

## Review

# Single-Atom Catalysts in Environmental Engineering: Progress, Outlook and Challenges

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**Abstract:** Recently, single-atom catalysts (SACs) have attracted wide attention in the field of environmental engineering. Compared with their nanoparticle counterparts, SACs possess high atomic efficiency, unique catalytic activity, and selectivity. This review summarizes recent studies on the environmental remediation applications of SACs in (1) gaseous: volatile organic compounds (VOCs) treatment, NO<sub>x</sub> reduction, CO<sub>2</sub> reduction, and CO oxidation; (2) aqueous: Fenton-like advanced oxidation processes (AOPs), hydrodehalogenation, and nitrate/nitrite reduction. We present the treatment activities and reaction mechanisms of various SACs and propose challenges and future opportunities. We believe that this review will provide constructive inspiration and direction for future SAC research in environmental engineering.

**Keywords:** single-atom catalysts; VOCs treatment; NO<sub>x</sub> reduction; CO<sub>2</sub> reduction; CO oxidation; fenton-like processes; hydrodehalogenation; nitrate and nitrite reduction

## 1. Introduction

Large amounts of pollutants are discharged into the environment as a result of economic growth, leaving serious pollution problems that require urgent treatment. Compared to traditional physical adsorption or biological treatments, chemical catalysis is considered an effective approach to quickly degrade pollutants [1], with less generation of secondary solid waste or sludge. Developing appropriate catalysts that can not only efficiently eliminate pollutants but also operate stably and sustainably is of great importance [2].

Conventional heterogeneous catalysts are typically designed on a nanometer scale. However, the atomic utilization of nanoparticles (NPs) is limited because only the outmost layer of atoms participates in the surface catalytic reaction [3], which hinders the further improvement of catalytic activity. Moreover, noble metal catalysts containing costly Pd, Pt, Au, Ru, etc. are required to achieve higher atomic efficiency to obtain economic benefits. To solve these issues, researchers have devoted themselves to decreasing the size of nanocatalysts to maximize the exposure of active surface sites, meanwhile achieving additional benefits such as quantum size effects [4,5] and unsaturated coordination [6].

The idea of single-atom catalysts (SACs) was first proposed by Zhang and coworkers [7] in 2011, which describes a type of catalyst reaching the theoretical size limit of “single-atom”. Compared to bulk nanocatalysts, single-atom catalysts possess several advantages. From the perspective of catalyst structure, the sufficient interactions generated by the chemical bond between the metal and the support provide higher numbers of interfaces and active sites for the catalytic reaction [8–11]. The unsaturated coordination facilitates the adsorption of pollutants on the SAC site and dynamic electron transport, contributing to a better redox reaction [7,10,12]. The strong metal-support bonding also prevents the aggregation of atoms [13,14] and the environmental risk of metal leaching [15]. With close to 100% atomic efficiency, the metal loading greatly decreases to achieve a similar degradation capacity as nanocatalysts, further reducing the cost of the catalyst.



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In the field of environmental engineering, remarkable progress has been made in SAC research (Figure 1), particularly involving CO oxidation [7,16,17], CO<sub>2</sub> reduction [18–21], NO<sub>x</sub> degradation [22–24], volatile organic compounds (VOCs) degradation [23,25], aqueous advanced oxidation processes (AOPs) [26–28], hydrodehalogenation [29], nitrate reduction [30,31], etc. To date, there are few systematic summaries and reviews of SACs' applications in environmental engineering. Therefore, in this review, we summarize recent studies on SAC applications in gaseous and aqueous pollution control, respectively, focusing on treatment efficiencies and reaction mechanisms. We further propose suggestions on the synthesis strategies and discuss the challenges and directions for future SAC research in the environmental engineering field.

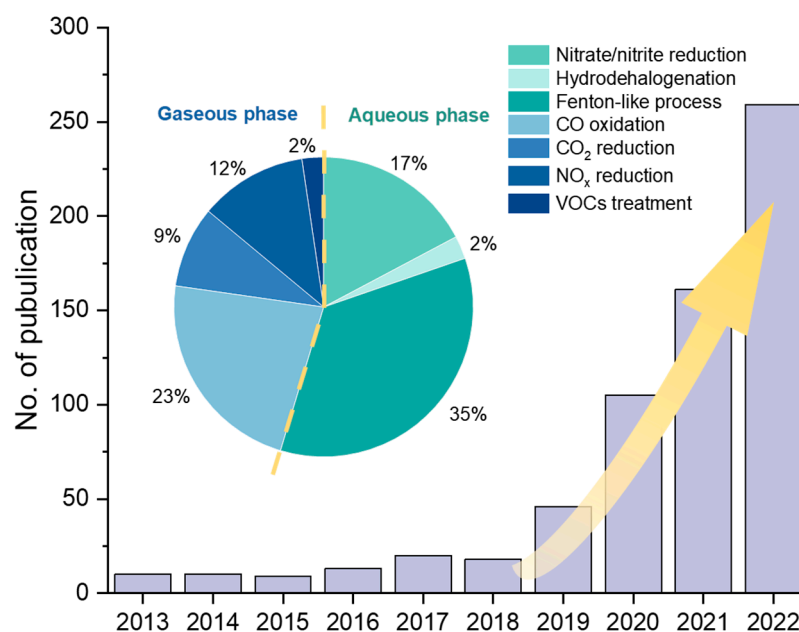


**Figure 1.** Number of publications of SAC research in environmental remediation applications and the proportion in various fields in the last decade. The publication data from 2013 to 2022 was collected from the Web of Science in April 2023.

## 2. Progress of SACs in Gaseous Pollution Control

### 2.1. VOC Treatments

Volatile organic compounds (VOCs) are ubiquitous air pollutants that are mainly emitted from fossil fuel combustion, transportation, and industrial and household activities [32,33]. There are a wide variety of VOCs, including non-methane hydrocarbons (e.g., alkanes, aromatics), oxygen-containing organic compounds (e.g., aldehydes, ketones, alcohols, ethers), halogenated hydrocarbons, nitrogen- and sulfur-containing compounds, etc. The outdoor VOCs are important precursors of photochemical smog [34], and the indoor VOCs are detrimental to human health, with the probability of causing cancer [35]. The Chinese Fourteenth Five-Year Plan (2021–2025) [36] proposes to further advance the comprehensive management of VOC emissions and requires a more than 10% reduction of the total VOC emissions compared to 2020. Given the adverse impacts of VOCs on the environment and the new legislation in place, it is critical to develop efficient and applicable technologies to reduce VOC emissions. Catalytic oxidation is one of the most promising approaches due to its desirable features, such as high efficiency and energy savings [37], among traditional VOC abatement technologies including adsorption, condensation, thermal incineration, and biological degradation [33].

SACs can maximize atomic efficiency, minimize the usage of noble metals, and achieve high activity and selectivity [9,38,39], thus attracting much attention in VOC treatments. In recent years, several noble metal SACs have been developed for VOC catalytic oxi-

ation and showed superior performance compared to their nanoparticle counterparts, including Ag [40,41], Au [23,42], Pt [43–45], and Pd [46]. The single-atom Ag based on nanostructured hollandite manganese oxide ( $\text{Ag}_1/\text{HMO}$ ) [40] prepared by a thermal diffusion method achieved 100% conversion of benzene oxidation at 220 °C at a GHSV of 23,000  $\text{h}^{-1}$  (Figure 2a). The isolated Ag adatoms possessed an excellent ability to activate lattice oxygen and gaseous  $\text{O}_2$  owing to their upshifted 4d orbitals. Comparably, the Ag atoms incorporated into cryptomelane-type manganese oxide (K/Ag–OMS-40) [41] showed higher benzene conversion, excellent stability, and enhanced tolerance to chlorine poisoning and moisture than 1 wt% Pd/ $\text{Al}_2\text{O}_3$  (Figure 2b) [40,41]. The increased number of Mn octahedral defects and newly formed Ag–O–Mn interaction entities accelerated charge transfer [41], facilitating the benzene conversion.

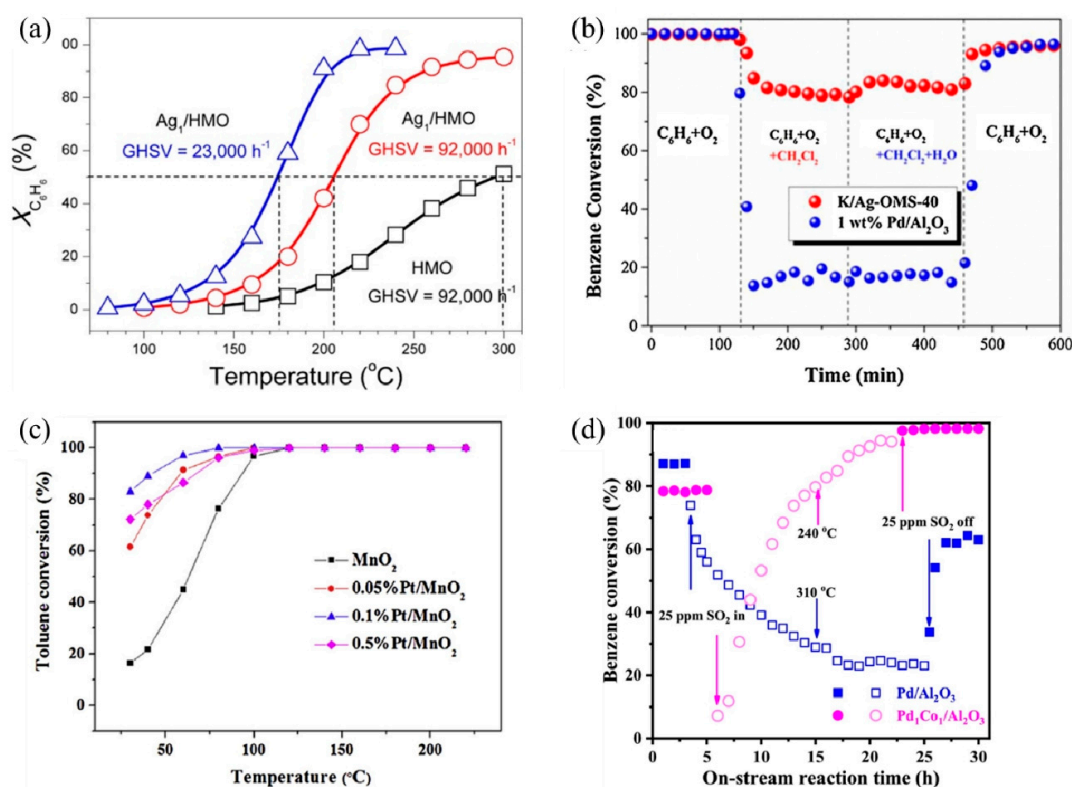


**Figure 2.** Catalytic performance of different SACs for several VOC treatments. (a) Conversion of benzene ( $X_{\text{C}_6\text{H}_6}$ ) as a function of temperature over  $\text{Ag}_1/\text{HMO}$  and HMO at different GHSVs. Reaction conditions: benzene, 200 ppm;  $\text{O}_2$ , 20% and balanced by  $\text{N}_2$ ; flow rate, 100  $\text{mL min}^{-1}$ . Copyright 2017, American Chemical Society [40]. (b) Comparison of  $\text{C}_6\text{H}_6$  conversion between K/Ag–OMS-40 (GHSV = 45,000  $\text{h}^{-1}$ ) and 1 wt% Pd/ $\text{Al}_2\text{O}_3$  (GHSV = 40,000  $\text{h}^{-1}$ ) and stability test in terms of chlorine and moisture tolerance at a temperature of 300 °C. Copyright 2018, Elsevier B.V. [41]. (c) Temperature-dependent toluene conversion by  $\text{MnO}_2$  and Pt-deposited  $\text{MnO}_2$  catalysts (toluene inlet concentration: 10 ppm, 21%  $\text{O}_2$ ,  $\text{N}_2$  as balance gas, GHSV: 60  $\text{L g}^{-1} \text{h}^{-1}$ ). Copyright 2019, Elsevier B.V. [43]. (d) Benzene conversion as a function of on-stream reaction time in the presence or absence of  $\text{SO}_2$  over the as-obtained samples. Copyright 2021, Elsevier B.V. [47].

