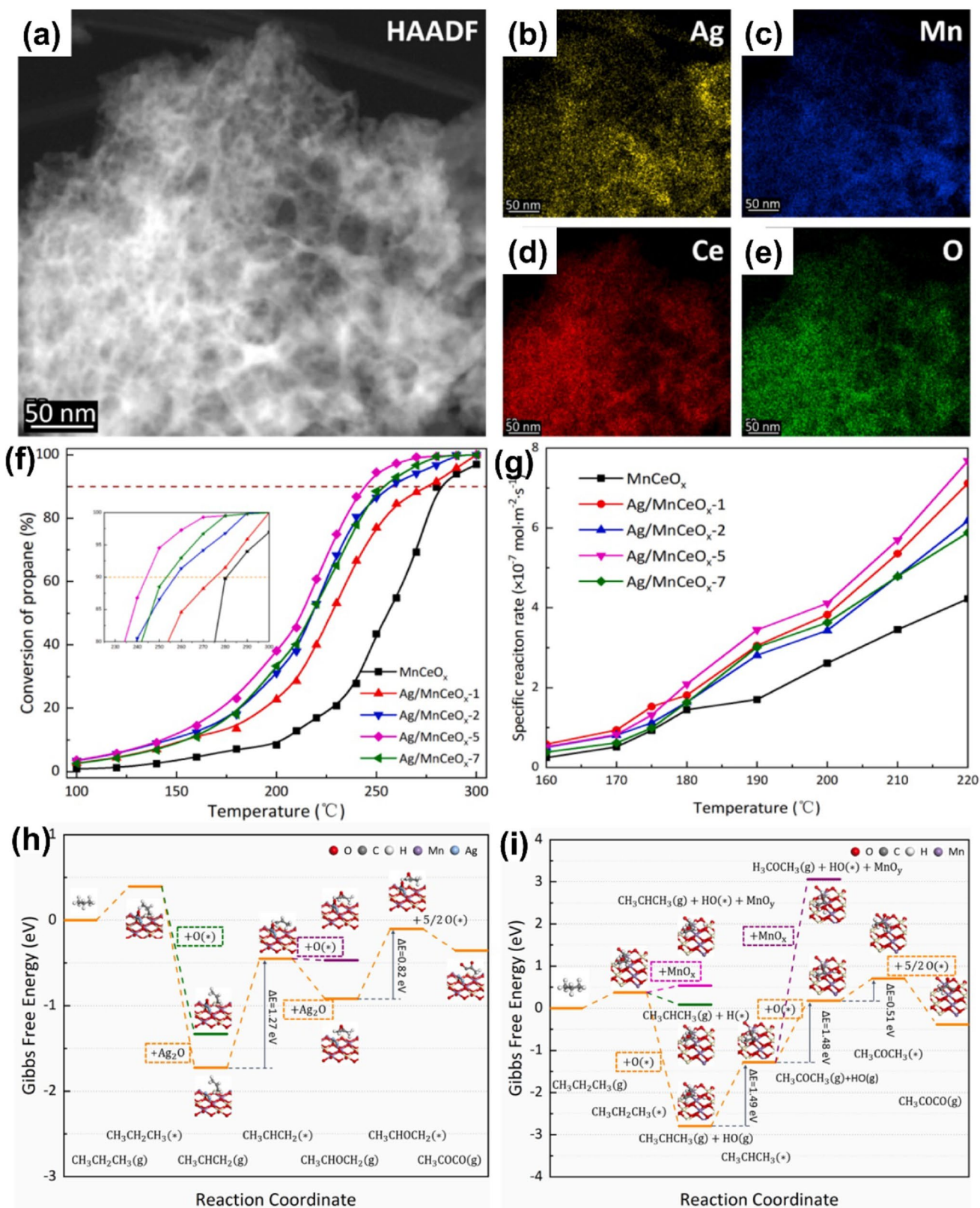
**Fig. 3** a–f SEM images of the  $\text{Co}_3\text{O}_4$  catalysts with different morphologies. **g** Catalytic performances of the  $\text{Co}_3\text{O}_4$  catalysts. **h** Stability test of the optimal sample. Reproduced with the permission from ref. [56], Copyright 2020, Elsevier

primarily originated from the low crystallinity, more surface defects, large specific surface area, and abundant oxygen vacancies.