Au SACs also play an important role in low-temperature HCHO oxidation.  $\text{Au}_1/\alpha\text{-MnO}_2$  [42] and  $\text{Au}_1/\text{CeO}_2$  [23] both exhibited remarkable activity and stability as the doped Au facilitates the formation of oxygen vacancies, active oxygen species, and charged Au species as active sites [23,42].  $\text{Au}_1/\alpha\text{-MnO}_2$  completely degraded the 500 ppm HCHO pollutant stream at 75 °C, with a WHSV of 6  $\text{L g}^{-1} \text{h}^{-1}$ . As for  $\text{Au}_1/\text{CeO}_2$ , among different  $\text{CeO}_2$  morphologies,  $\text{CeO}_2$  rod-supported Au ( $\text{Au}/\text{r-CeO}_2$ ) as an optimal catalyst successfully achieved complete mineralization of HCHO at 85 °C. Additionally, Pt SACs exhibit good VOC catalytic performance as well. For example, the  $\text{Pt}_1/\text{MnO}_2$  [43] synthesized

via hydrothermal process achieved 100% conversion of indoor-level toluene at ambient temperature due to the formation of surface active oxygen species, including hydroxyl radicals ( $\cdot\text{OH}$ ) (Figure 2c). Chen et al. [45] screened out 0.47 wt%  $\text{Pt}_1/\text{Mn-TiO}_2$  as the optimal catalyst with extraordinary activity and acceptable cost, which completely eliminated HCHO (100 ppm) at room temperature.

Moreover, non-noble metal SACs are also applied in VOC catalytic oxidation. An Al SAC-doped graphene was proposed through density functional theory (DFT) calculations for the catalytic oxidation of HCHO at room temperature [48]. Through a pathway of  $\text{HCHO} \rightarrow \text{HCOOH} \rightarrow \text{CO} \rightarrow \text{CO}_2$ , the energy barriers for breaking the C–H bond in HCHO and the C–O bond in HCOOH were both 0.82 eV, serving as the kinetic limiting steps. A bimetal single-atom  $\text{Pd}_1\text{Co}_1/\text{Al}_2\text{O}_3$  catalyst with double active sites showed enhanced catalytic performance and sulfur resistance for benzene oxidation, over which a 90% benzene conversion was realized at 256 °C, and a gradual recovery of activity after the introduction of 25 ppm  $\text{SO}_2$  was observed (Figure 2d) [47]. In situ temperature-programmed experiments, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and X-ray absorption fine structure (XAFS) characterizations demonstrated the synergistic behaviors between  $\text{Co}_1$  and  $\text{Pd}_1$  sites. The  $\text{O} = \text{Co} = \text{O}$  species formed rapidly on the  $\text{Co}_1$  site to activate oxygen, while benzene selectively tended to adsorb on the  $\text{Pd}_1$  site. According to previous studies, due to the  $\pi$ -bond in the benzene molecule, a parallel or flat configuration is formed on the close-packed transition metal surfaces [49]. The  $\text{Pd}_1$  and  $\text{Co}_1$  double active sites inhibited the competitive adsorption between benzene and oxygen, thus enhancing the reactivity. Meanwhile, the  $\text{PdO-SO}_3$  complex formed after the addition of  $\text{SO}_2$  was decomposed into PdO, reactive oxygen species (ROS), and aluminum sulfite at low temperatures, while ROS and PdO sites continued to participate in the reaction, leading to high sulfur resistance.

## 2.2. CO Oxidation

Carbon monoxide (CO), an odorless and toxic gas due to its high affinity with hemoglobin in the blood [50], widely exists in the exhaust of the automobile and multiple industrial processes [51]. Over the past few decades, CO oxidation methods have been investigated to deal with CO emissions [52]. To overcome the low activity, poor stability, and high cost of current catalysts [53,54], numerous SACs have attracted considerable attention in CO oxidation both experimentally and theoretically, including noble metal catalysts (Pt (Figure 3) [7], Au [55–58], Pd [59]), non-noble metal catalysts (Fe [60], Co [61], Ni [62]), and metal-free catalysts (Si [63], B and S [64]).

Gold nanocatalysts have shown outstanding performance in low-temperature CO oxidation [55–58]. As large Au particles are inert for  $\text{O}_2$  activation, it is important to reduce the particle size. The  $\text{Au}_1/\text{FeO}_x$  SAC [65] with an extremely low loading of 0.015 wt% achieved a high turnover frequency (TOF) of  $0.49 \text{ s}^{-1}$  at 24 °C, which was almost 10 times higher than that of the  $\text{Au/Fe}_2\text{O}_3$  catalyst with a loading of 4.4 wt% at 27 °C [66]. It also achieved higher sintering resistance than Au nanocatalysts. By means of extensive first-principles calculations [67], undergoing a local reconstruction, single-atom Au in Ni- and Cu-doped  $\text{Au@TiO}_2$  were atomically deposited at oxygen vacancies on the  $\text{TiO}_2$  and formed stable “O–Au–O” species. The oxidation states of the Au cation SAC can be tuned via substrate doping with a transition metal to further improve the  $\text{O}_2$  activation. The highly oxidized Au single atom showed magnetism and promoted activity and stability for  $\text{O}_2$  activation and CO oxidation.

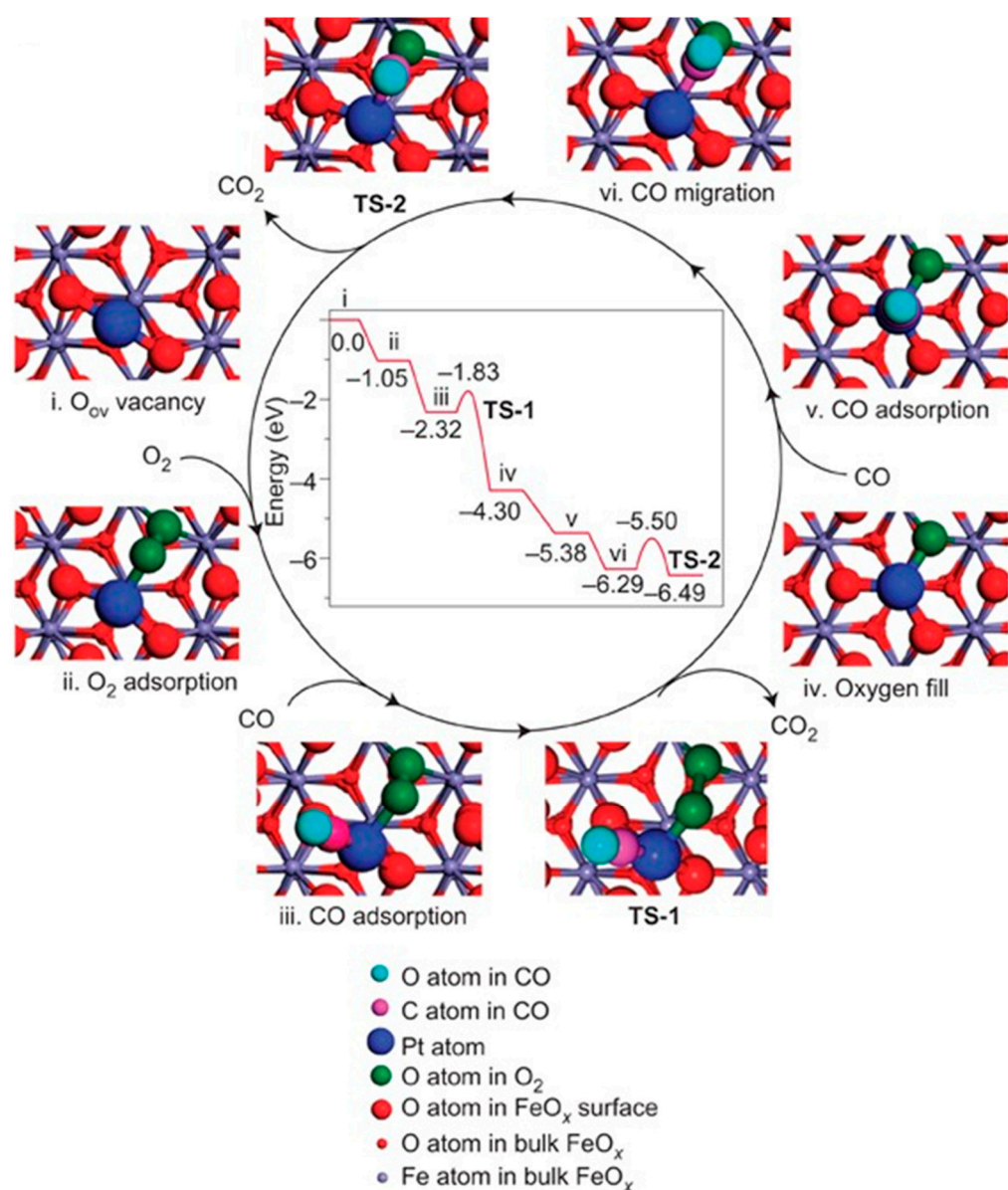


**Figure 3.** The proposed reaction pathways and energy profile (in eV) for CO oxidation on the single-atom catalyst Pt<sub>1</sub>/FeO<sub>x</sub>. Copyright 2011, Nature Publishing Group [7].

The high cost of noble metals can be an obstacle to their practical application, so it is necessary to exploit non-noble and non-metal catalysts. It was elucidated theoretically that the Fe<sub>1</sub>/C<sub>2</sub>N monolayer can catalyze CO oxidation via a two-step mechanism due to the localized metal 3d orbitals near the Fermi level [60]. The mechanism of CO oxidation mediated by single Cu atom-doped clusters CuAl<sub>4</sub>O<sub>7-9</sub><sup>−</sup> was experimentally identified, and CO was found to be crucial to stabilizing Cu in CuAl<sub>4</sub>O<sub>9</sub><sup>−</sup> around the +1 oxidation state [68]. Moreover, the single-atom Si can be stably embedded into the center of N<sub>4</sub> in graphene (Si-GN<sub>4</sub>) and effectively regulate the electronic structure of the GN<sub>4</sub> system, enhancing O<sub>2</sub> adsorption [63]. According to the first-principles method, Si-GN<sub>4</sub> had excellent stability and catalytic activity at high temperatures. The steps of the complete CO oxidation on Si SAC were as follows: CO + O<sub>2</sub> → OOCO → CO<sub>2</sub> + O<sub>ads</sub>, 0.57 eV, followed by a second reaction: CO + O<sub>ads</sub> → CO<sub>2</sub>, 0.72 eV. Lee and Yan et al. [64] reported the CO oxidation mechanism on a sulfur-doped hexagonal boron nitride (*h*-BN) non-metal catalyst. The sulfur-doped *h*-BN accelerated the oxidation of CO by reducing the energy barrier of O<sub>2</sub> chemisorption.

### 2.3. NO and N<sub>2</sub>O Reduction

High volumes of NO<sub>x</sub> exist in gaseous wastes from industrial activities and automobile exhaust gas. Selective catalytic reduction (SCR) is the key industrial technology for NO<sub>x</sub> removal by converting it to N<sub>2</sub> with reducing gases (e.g., H<sub>2</sub> and NH<sub>3</sub>) at high temperatures. Conventionally, metal oxides and molecular sieves ((M)<sub>2</sub>/nO·Al<sub>2</sub>O<sub>3</sub>·xSiO<sub>2</sub>·pH<sub>2</sub>O) are commonly used as supports to load active metals for NO<sub>x</sub> SCR. However, the additional secondary metals (usually in the oxide form) tend to aggregate into large nanoparticles, decreasing the distribution of active sites and inhibiting metal–metal interactions for good NO<sub>x</sub> reduction performance.

Therefore, in recent years, researchers have started to design bimetallic catalysts in the single-atom alloy (SAA) structure. In SAA, a small amount of an active metal is well distributed on the surface of another less active or less expensive metal to improve activity via enhancing metal–metal and metal–NO<sub>x</sub> interactions. For example, Wen et al. investigated the reduction of NO with H<sub>2</sub> on pure Ni and single-atom-Ir-doped Ni (Ir/Ni) surfaces by DFT calculations and microdynamics models [69]. The results showed that the doping of Ir greatly reduced the energy barrier of N<sub>2</sub> generation and increased the energy barrier of N<sub>2</sub>O production (Figure 4a,b). In another study, a Cu–Pd dual-atom alloy (DAA) using Al<sub>2</sub>O<sub>3</sub> as the support completely converted NO to N<sub>2</sub> at 175 °C [70], with the N–O bond breaking of the (NO)<sub>2</sub> dimer determined as the rate-limiting step. Single-atom Pd isolated by a large amount of Cu (Cu/Pd = 5) significantly improved the catalytic activity and N<sub>2</sub> selectivity. After N–O bond breaking, N<sub>2</sub>O is decomposed into N<sub>2</sub> smoothly on the Cu surface, which makes Cu and Cu-rich catalysts have high N<sub>2</sub> selectivity. Both single-atom Pd and Cu active sites contribute to this highly efficient deNO<sub>x</sub> system.

Tang's group has systematically designed several SAAs for NO<sub>x</sub>-SCR. A single-atom Mo<sub>1</sub>/Fe<sub>2</sub>O<sub>3</sub> catalyst was synthesized for NO SCR [71], in which atomic Mo was anchored on reducible α-Fe<sub>2</sub>O<sub>3</sub>(001), thus a single-atom Mo ion and an adjacent Fe ion were constructed as a dinuclear site. In Mo<sub>1</sub>/Fe<sub>2</sub>O<sub>3</sub>, Mo ions provided Brønsted acid sites that converted to Lewis acid sites during SCR. This dinuclear structure showed high SCR TOFs comparable to V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>. Further, this group assembled single-atom V<sub>1</sub> and W<sub>1</sub> loaded on TiO<sub>2</sub> (V<sub>1</sub>–W<sub>1</sub>/TiO<sub>2</sub>) [72], which realized tunable electronic interactions, thus performing significantly higher SCR rates (Figure 4c). Experimental and theoretical results indicated that the synergistic electron effect between V<sub>1</sub> and W<sub>1</sub> enriches high-energy spin charge around the Fermi level, enhancing the adsorption of reactant (NH<sub>3</sub> or O<sub>2</sub>) and accelerating the surface reactions compared to individual V or W atoms. Besides, a dinuclear Ce<sub>1</sub>–W<sub>1</sub>/TiO<sub>2</sub> catalyst was also developed to explore the synergistic effect between Ce and W in SCR [73]. The synergy of Ce<sub>1</sub>–W<sub>1</sub> reduces the lowest unoccupied states of Ce<sub>1</sub> near the Fermi level, boosting adsorption and oxidization of NH<sub>3</sub>, and renders the frontier orbital electrons of W<sub>1</sub>, speeding up O<sub>2</sub> activation. Due to the strong electronic interaction within Ce<sub>1</sub>–W<sub>1</sub> atom pairs, the TOF of Ce<sub>1</sub>–W<sub>1</sub>/TiO<sub>2</sub> at 250 °C was four times higher than the sum of Ce<sub>1</sub>/TiO<sub>2</sub> and W<sub>1</sub>/TiO<sub>2</sub> (Figure 4d).

With CO as the reducing agent, CO-SCR is regarded as a promising NO-SCR route because of its capacity to control two pollutant gases at the same time. However, the narrow reaction temperature window and the weak resistance to SO<sub>2</sub> and O<sub>2</sub> limit the application of CO-SCR. Ji et al. [74] developed a novel Ir SAC (IrW–WO<sub>3</sub>/KIT-6), with 1% Ir loaded on mesoporous SiO<sub>2</sub> (KIT-6), and formed Ir–W intermetallic nanoparticles. At 250 °C and in the presence of 1% O<sub>2</sub>, NO was completely converted to N<sub>2</sub> with 100% selectivity. At a wide temperature window (250–400 °C), the NO conversion rate of 80% and the N<sub>2</sub> selectivity of 95% were achieved, better than those of Ir isolate-single-atomic-sites (Ir<sub>1</sub>–WO<sub>3</sub>/KIT-6) and Ir nanoparticles (Ir<sub>n</sub>–WO<sub>3</sub>/KIT-6); IrW–WO<sub>3</sub>/KIT-6 also showed excellent SO<sub>2</sub> resistance. Furthermore, the team also developed a Pt SAC with negatively charged single-atom Pt (0.02 wt%) embedded on CuO squares and supported by CoAlO nanosheets (Pt–CuO/CoAlO) [75], showing 91% NO conversion and 80% N<sub>2</sub> selectivity in 3% O<sub>2</sub> at 200 °C. The interfacial electron transfer from CoAlO to CuO improved the electron density near Pt, thus enhancing NO adsorption, while Cu served as the adsorption

site for CO. The Pt–CuO/CoAlO also showed no activity loss after 200 ppm SO<sub>2</sub> heating for 15 h due to weakened SO<sub>2</sub> adsorption on active sites.

The reaction between CO and NO also has implications for automobile exhaust treatment. SACs were also found to be efficient in emission control, typically in three-way catalysts (TWCs), achieving synergistic treatment of NO, CO, and hydrocarbons (HCs). Wang et al. [76] reported a dual-site catalyst composed of strongly coupled atomic Pt and Pd on CeO<sub>2</sub>, which was fabricated via a multi-step heating strategy. Compared with Pt SAC and Pd SAC, Pt–Pd SAC showed a lower T<sub>90</sub> of NO and C<sub>3</sub>H<sub>6</sub> conversion, while the T<sub>90</sub> of CO oxidation was Pt–Pd SAC ≈ Pt SAC > Pd SAC.

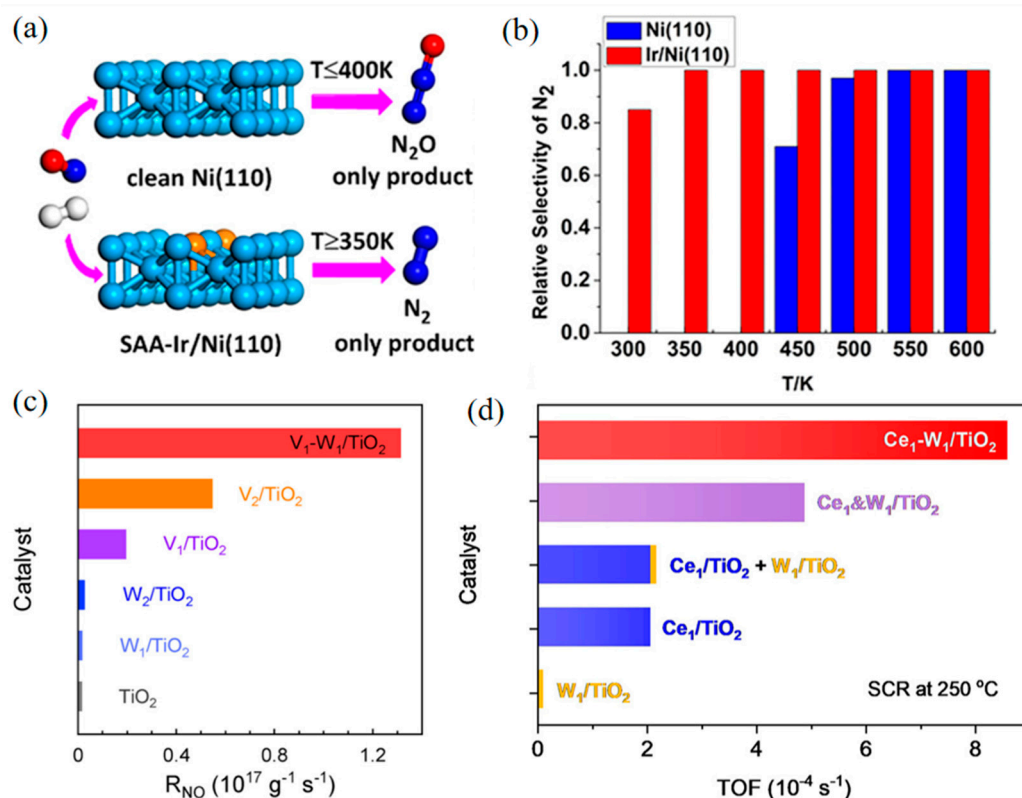


**Figure 4.** The single-atom alloy (SAA) Ir/Ni (110) promotes the reduction of NO into N<sub>2</sub>. (a) Mechanism diagram. (b) Relative selectivity of N<sub>2</sub>. Copyright 2019, American Chemical Society [69]. (c) Catalytic activities in terms of the reaction rates over the samples in SCR. Copyright 2022, Wiley-VCH [72]. (d) TOFs in SCR over Ce<sub>1</sub>&W<sub>1</sub>/TiO<sub>2</sub>, Ce<sub>1</sub>&W<sub>1</sub>/TiO<sub>2</sub>, Ce<sub>1</sub>/TiO<sub>2</sub> + W<sub>1</sub>/TiO<sub>2</sub>, Ce<sub>1</sub>/TiO<sub>2</sub>, W<sub>1</sub>/TiO<sub>2</sub>, and TiO<sub>2</sub> at 250 °C. Copyright 2022, American Chemical Society [73].