Besides, heteroatom doping can also increase the concentration of high-valence metal ions and facilitate the surface oxygen migration capability, which is also favorable for the adsorption and dissociation of VOCs. As demonstrated by Li and coworkers, they reported the synthesis of Ag-doped  $\text{MnCeO}_x$  catalyst to boost the catalytic oxidation of propane (Fig. 4a–e) [72]. After a systematic test, it is demonstrated that the Ag-doped  $\text{MnCeO}_x$  catalyst with an Ag loading of 5 wt% could exhibit the highest catalytic activity and

durability (Fig. 4f, g). Mechanism study reported that the addition of Ag species can effectively convert the propane into propylene and thus reduce the activation energy barrier, which account for the extraordinary catalytic performance (Fig. 4h, i).

More recently, Li et al. synthesized the Fe doped  $\delta\text{-MnO}_2$  catalyst to boost the VOC oxidation [73]. It is discovered that the  $\text{Fe}_1\text{Mn}_5$  oxide can achieve the optimum catalytic performance for toluene oxidation with a  $T_{90}$  of 209 °C, along with outstanding durability and good water resistance. Upon the combination of mechanism study and experimental results, it is uncovered that Fe doping method can induce the



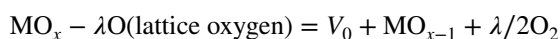
**Fig. 4** **a** STEM image and **b–e** elemental mapping images of the Ag-doped MnCeO<sub>x</sub>. **f** Propane total oxidation activity and **g** specific surface activity. Primitive steps and Gibbs free energy diagram of

propane oxidation over the slab model of **h** Ag<sub>2</sub>O-Ce(Mn)O<sub>2</sub> and **i** Ce(Mn)O<sub>2</sub> surface. Reproduced with the permission from ref. [72], Copyright 2023, Elsevier

formation of high concentration of oxygen vacancy, which improve the lattice oxygen mobility and oxygen species activity (Fig. 5).

### Oxygen vacancy engineering

Oxygen vacancy is first proposed in 1960, which has been used to study the mechanism of interaction between gases and solid metal oxides [74]. Specific external environment can cause the detachment of oxygen in the lattice, leading to oxygen deficiency and the formation of oxygen vacancies [75], which can be described as the following equation:



In short, a defect is formed by the removal of an oxygen atom from a metal oxide lattice. For metal oxides, their oxygen vacancies are a type of defect (point defect) [76, 77]. As well known, in metal oxides, the electronegativity of other elements is generally lower than that of oxygen, so when oxygen is lost, it is equivalent to take one oxygen atom and add two positively charged electron holes [78]. If these two electron holes are bound to the oxygen vacancy, the oxygen vacancy is generally positively charged.

The creation of oxygen vacancies has been demonstrated to be favorable for boosting the catalytic reactions. On the one hand, creating oxygen vacancies can regulate the electronic structure of metal oxides to regulate the energy band structure [79]. And the presence of oxygen vacancies causes the Fermi level of the oxide to shift upwards, resulting in defect energy levels in the band gap that decrease the band width [80]. As a result, it can substantially improve the light absorption, promote the carrier separation, and accelerate surface reduction reaction via promoting carrier separation. On the other hand, oxygen vacancies can also generate

unsaturated coordination sites on the surface (edges, corners, or terraces), which can function as active site [81, 82]. Oxygen vacancies can optimize the adsorption energy of reactants on the catalyst surface, thereby reducing the reaction energy barrier and promoting molecular activation [83, 84]. Moreover, there is a synergistic effect between oxygen vacancies and nearby active metal sites in the catalyst.

Inspired by these, creating oxygen vacancies in metal oxide catalysts have been demonstrated to be a promising strategy for optimizing their catalytic performance. For example, Lu and coworkers engineered a composite of Au-modified hollow Ni–Mn nanospheres with abundant oxygen vacancies and used for boost toluene and benzene oxidation reaction (Fig. 6a–c) [85]. It is indicated that the synergistic role of defects from surface and intrinsic O-vacancies between different components benefits for the generation of many adsorbed oxygen species, which are conducive to the oxidation-reduction cycle and promote the catalytic activity of toluene oxidation (Fig. 6d). Moreover, the oxygen vacancies can also effectively activate the lattice oxygen and enable them to migrate to react with the adsorbed toluene. As a result, the optimal catalyst can exhibit extraordinary toluene and benzene oxidation performance, obtaining 100% conversion at 155 and 148 °C with a WHSV of 36,000 mL g<sup>-1</sup> h<sup>-1</sup> (Fig. 6e, f).

Liu et al. synthesized the CoCuO<sub>x</sub> catalysts with abundant oxygen vacancies to boost the catalytic oxidation of VOCs [27]. To be specific, the CoCuO<sub>x</sub> catalysts were synthesized by depositing the Cu(OH)<sub>2</sub> nanorod on the surface of Cu foam and then growing the CoCu-MOF (Fig. 7a, b). After a post treatment, the composites can be converted into CoCuO<sub>x</sub> catalysts that enriched with oxygen vacancies. It is reported that the mutual contact between Cu and Co benefits for the formation of oxygen vacancies and boosting the electron transfer to molecular oxygen, thereby accounting for the

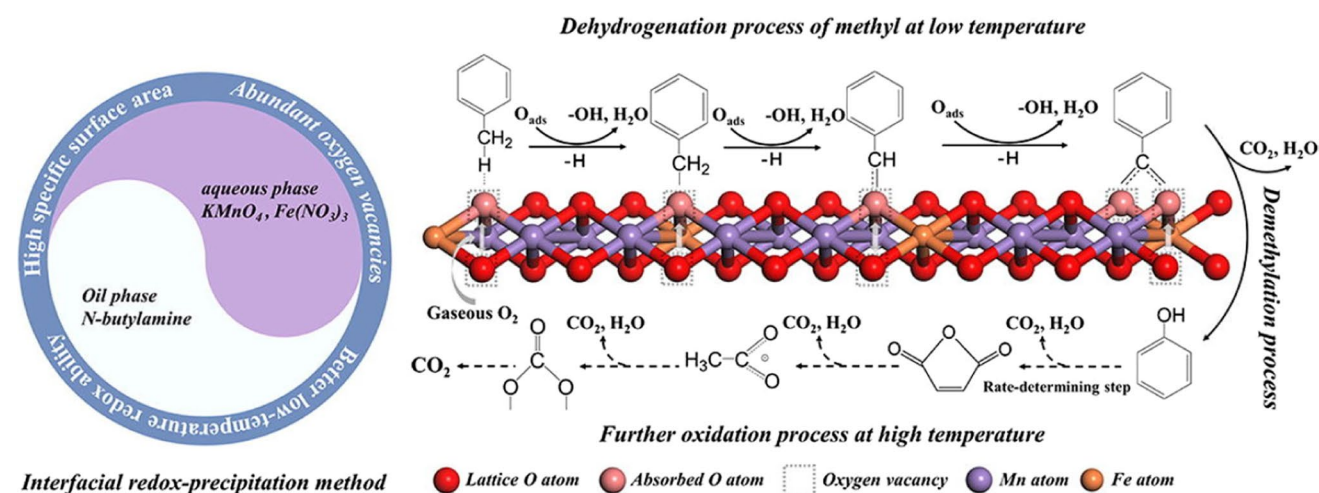
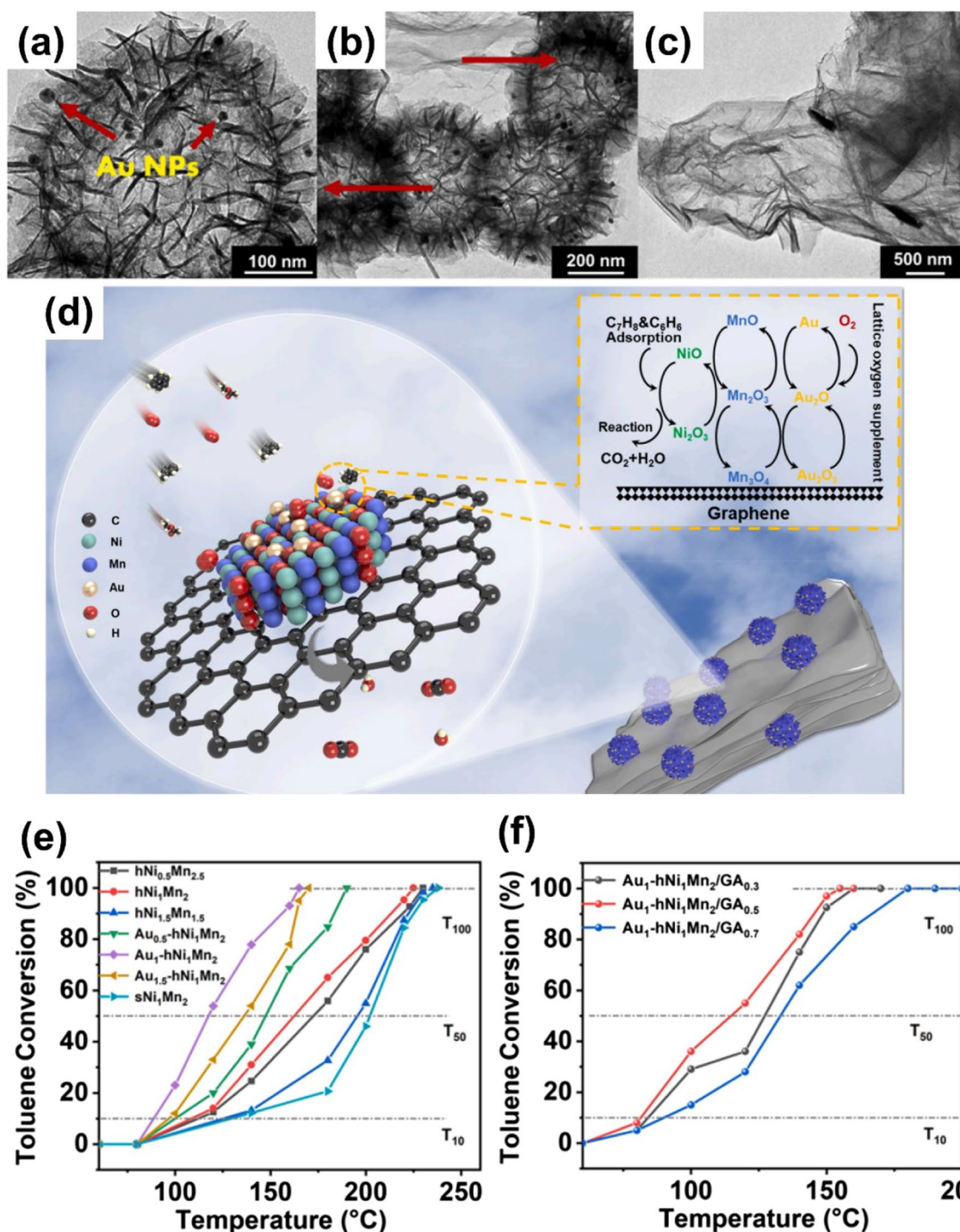