N<sub>2</sub>O largely exists in the gas exhausts of nitric acid, adipate, and caprolactam industrial production and is also a byproduct during NH<sub>3</sub>–SCR to treat NO<sub>x</sub>. With an extremely high global warming potential (GWP) that is 298 times CO<sub>2</sub>-equivalent and 25 times CH<sub>4</sub>-equivalent, N<sub>2</sub>O is an important greenhouse gas [77]. For N<sub>2</sub>O direct decomposition (deN<sub>2</sub>O), it is generally decomposed at high temperatures (500–600 °C) by metal-loaded oxides or molecular sieves. In order to reduce the amount of noble metals, they are usually loaded on carriers with large specific surface areas, such as NiO, Co<sub>3</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and SiO<sub>2</sub>, to make them dispersed and improve deN<sub>2</sub>O activity. The catalytic performance of SACs depends largely on the coordination environment of metal sites. For example, Xie et al. obtained two different Rh<sub>1</sub>/CeO<sub>2</sub> SACs with high and low coordination numbers (CN) by adjusting synthesis procedures [78]. The Rh<sub>1</sub>/CeO<sub>2</sub> with higher Rh CN (Rh/CeO<sub>2</sub>-H) was more active in deN<sub>2</sub>O, which resulted from faster O<sub>2</sub> desorption, more surface oxygen vacancies, and higher reducibility (Figure 5a,b). Li's group loaded rare earth elements Sm [79] and Pr [80] onto Co<sub>3</sub>O<sub>4</sub>, respectively. By introducing Sm into Co<sub>3</sub>O<sub>4</sub>, the presence

of Sm promoted the regeneration of the active site and improved the reducibility and oxygen desorption capacity of  $\text{Co}_3\text{O}_4$ . The catalytic performance of  $\text{Sm}_{0.1}\text{-Co}_3\text{O}_4$  showed  $\sim 52\%$   $\text{N}_2\text{O}$  decomposition at  $325^\circ\text{C}$  and over  $90\%$   $\text{N}_2\text{O}$  decomposition at  $375^\circ\text{C}$  (Figure 5c). In addition, in  $\text{Pr-Co}_3\text{O}_4$ , the “Pr 4f–O 2p–Co 3d” network generated by Pr single-atom doping in  $\text{Co}_3\text{O}_4$  redistributed electrons in the  $\text{Co}_3\text{O}_4$  lattice, which greatly improved the  $\text{N}_2\text{O}$  decomposition performance (Figure 5d). The  $T_{50}$  decreased from  $\sim 430^\circ\text{C}$  of  $\text{Co}_3\text{O}_4$  to  $\sim 320^\circ\text{C}$  of  $\text{Pr}_{0.06}\text{Co}$ , and the  $T_{90}$  decreased from  $\sim 500^\circ\text{C}$  of  $\text{Co}_3\text{O}_4$  to  $\sim 367^\circ\text{C}$  of  $\text{Pr}_{0.06}\text{Co}$ .

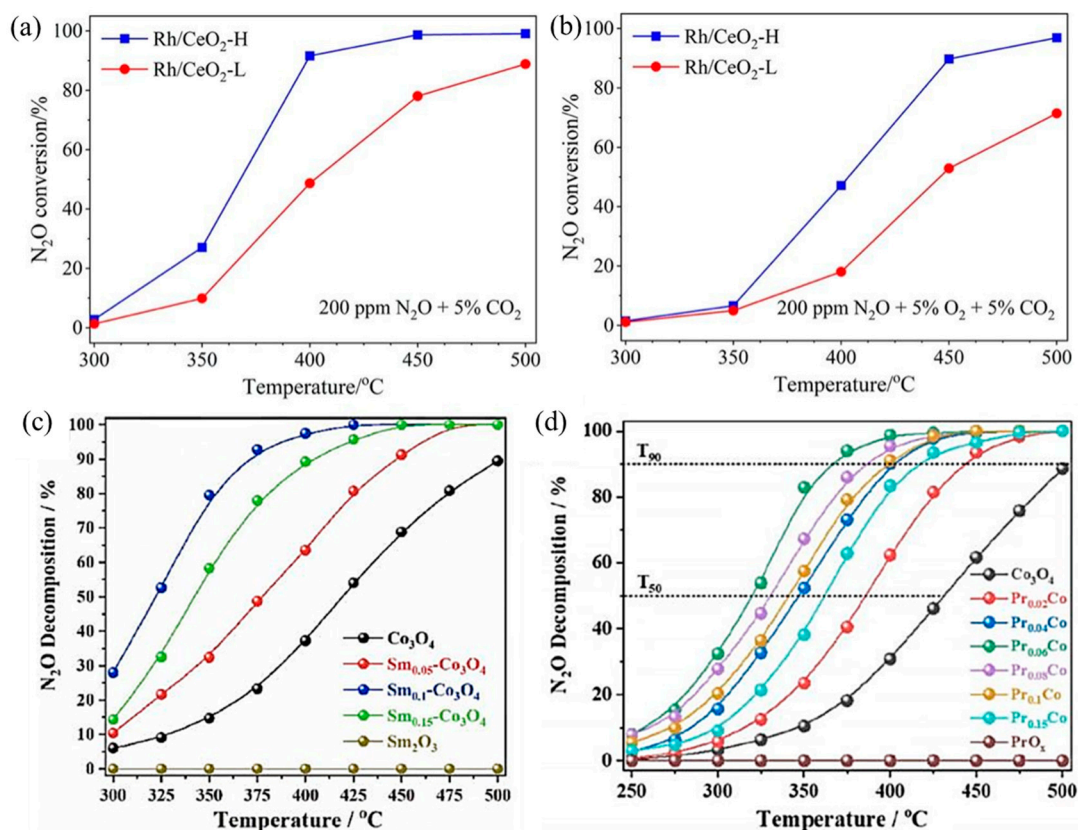


**Figure 5.** Catalytic performance for  $\text{N}_2\text{O}$  decomposition over  $\text{Rh/CeO}_2\text{-L}$  and  $\text{Rh/CeO}_2\text{-H}$  catalysts under conditions of (a)  $0.02\%$   $\text{N}_2\text{O}$  +  $5\%$   $\text{CO}_2$  and (b)  $0.02\%$   $\text{N}_2\text{O}$  +  $5\%$   $\text{O}_2$  +  $5\%$   $\text{CO}_2$ ; Ar balanced. Weight hour space velocity (WHSV) was fixed at  $100,000\text{ mL g}^{-1}\cdot\text{h}^{-1}$ . Copyright 2023, Chinese Society of Rare Earths [78]. (c)  $\text{N}_2\text{O}$  decomposition activity normalized by specific surface area ( $S_{\text{BET}}$ ) on  $\text{Co}_3\text{O}_4$  and Sm-doped  $\text{Co}_3\text{O}_4$  samples. Copyright 2021, Elsevier B.V. [79]. (d)  $\text{N}_2\text{O}$  decomposition activity normalized by  $S_{\text{BET}}$  on  $\text{Co}_3\text{O}_4$  and Pr-doped  $\text{Co}_3\text{O}_4$  samples. Copyright 2022, American Chemical Society [80].

#### 2.4. $\text{CO}_2$ Reduction

Electrochemical reduction of  $\text{CO}_2$  into various chemical feedstocks and fuels not only reduces the negative environmental impact of  $\text{CO}_2$  but also alleviates the problem of fossil fuel shortage [81–83]. In recent years, researchers have developed SACs as efficient catalysts for the electrochemical reduction of  $\text{CO}_2$  ( $\text{CO}_2\text{RR}$ ). Numerous heterogeneous catalysts, for example, metals [84–86], metal oxides [87,88], metal sulfides [89], metal organic frameworks (MOFs) [90], and their composites [91], have been used. In general, Ni and Fe SACs exhibited superior catalytic performance for CO evolution, while Co, Mn, and Zn SACs were relatively inert to  $\text{CO}_2\text{RR}$  [92].

In a study by Zhang et al. [93], an isolated nickel monatomic electrode was prepared with high-density Ni(I) sites anchored to a nitrogen-doped carbon nanotube array and further encapsulated in a nickel–copper alloy on carbon fiber paper ( $\text{Ni}^{\text{I}}\text{-NCNT@Ni}_9\text{Cu}$ ). The nickel–copper alloy was encased in the carbon-fiber paper. The combination of the

single-atomic Ni(I) site and the self-supported array structure resulted in excellent CO<sub>2</sub>RR performance. The electron configuration of the *d* band of Ni was modified by introducing Cu, which enhanced the adsorption of hydrogen, thus hindering the hydrogen evolution reaction (HER). The specific current density of a single Ni atom electrode was 32.87 mA cm<sup>−2</sup>, with a TOF of 1962 h<sup>−1</sup> at an overpotential of 620 mV and a Faradaic efficiency of 97% at around −0.73 V vs. RHE. Tang's group [94] developed a Fe–N–C catalyst for CO<sub>2</sub>RR via a novel one-step calcination method, which achieved high selectivity of CO<sub>2</sub>RR to CO. Compared with pristine N–C material, Fe–N–C achieved a higher maximum Faradaic efficiency of 73% and a Tafel slope of 68 mV dec<sup>−1</sup>, respectively. The excellent CO<sub>2</sub>RR performance of the catalyst was ascribed to the active Fe–N<sub>x</sub> sites, rich functional groups, and abundant microporous structure.

As for noble metal catalysts, Au and Ag show relatively high CO<sub>2</sub>RR catalytic activity. It was shown that when comparing Ag and Au, when the NP size decreases, Au NPs will lead to the enhancement of the competitive HER, resulting in an increase in by-products, while Ag NPs can selectively enhance CO<sub>2</sub>RR [95]. Zhang et al. synthesized Ag<sub>1</sub> monatomic catalyst (Ag<sub>1</sub>/MnO<sub>2</sub>) by thermal conversion of Ag NPs and surface reconstruction of MnO<sub>2</sub> [96]. Ag<sub>1</sub>/MnO<sub>2</sub> exhibited a Faradaic efficiency of 95.7% at −0.85 V vs. RHE (Figure 6b), with excellent stability in the reaction (Figure 6c). The Ag<sub>1</sub>/MnO<sub>2</sub> showed improved CO<sub>2</sub>RR performance than conventional Ag nanocatalysts (AgNP/MnO<sub>2</sub>) and other reported Ag-based catalysts (Figure 6a,b,d). For current SACs in CO<sub>2</sub>RR, the low density of active sites, poor conductivity, and mass transfer resistance towards single atomic electrodes still limit their catalytic performance. In order to prevent metal aggregation on the cathode during reductive reactions and maintain the atomic dispersion, most current studies have only achieved a relatively low SAC metal loading below 5 wt%. Therefore, further research is still needed to improve the metal loading capacity of SACs.