Fig. 5 The toluene oxidation mechanism over Fe doped  $\delta$ -MnO<sub>2</sub>. Reproduced with the permission from ref. [73] Copyright 2023, Elsevier





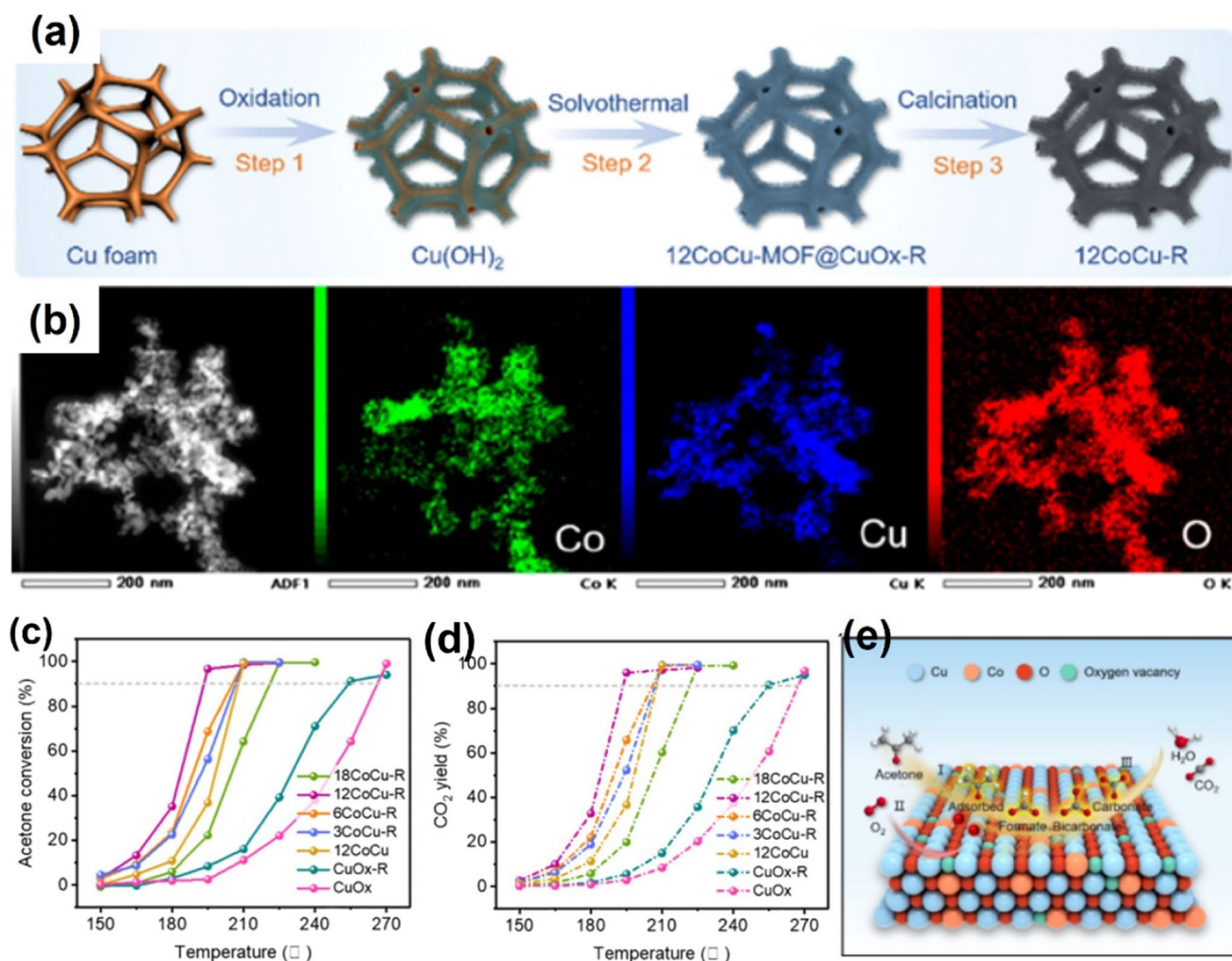
**Fig. 6** a–c TEM images of the Au-modified hollow Ni–Mn nanospheres. **d** Schematic illustration of the reaction mechanism of toluene and benzene oxidation. **e, f** Toluene conversion of the different

samples in each step. Reproduced with the permission from ref. [85] Copyright 2023, Elsevier

enhanced oxygen activation performance (Fig. 7c–e). As a result, such catalyst can exhibit superb stability in long-time cycle and good water resistance. These works demonstrated that the oxygen vacancy engineering posed a great influence on the catalytic performance.

### Multicomponent composites

Given that the performance of single component catalysts is still unsatisfactory, combining two or more catalytic materials to fabricate composites is now emerging as a