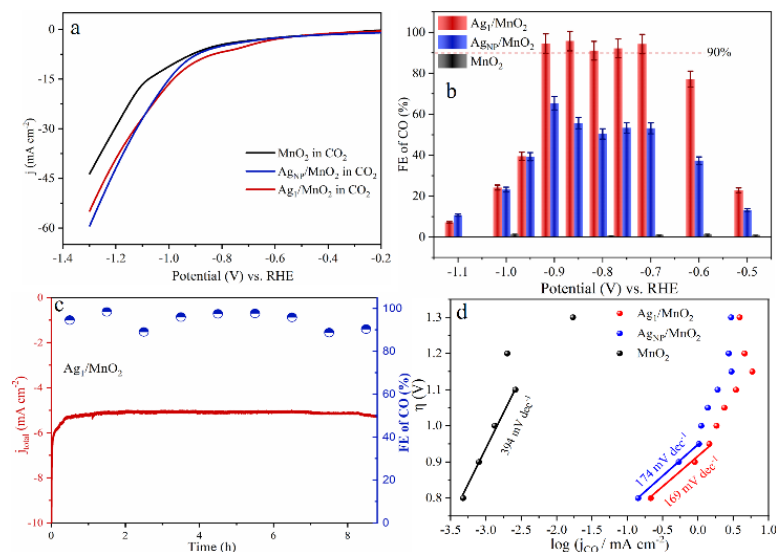


**Figure 6.** (a) Linear Sweep Voltammetry (LSV) curves of MnO<sub>2</sub>, AgNP/MnO<sub>2</sub>, and Ag<sub>1</sub>/MnO<sub>2</sub> in a CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> electrolyte. (b) Faradaic efficiency of CO. (c) Long-term electrolysis experiments on Ag<sub>1</sub>/MnO<sub>2</sub> at electrolysis potentials of −0.9 V vs. RHE. (d) Tafel plots of three samples. Copyright 2021, Angew Chem Int Ed Engl. [96].

### 3. Progress of SACs in Aqueous Pollution Control

#### 3.1. H<sub>2</sub>O<sub>2</sub>-Based Fenton-like Processes

Fenton process with H<sub>2</sub>O<sub>2</sub> generates strongly oxidizing •OH for aqueous organic pollutant decomposition. The traditional Fe-based catalysts have been reported the most, among which Fe SACs have a better catalytic ability than nanoparticle catalysts. Yin et al. [97] reported a SAFe–SBA catalyst with single-atom Fe dispersed into the nanopores of SBA-15. The well-dispersed Fe atoms promoted the decomposition of H<sub>2</sub>O<sub>2</sub> into •OH,

leading to a better catalytic performance of SFe-SBA than aggregated iron sites (AGFe-SBA). The degradation efficiency of both HBA and phenol reached 100% after 180 min (Figure 7a,b). In addition, the Fe SACs formed by Fe sites embedded in g-C<sub>3</sub>N<sub>4</sub> effectively degraded a variety of dyes and organic pollutants (methylene blue (MB), methyl orange (MO), rhodamine B (RhB), and phenol) (Figure 7c), owing to the improved production of  $\bullet$ OH from H<sub>2</sub>O<sub>2</sub> activated by Fe(II)-N<sub>x</sub> active sites [28].

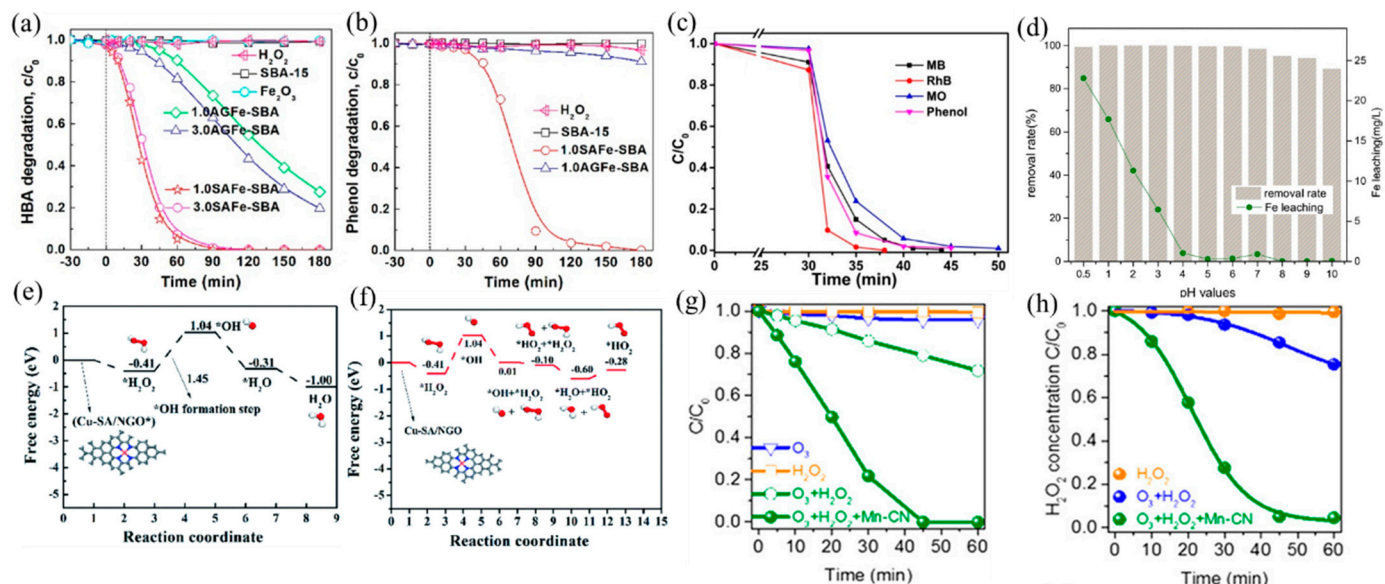


**Figure 7.** (a) HBA and (b) phenol adsorption and oxidation by H<sub>2</sub>O<sub>2</sub> activation on catalysts. Copyright 2019, American Chemical Society [97]. (c) Removal efficiency of different organic pollutants using an I-FeN<sub>x</sub>/g-C<sub>3</sub>N<sub>4</sub>-5 catalyst [28]. Reaction conditions: 200 mg L<sup>−1</sup> organics (MB, MO, RhB, and phenol), 77 mM H<sub>2</sub>O<sub>2</sub>, 0.5 g L<sup>−1</sup> catalyst, 308 K, and visible light. Copyright 2018, American Chemical Society. (d) Effect of pH values on AR 73 removal and Fe leaching. Copyright 2016, Elsevier B.V. [98]. Free energy diagrams for Cu-SA/NGO in  $\bullet$ OH generation under acidic (e) and neutral (f) conditions. Copyright 2020, The Royal Society of Chemistry [26]. (g) Degradation curves of OA in ozonation, the H<sub>2</sub>O<sub>2</sub> process, and the peroxone process with or without Mn-CN. (h) Corresponding H<sub>2</sub>O<sub>2</sub> decay curves in the H<sub>2</sub>O<sub>2</sub> process, peroxone process, and peroxone process with Mn-CN. Copyright 2019, American Chemical Society [99].

The narrow pH range (2–4) hinders the real application of the Fenton processes [100], which can be improved by adjusting the support and coordination environment of the catalyst. Ma et al. [98] found that dispersing SA Fe-g-C<sub>3</sub>N<sub>4</sub> onto graphitized mesoporous carbon composite (GMC) broadened the working pH window. The obtained catalyst exhibited high catalytic activity in the range of pH = 4–10, attributable to the well-dispersed Fe-N<sub>x</sub> and  $\pi$ - $\pi$  stacking of GMC that promoted the adsorption and decomposition of H<sub>2</sub>O<sub>2</sub> (Figure 7d). Besides, Wu and coworkers [26] prepared a high density of Cu SACs on N-doped graphene (Cu-SA/NGO), which also achieved efficient H<sub>2</sub>O<sub>2</sub> decomposition at neutral pH facilitated by Cu-N<sub>4</sub> active sites and low energy barriers of reaction (Figure 7e,f). At acidic conditions, H<sub>2</sub>O<sub>2</sub> can easily be adsorbed on Cu-N<sub>4</sub> sites and generate OH\* and  $\bullet$ OH, while at neutral conditions, OH\* s formed when adsorbed H<sub>2</sub>O<sub>2</sub> reacted with another H<sub>2</sub>O<sub>2</sub> molecule to form oxidative HO<sub>2</sub>\*. Gong and coworkers [99] developed Mn-N<sub>4</sub>-doped g-C<sub>3</sub>N<sub>4</sub> (Mn-CN), which catalyzed the formation of  $\bullet$ OH with H<sub>2</sub>O<sub>2</sub> and additional oxidant O<sub>3</sub> and degraded oxalic acid (OA). Because of the dispersion of isolated Mn atoms, Mn-CN showed excellent catalytic performance, and oxalic acid was completely degraded within 45 min (Figure 7g,h). Different from the traditional H<sub>2</sub>O<sub>2</sub> reaction, this work proposed a new pathway: H<sub>2</sub>O<sub>2</sub> adsorbed on Mn-N<sub>4</sub> sites formed HOO-Mn-N<sub>4</sub> species, which reacted with O<sub>3</sub> to generate HO<sub>2</sub>\* and O<sub>3</sub>\*<sup>−</sup>, finally producing  $\bullet$ OH.

### 3.2. Persulfate-Based Fenton-like Processes

In recent years, persulfate-based AOPs have been widely applied in water purification, which is mainly based on the chain reactions initiated by persulfate (PMS, PDS) molecules, generating strongly oxidizing ROS including  $\text{SO}_4^{\bullet-}$ ,  $\bullet\text{OH}$ ,  $\text{O}_2^{\bullet-}$ , and  $^1\text{O}_2$  [101,102]. The process has a strong oxidation capacity and a wide range of solutions for environmental adaptation. In persulfate-AOPs, Co-based, Fe-based, Cu-based, and Mn-based catalysts are widely studied.