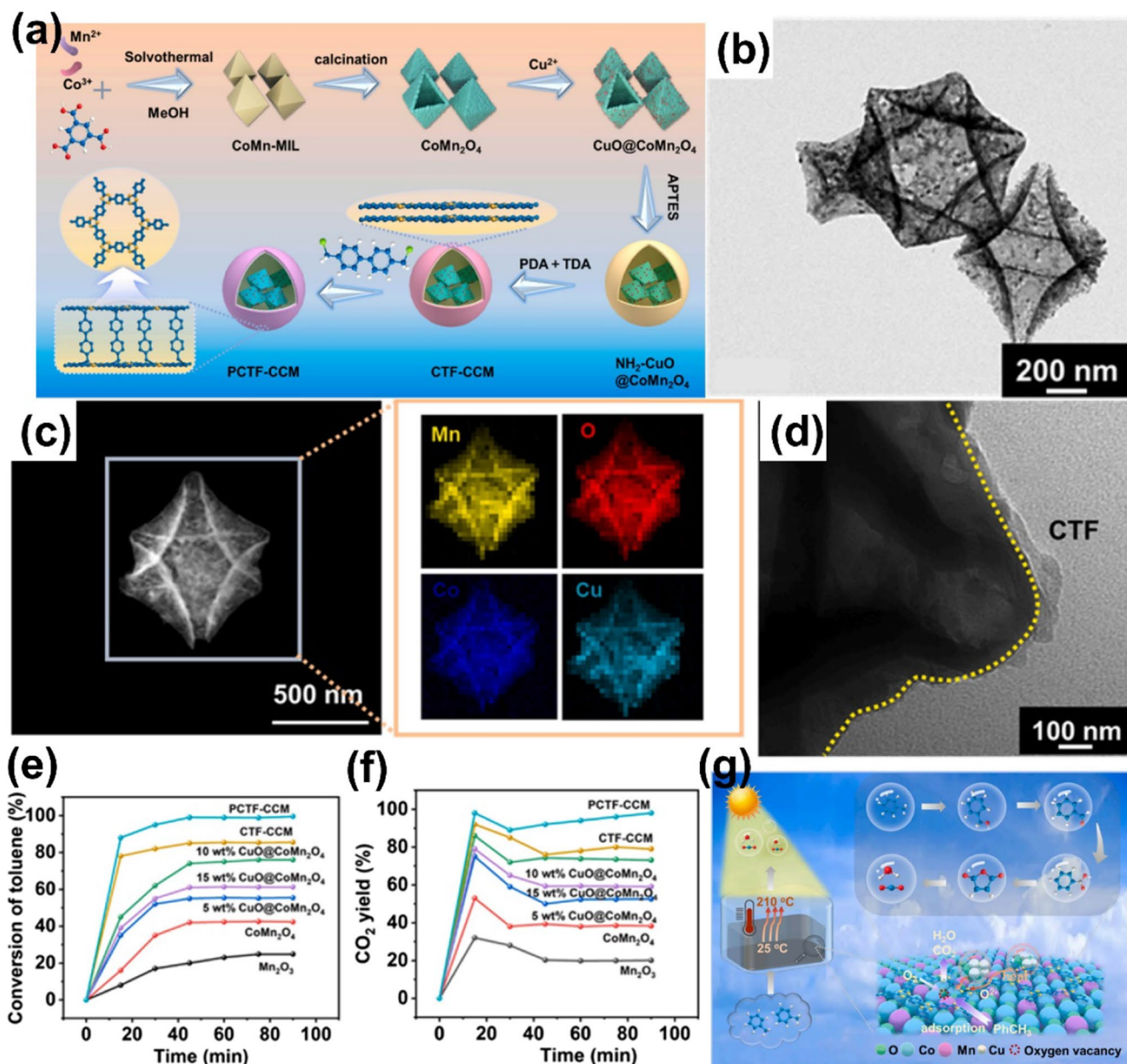
**Fig. 7** **a** Scheme of the synthesis of the 12CoCu-R catalyst on the Cu foam. **b** Elemental mapping images of the 12CoCu-R catalyst. **c** Acetone conversion and **d** CO<sub>2</sub> yield over different catalysts. **e** Sketch

map of reaction mechanism and the effect of oxygen vacancies on catalytic reaction. Reproduced with the permission from ref. [27], Copyright 2021, American Chemical Society

promising avenue for improving the catalytic performance [86–89]. As well known, constructing multicomponent can not only induce the electron redistribution and, but also generate new heterointerfaces by varying the composition and crystal phase of the structure [37, 90–92]. Generally, the advantages of multicomponent composites are included as the following aspects: (1) synergistic effect—the bond cooperation between different component interfaces can increase the electron transfer rate. By combining with different materials, the conductivity, hydrophilicity, chemical stability, and active site density of composites can be tailored [93–95]. (2) Strain effect—different chemical components and crystal structures in composites can cause lattice strains such as stretching and compression, affecting the adsorption energy of sites on intermediates, and improving the catalytic activity of materials [96, 97]. (3) Electronic interaction—in composites, the arrangement of energy bands in different

phases can lead to charge transfer at the interface, which is beneficial for surface electron modulation of the composites [98, 99]. Owing these favorable terms, constructing metal oxide composites has attracted great interest in recent years, and enormous endeavors have been devoted to the design and fabrication of advanced metal oxide composites toward VOC oxidation.