In PMS-based AOPs, Co-based SACs have been extensively studied [101]. Single Co atoms anchored onto porous N-doped graphene showed dual reaction sites [103]: the Co atom was the reaction site, while the adjacent pyrrolic N was the adsorption site (Figure 8a). It activated PMS to degrade BPA with high efficiency because the dual reactive sites reduced the transport distance of ROS and improved the mass transfer efficiency. Likewise, Kim's group [104] reported pyridine N-coordinated single-atom Co loaded on a polyromantic macrostructure (Co-TPML) (Figure 8b), which also showed outstanding PMS activation and achieved high pollutant removal efficiency, resulting from a high-density and ultrafine dispersion of Co single atoms. With beneficial  $\pi$ -conjugation of TPML and strong metal-support interactions, peroxide adsorption and activation were enhanced. Furthermore, this group developed a single-atom Co-loaded 2D Graphene Oxide (GO)-based membrane [105], in which vitamin C was applied as a mild reducing agent to improve the atomically Co dispersion and maintain the structure of GO layers. This study observed that the  $\text{Co}_1$ -GO membrane showed excellent ability for 1,4-dioxane degradation with the addition of PMS. The kinetics of 1,4-dioxane degradation were over 640 times greater than those in suspension, which was the highest among reported studies in persulfate-based 1,4-dioxane degradation. This catalyst-membrane combination was able to repel macromolecular organic matter, reducing its scavenging effect on free radicals. In addition, studies have found that the porous carbon material support can promote electron transfer [106], which is conducive to improving the efficiency of PMS-based AOPs.

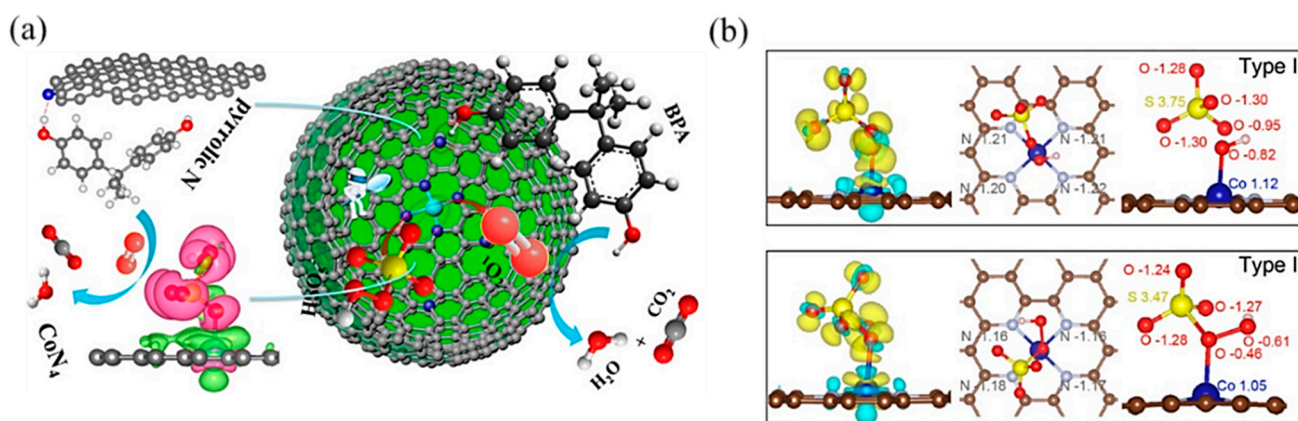


**Figure 8.** (a) The proposed overall Fenton-like reaction mechanism on a single-Co-atom catalyst. Copyright 2018, American Chemical Society [103]. (b) Adsorption configuration and charge density of PMS on Co-TPML through coordination with H-adjacent (Type I) and S-adjacent (Type II) O atoms in the peroxide bond, respectively. Yellow and cyan denote the electron accumulation and electron depletion, respectively. Copyright 2020, American Chemical Society [104].

Compared with PMS, PDS is more difficult to activate with a short peroxide O–O bond (1.322 Å) in the structure of  $-\text{O}_3\text{S}-\text{O}-\text{O}-\text{SO}_3-$  [107]. Because of its cheaper cost, lower toxicity, and lower pH limits, PDS is expected to be more widely applied in actual water treatment. Generally, in PDS/SAC systems, synergistic effects between the atomic metal and the support play an important role [15]. Li and coworkers [108] developed Cu single sites dispersed on carbon nitride (SAS- $\text{Cu}_{1.0}$ ), showing remarkable performance in tetracycline degradation due to the enhanced PDS adsorption and activation. Under

UV light and 0.1 mM sodium persulfate, the tetracycline (TC) degradation rate of SAS-Cu<sub>1.0</sub> reached 82.5% in 30 min, while the degradation rates of carbon nitride (CN) and CN-NanoCu were 53.5% and 78.1%, respectively. The result revealed that the degradation mechanism on single-atom Cu involved both radical and nonradical pathways, leading to the promotion of charge separation and transfer.

### 3.3. Electrocatalytic Hydrodehalogenation

Organic halides that contain C–X bonds (X = Cl, Br, I, and F), such as chlorobenzene, 4-chlorophenol, and bromophenol, are commonly found in water bodies contaminated by pharmaceuticals, pesticides, surfactants, and after disinfection by chlorine [109]. Due to their strong carbon–halogen bonds and the ability to destruct biological enzymes, organohalogens are difficult to destroy by biological methods, leading to their persistent existence in water and posing a serious threat to human health, the ecological environment, and agricultural production. To solve this problem, hydrodehalogenation is proposed as an effective dehalogenation scheme in which two distinct partially charged H<sup>δ−</sup> and H<sup>δ+</sup> atoms formed from H atoms are utilized to attack carbon–halogen bonds [110,111]. Direct catalytic hydrodehalogenation is the most studied dehalogenation method at present. Numerous mono-metal and bimetallic catalysts have been developed. However, high catalyst costs, strict reaction conditions, and unsatisfactory catalytic efficiency make this technology a dilemma. In comparison, electrocatalytic and photocatalytic hydrodehalogenation, which are environmentally friendly and energy saving, have become a hot research field in recent years. In 1975, Geer et al.'s experiment on hydrodehalogenation of hexachlorobenzene (HCB) by electrocatalysis proved that the complete degradation of chlorinated organic compounds could be achieved by controlling the potential [112].

Transition metal-based SACs have been used due to their excellent electrocatalytic hydrodehalogenation performance. Wang et al. [113] synthesized single-atom Co on sulfide graphene (Co–SG), achieving high atomic H<sup>\*</sup> production by electrochemical reduction of H<sub>2</sub>O and electrolysis of hydrogen. With the synergistic effects among Co active sites, S-doped graphene, and the interfacial structure, the conversion rate of 2,4-DCBA reached 91.1% and the TOC concentration was reduced by 80% (Figure 9a,b). Zhao and coworkers [114] developed a Fe/Cu bimetallic single-atom catalyst dispersed on N-doped porous carbon (FeCuSA–NPC), leading to a stronger chlorinated pollutant degradation effect. In this process, dichlorination on the Cu single atom and hydroxyl radical oxidation on the Fe single atom formed a synergistic effect, which led to a high removal activity for 3-chlorophenol (3-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP), with kinetics between 545.1 and 1374 min<sup>−1</sup> g<sub>metal</sub><sup>−1</sup>.

Apart from transition metal catalysts, noble metal catalysts are also efficient in electrocatalytic hydrodehalogenation, among which, Pd-based catalysts have been studied in depth. Huang et al. [115] synthesized a single-atom Pd loaded on reduced graphene oxide (Pd<sub>1</sub>/rGO), which was more effective in chlorinated phenol dichlorination and showed higher atomic efficiency than Pd nanoparticle counterparts (Figure 9c). Mechanistic studies showed that this promotion effect was attributed to two aspects: (1) a strong interaction between the metal and support enhanced interfacial electron transfer through Pd–O bonds; (2) Pd<sub>1</sub> restrained H<sub>2</sub> evolution, contributing to atomic H (H<sup>\*</sup>) utilization (Figure 9d). Further, Chu et al. [116] proposed that neighboring Pd single-atom catalysts, with shorter distances and more adjacent active sites between atoms, performed higher activity and selectivity in hydrogenating carbon–halogen bonds than isolated single-atom Pd. DFT calculations (Figure 9e) revealed that the cooperative effect between neighboring Pd atoms decreased the energies of water desorption and hydrogenated product desorption, which were the key meta-stable reaction steps. Besides, the neighboring structure was conducive to selectively hydrogenating the C–Cl bond without affecting the other bonds.

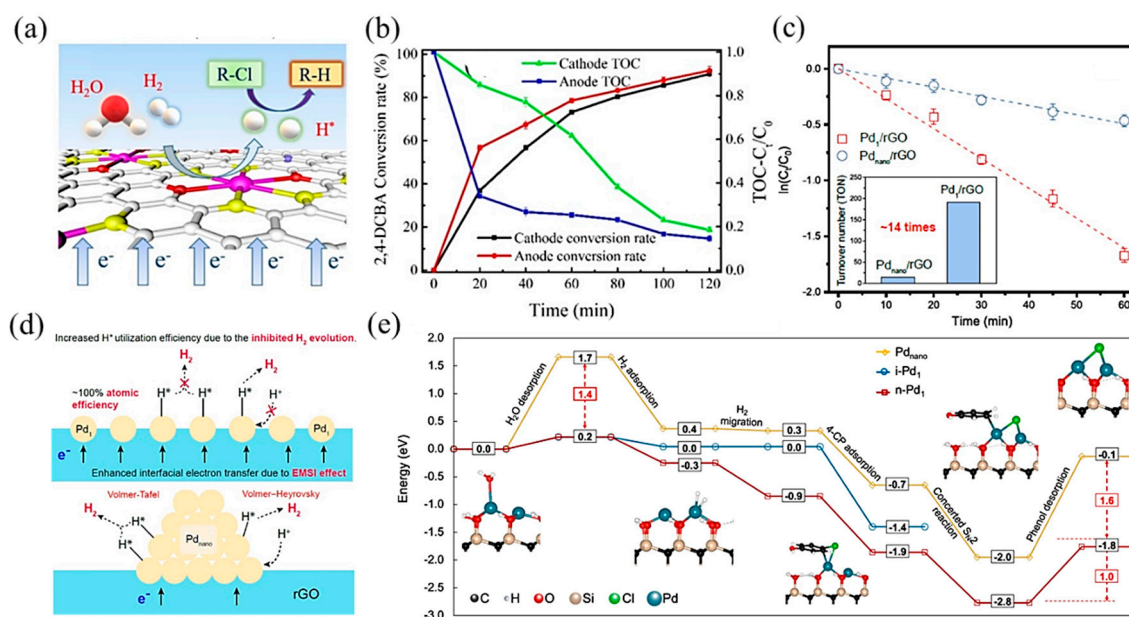


**Figure 9.** (a) Schematic illustration of the electrocatalytic hydrodechlorination reaction mechanism. (b) Total Organic Carbon (TOC) concentration ratio and conversion rate of 2,4-DCBA over time. Copyright 2020, American Chemical Society [113]. (c) Pseudo-first-order kinetic plots of 4-CP dechlorination with Pd<sub>1</sub>/rGO and Pd<sub>nano</sub>/rGO electrodes. The inset indicates the turnover number per Pd atom based on a reaction time of 30 min. (d) Proposed mechanism of enhanced cathodic hydrodechlorination with Pd<sub>1</sub>/rGO versus Pd<sub>nano</sub>/rGO. Copyright 2021, American Chemical Society [115]. (e) Hydrodehalogenation on i-Pd<sub>1</sub>, n-Pd<sub>1</sub>, and Pd<sub>nano</sub>. The blue, black, red, tan, and white spheres in geometrical models are Pd, C, O, Si, and H atoms, respectively. The solid and dashed lines represent the minimum energy path and other reaction pathways, respectively. Copyright 2021, Springer Nature [116].

### 3.4. Photocatalytic Hydrodehalogenation

Photocatalytic hydrodehalogenation realizes the fracture of carbon–halogen bonds through photoexcitation and electron transfer. Numerous studies have proved that semiconductor catalysts doped with noble metals display superior photocatalytic hydrodehalogenation.

Kim's team has reported single-atom Pt supported on SiC (Pt<sub>1</sub>/SiC) [29] and TiO<sub>2</sub> (Pt<sub>1</sub>/TiO<sub>2</sub>) [117], respectively, achieving hydrodehalogenation of perfluorooctanoic acid (PFOA) by cleaving C–F bonds. As for Pt/SiC (Figure 10a), due to the high work function of Pt (~5.65 eV), it tended to attract photogenerated electrons from the SiC conduction band, and then H atoms were selectively reduced and formed Pt–H bonds through the Volmer reaction. Finally, H atoms spillover from Pt–H bonds were transferred to SiC to form Si–H, which was then redistributed with the C–F bond, thus achieving hydrodehalogenation. Likewise, Pt single atoms in Pt/TiO<sub>2</sub> drove the photogenerated electrons on the conduction band to generate H atoms and spill over onto the TiO<sub>2</sub> surface, further forming Ti–H bonds to break C–F (Figure 10b). On the contrary, Pt nanoparticles consumed photogenerated electrons to reduce O<sub>2</sub>, instead of hydrodehalogenation.

In addition, single-atom Ag was confirmed as an ideal catalyst to selectively dehalogenate under visible-light irradiation by Wang et al. [118]. Under mild visible light irradiation, AgF was successfully reduced to Ag(0) single atoms and Ag nanoparticles. Theoretical and experimental investigations suggested that such mixed species (MS-Ag) showed outstanding hydrodehalogenation and deiodination-arylation performance, resulting from the synergistic effects of the Ag single atoms and the light-harvesting unit of Ag nanoparticles. Notably, the yield of selective hydrodehalogenation of 4-iodoanisole was up to 99% when CsF was added.

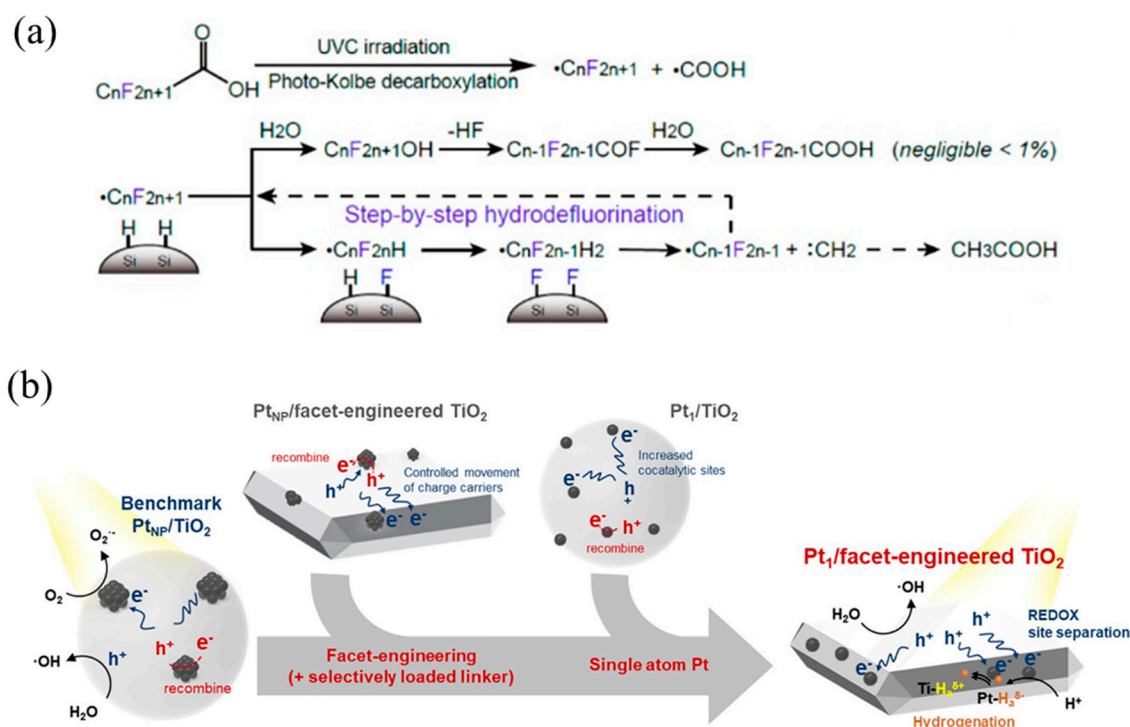


**Figure 10.** (a) PFOA decomposition mechanism with  $\text{Pt}_1/\text{SiC}$  showing photo-Kolbe decarboxylation and subsequent hydrodefluorination. Copyright 2018, American Chemical Society [29]. (b) Photocatalysis mechanisms of Pt nanoparticle-loaded  $\text{TiO}_2$ , Pt single-atom-loaded  $\text{TiO}_2$ , Pt nanoparticle-loaded facet-engineered  $\text{TiO}_2$ , and Pt single-atom-loaded facet-engineered  $\text{TiO}_2$ . Copyright 2021, American Chemical Society [117].

### 3.5. Nitrate and Nitrite Reduction

Nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) are common inorganic nitrogen-containing pollutants in the aqueous phase and the main causes of eutrophication and algae blooms. Due to the excessive use of agricultural fertilizers and improper treatment of sewage,  $\text{NO}_3^-$  is prevalent in groundwater and surface water bodies, posing a great threat to human health and the environment.  $\text{NO}_3^-$  in sewage can be converted into  $\text{NO}_2^-$  by microorganisms, which will destroy the oxygen transport ability of hemoglobin when entering the human body, and even lead to poisoning or cancer. Nitrate reduction reaction ( $\text{NO}_3\text{RR}$ ) is a promising strategy to reduce the environmental pollution caused by  $\text{NO}_3^-$ , while producing  $\text{N}_2$  or  $\text{NH}_3$  as a valuable energy source.

Single-atom electrocatalysts can realize efficient  $\text{NO}_3\text{RR}$  and selectively obtain  $\text{NH}_3$ , such as Fe- and Cu-based SACs. Primarily, the active center of the Fe-based catalyst is  $\text{Fe-N}_x$ . According to Wang et al. [30], isolated Fe single atoms in the form of  $\text{Fe-N}_4$  hindered N–N coupling, resulting in higher affinity towards N–H coupling and  $\text{NH}_3$  formation. Benefiting from these structure advantages, the nitrogen-coordinated Fe sites dispersed on carbon matrix exhibited remarkable capacities in  $\text{NO}_3\text{RR}$  with a Faradaic efficiency of ~75% and a high  $\text{NH}_3$  yield of  $\sim 20,000 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  (Figure 11a,b). In addition, Liu et al. [31] prepared a highly active and selective Fe–CNS consisting of Fe single atoms loaded on S and N-doped carbon supports. S-doping created more defects on the support surface, which was beneficial to enhancing the stability of Fe single atoms. Along with  $\text{Fe-N}_4$ , the presence of S sites adjusted the coordination environment and formed  $\text{FeN}_4\text{S}_2$  as the dominant active site. The experimental results of  $\text{NO}_3\text{RR}$  revealed that the prepared Fe–CNS catalyst performed excellent activity with a nitrate removal capacity of  $7822 \text{ mg-N g}^{-1} \text{Fe}$  and a high ammonia Faradaic efficiency of 78.4%. Yu et al. [119] found that nitrate preoccupied on  $\text{Fe(II)-N}_x$  and hindered the adsorption of  $\text{H}_2\text{O}$ , thus inhibiting the competitive reaction of HER. In addition, the special thermodynamic and kinetic properties of the Fe SACs resulted

in a more positive and narrower range of redox potentials than the Fe NPs (Figure 11c). As a result, Fe SACs achieved a higher  $\text{NH}_3$  yield and selectivity, with a maximum yield rate of  $2.75 \text{ mg}_{\text{NH}_3} \text{ h}^{-1} \text{ cm}^{-2}$  and close to 100% Faradaic efficiency (Figure 11d). The TOFs of the Fe-PPy SACs reached  $0.006\text{--}0.7 \text{ s}^{-1}$  at  $0\text{--}0.7 \text{ V}$  vs. RHE, while the TOFs of the Fe NPs were  $0.00015\text{--}0.06 \text{ s}^{-1}$  (Figure 11e).