For instance, Lu and coworkers have synthesized the spinel oxide coated with porous covalent triazine frameworks (COFs) and used for improved photothermal catalytic oxidation of toluene [100]. As illustrated in Fig. 8a, the CuO@CoMn<sub>2</sub>O<sub>4</sub> was first synthesized via hydrothermal method (Fig. 8b), followed by the amino modification and polymerization reaction (Fig. 8c, d). Upon the characterizations, it was found that the CuO@CoMn<sub>2</sub>O<sub>4</sub> was enriched with oxygen vacancies. In addition, after the modification of COFs, the adsorption of toluene was



**Fig. 8** a Schematic illustration of the synthesis of CuO@CoMn<sub>2</sub>O<sub>4</sub>@COF. b TEM image of the CuO@CoMn<sub>2</sub>O<sub>4</sub>. c HAADF-STEM image and corresponding elemental mapping image of the CuO@CoMn<sub>2</sub>O<sub>4</sub>@COF. d TEM image of the CuO@CoMn<sub>2</sub>O<sub>4</sub>@COF. e

Toluene and f CO<sub>2</sub> conversion of different catalysts. g The proposed mechanism of photothermal catalytic oxidation of toluene. Reproduced with the permission from ref. [100], Copyright 2023, Elsevier

significantly improved, and the catalytic reaction rate was also largely enhanced. Owing to the synergistic contribution of these advantageous merits, such composite can exhibit extraordinary catalytic toluene oxidation performance, in which the toluene conversion and CO<sub>2</sub> yield were as high as 100% and 98% within 40 min, respectively (Fig. 8e–g).

### Conclusions and prospects

The increasing emissions of VOCs in recent years have led to the formation of tropospheric ozone and secondary organic aerosols. Catalytic oxidation over transition metal oxides have been demonstrated to be a promising strategy

for VOC abatement. This comprehensive review summarizes the recent progress of catalysts used for VOC oxidation, with the special focus on the categories of VOCs and their features. In addition, many effective strategies for further improving the catalytic performance of VOC oxidation over transition metal oxides are also manifested, which pose great influence on the catalytic performance. The proposed strategies have been demonstrated to be favorable for further improving the catalytic performance of metal oxides. However, there are still some challenges that should be addressed before the industrial applications.

The facets of metal oxides can also greatly affect the catalytic oxidation performance for VOCs. It is still difficult to realize the controllable synthesis of metal oxides with highly active facets, and more advanced strategies should be further developed and proposed.

As well known, the catalytic VOC oxidation is a typical redox process, in which the electron transfer is crucial to determining their catalytic performance. However, the poor conductivity of the metal oxides may limit the electron transfer and result in poor catalytic activity. Therefore, it is imperative to substantially improve the conductivity of metal oxides by developing some effective strategies.

Oxygen vacancies play a critical role in affecting the catalytic performance of metal oxides. However, the construction strategy for the oxygen vacancies should be further optimized to control the building accurately. In this regard, it is necessary to explore new synthetic strategy for realizing the controllable and straightforward fabrication of oxygen vacancies. In addition, the identification, distribution, and function of oxygen vacancies are still unclear. More endeavors should be devoted to the exploration and understanding of these crucial factors.

To further elevate the catalytic performance, a better understanding on the interaction between metal oxides and VOCs is necessary, which can help researchers to develop cost-effective catalytic reactors. In addition, the scale-up production of high-performing metal oxide catalysts is also highly important as the industrial VOC removal requires a large number of advanced catalysts.

Although metal oxides have been demonstrated to be highly active toward VOC oxidation, they can only catalytic no more than three VOC oxidation. However, the VOCs all existed in the form of mixtures. Therefore, systematic studies of various VOCs removal should be carried out, and metal oxides with multifunction should also be designed and developed.

The selectivity and long-term stability are two crucial parameters evaluating the performance and potential of metal oxide catalysts for VOC oxidation. However, for the practical applications, the metal oxide catalyst should not only possess high selectivity but also extraordinary long-term cycle stability.

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**Author contribution** Hui Zhao: conceptualization, formal analysis, writing. Jipeng Wang: writing, review, editing, project administration

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**Data availability** The results/data/figures in this manuscript have not been published elsewhere, nor are they under consideration by another publisher. The corresponding author declares that all the data and materials are available.

## Declarations

**Ethical approval** This work is not applicable to both human and/or animal studies.

**Competing interests** The authors declare no competing interests.

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