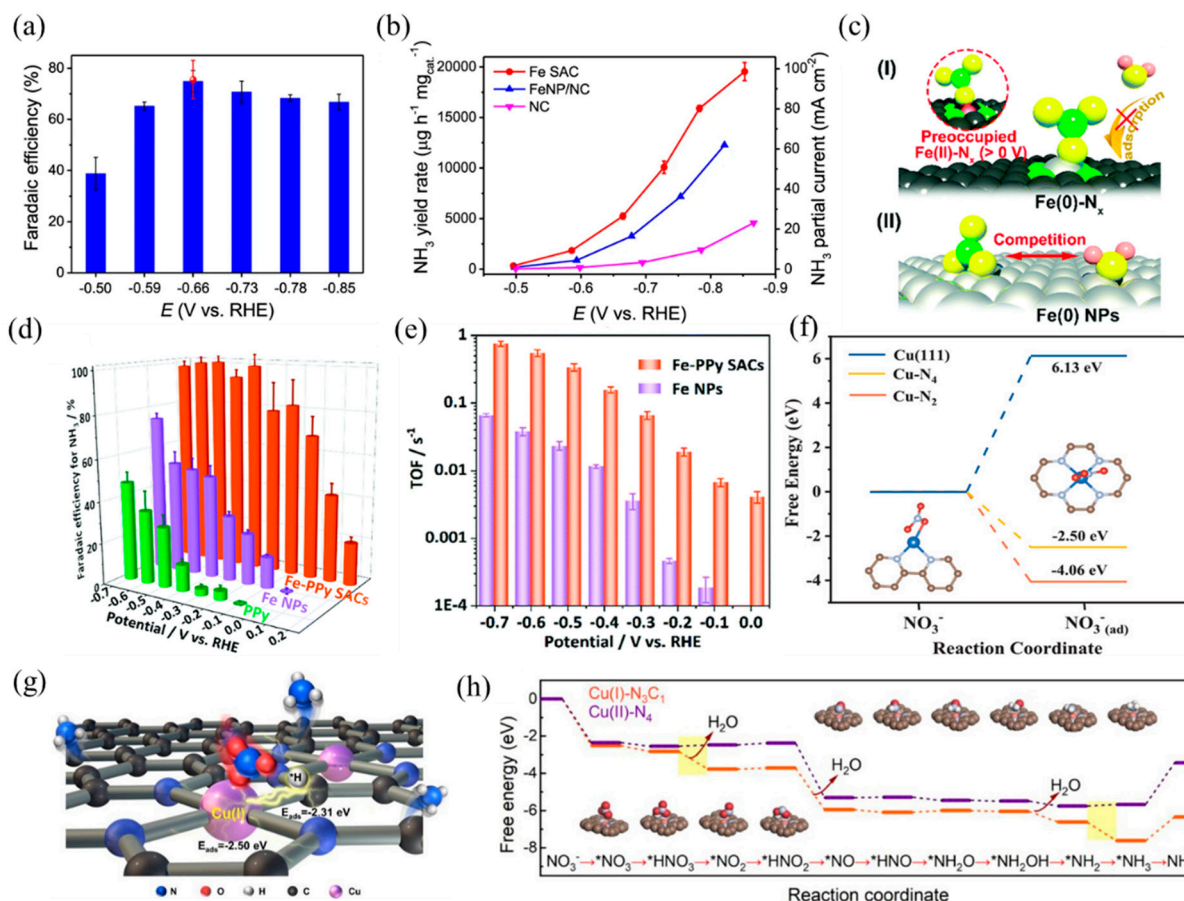


**Figure 11.** (a)  $\text{NH}_3$  Faradaic efficiency of Fe SAC at each given potential. Red dot is Faradaic efficiency estimated by three independent NMR tests. (b)  $\text{NH}_3$  yield rate and partial current density of Fe SAC, FeNP/NC, and NC. Copyright 2021, Springer Nature [30]. (c) The proposed preoccupied  $\text{NO}_3\text{RR}$  mechanism for the single-site center (I) and the classical competitive mechanism for the bulk surface (II). (d) Faradaic efficiency for ammonia and (e) TOFs of the Fe-PPy SACs and Fe NPs based on the result of SI-SECM for ammonia production. Copyright 2021, The Royal Society of Chemistry [119]. (f) Calculated free energies for  $\text{NO}_3^-$  adsorption on Cu (111),  $\text{Cu-N}_4$ , and  $\text{Cu-N}_2$  surfaces, respectively. The brown, gray, blue, and red balls represent C, N, Cu, and O atoms, respectively. Copyright 2020 Wiley-VCH [120]. (g) TOC and (h) calculated activation energy for  $\text{NO}_3\text{RR}$  using  $\text{Cu(I)-N}_3\text{C}_1$  and  $\text{Cu(II)-N}_4$  as models. Copyright 2022, American Chemical Society [121].

Besides, Cu-based SACs with the  $\text{Cu-N}_x$  coordination structure are also suitable for  $\text{NO}_3\text{RR}$ , according to previous studies. Feng et al. [120] reported a Cu SAC anchored on nitrogen-doped carbon nanosheets ( $\text{Cu-N-C}$ ) with high activity, selectivity, and stability in  $\text{NO}_3\text{RR}$ . XAFS analysis and DFT calculations revealed that the mixed coordination structures of  $\text{Cu-N}_2$  and  $\text{Cu-N}_4$  dispersed on carbon caused the adsorption of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (Figure 11f), inhibiting the release of  $\text{NO}_2^-$ . At  $-1.3 \text{ V}$  vs. SCE with an initial  $50 \text{ mg L}^{-1}$   $\text{NO}_3\text{-N}$ , the selectivity of the  $\text{NO}_2\text{-N}$  product was only 5%. Fan and coworkers [121] studied the  $\text{NO}_3\text{RR}$  properties of atomic Cu supported on micro/mesoporous nitrogen-doped carbon (Cu MNC). The Cu(I) sites ( $\text{Cu(I)-N}_3\text{C}_1$ ) concentrated the charge around the center Cu atoms, causing the adsorption of  $^*\text{NO}_3$  and  $^*\text{H}$  to adjacent Cu and C sites by balanced

adsorption energy. Compared with Cu(II)-N<sub>4</sub>, Cu(I)-N<sub>3</sub>C<sub>1</sub> decreased the activation energy of rate-limiting steps, thus promoting the formation of NH<sub>3</sub> (Figure 11g,h). When applied to nitrate reduction (100 mg-N L<sup>-1</sup>), Cu MNC achieved a promising NH<sub>3</sub> yield rate per active site of 5466 mmol g<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup> and a conversion rate of 94.8% within 6 h.

As for noble metal SACs, isolated Ru sites dispersed on nitrogen-doped carbon (Ru SA-NC) were demonstrated to be an effective catalyst for both nitrate and nitrite electroreduction to NH<sub>3</sub> [122]. Ru SA-NC achieved Faradaic efficiencies of 97.8% at -0.6 V vs. RHE (NO<sub>2</sub><sup>-</sup> reduction) and 72.8% at -0.4 V vs. RHE (NO<sub>3</sub><sup>-</sup> reduction), respectively. A bimetallic catalyst with a single-atom Ru-modified Cu nanowire array loaded on Cu foam (Ru-Cu NW/CF) was proposed by Lee's group [123], which showed efficient electrocatalytic nitrite reduction. Due to the inhibition of N-N coupling by the active site of single-atom Ru, at the overpotential of -0.6 V vs. RHE, the Faradaic efficiency reached 94.1% and the NH<sub>3</sub> yield was up to 211.73 mg h<sup>-1</sup> cm<sup>-2</sup>. Kamiya et al. [124] prepared an atomically dispersed Pt-modified covalent triazine framework hybridized with carbon nanoparticles (Pt-CTF/CP), which showed a NO<sub>2</sub><sup>-</sup> reduction activity comparable to that of bulk Pt surfaces. It is worth noting that nitrate reduction reactions were almost not detectable. Since nitrate adsorbed on the single Pt atom is in an unstable monodentate form, the nitrate may not have enough adsorption energy to be activated.

#### 4. Conclusions and Outlook

With close to 100% atomic efficiency and high catalytic activity, SACs are considered to bring new opportunities for environmental pollution remediation and are becoming a prevalent research frontier. The well-controlled atomically dispersed structure of SACs fills the gap between heterogeneous and homogeneous catalytic reactions and provides a new direction for understanding the catalytic mechanism at the atomic level. Compared with bulk NPs, SACs' unique electronic characteristics and atomic sites help them achieve reactions that cannot be catalyzed by NPs. Additionally, with higher atomic utilization and less metal loading, SACs have a lower cost of raw materials, showing economic advantages in practical engineered applications. In the past decade, researchers have developed a variety of SACs that have been successfully applied to solve practical environmental problems, such as the purification of industrial gaseous pollutants and the treatment of organic pollutants in wastewater. In general, SACs show excellent catalytic activity, selectivity, and stability in various catalytic reactions.

However, current SACs still have non-negligible shortcomings that should be overcome. Due to ultra-low metal loading, the catalytic efficiency of SACs is unsatisfactory. To improve the reaction efficiency, it is a tough challenge to avoid single-atom aggregation when increasing the metal content. From the above discussions, we found that the coordination structure and interactions between the atomic metal and the support have an important impact on the physicochemical properties and catalytic performances of SACs. Nevertheless, there is still a lack of clarity on the structure-catalytic correlation. Besides, unlike laboratory experiments, complex compositions in the actual gas or water bodies might interfere with the catalytic reaction via surface contamination and deactivation of the catalyst. A long-term reaction may also lead to the loss of metal atoms or aggregation. In engineering applications, the integration of SACs into existing devices or systems is also an important issue. To promote further development of SACs in environmental engineering, the following research directions are proposed:

- (1) **Development of new synthetic strategies:** Increasing the number and density of coordination sites can effectively improve the loading of metal single atoms. More loading sites can be created by fabricating defects and unsaturated coordination centers. The methods for synthesizing stable SACs with relatively high metal loadings should be further developed. Studies revealed that when the SAC content increases from ~1% to ~5%, monatomic metals will form neighboring SACs or SAC ensembles without metal-metal bonding. However, it still maintains high atomic utilization and a unique coordination environment [101]. Recently, atom-trapping methods have

been applied to load 1–3 wt% of SACs onto reducible supports (e.g.,  $\text{CeO}_2$ ,  $\text{FeO}_x$ ), preventing metal aggregation at high temperatures [17]. It was demonstrated that a single-atom Cu catalyst prepared by atom-trapping on  $\text{CeO}_2$  effectively prevented sintering and deactivation via the regulated charge state of the Cu through facile charge transfer between the active site and the support [125]. Moreover, using graphene quantum dots as the carbon carrier, the transition metal SAC content was further increased to nearly 40% [126]. Appropriate supports, such as porous carbon and MOF, can strengthen metal–substrate interactions. In addition, it is important to develop a synthetic strategy that can precisely regulate the atomic active center and create more selective metal active centers for a specific catalytic reaction. Through doping heteroatoms and designing bimetallic sites, creating synergistic interactions between various elements may greatly contribute to the enhancement of SAC performance.

- (2) **Study on catalytic mechanisms:** At present, most of the characterization techniques are ex situ, such as high-angle annular dark-field–scanning transmission electron microscopy (HAADF–STEM) and X-ray absorption spectroscopy (XAS), which make it difficult to provide in situ characterization of the alterations of the physicochemical properties and electronic structures of SACs during the reactions. Hence, it is necessary to develop advanced in situ characterization technology to further study the complex pathways of catalytic reactions at the atomic level. Nowadays, some cutting-edge in situ characterization techniques have been reported to detect the evolution of catalyst sites and the interactions between active sites and reactants during the reaction process. For example, Hensen et al. [59] used an in situ near ambient pressure X-ray photoelectron spectrometer (NAP–XPS) to follow the surface electronic structure of Pd– $\text{CeO}_2$  SAC during CO oxidation and in situ infrared spectroscopy to probe the interaction between surface sites and reactants. Thereby, the structure–function relationships of Pd/ $\text{CeO}_2$  catalysts were established. In addition, in situ and operando infrared and XAS were used to detect CO oxidation mechanisms on an Ir single atom, detailing reaction steps [127]. Datye et al. [128] also used CO as a probe molecule during in situ DRIFTS to effectively detect the property changes of  $\text{Pt}_1/\text{CeO}_2$  under reaction conditions. The model establishment and theoretical calculations by DFT are beneficial to understanding the formation of the intermediate products and energy barriers (i.e., the rate-determining step) during the reaction, which can guide the design of future catalysts. However, when faced with complicated environmental media and operating parameters, DFT is not suitable due to the high cost of time. As a more handy and advanced technology, machine learning (ML) and quantitative structure–activity relationship (QASR) can efficiently establish the relationship between catalyst performance and certain specific descriptors, such as operational parameters.
- (3) **Optimization for practical applications:** To stabilize the interactions between metal atoms and support, the synthesis methods of a certain metal–support combination are specific, which may hinder the large-scale synthesis of SACs. Developing a simple and general synthesis strategy is beneficial to reducing the cost of large-scale SAC production. The integration of SACs into reactors or systems to achieve pilot-scale and large-scale is another troublesome challenge to overcome. Besides, it is of great importance to improve the adaptability to different complex environments and the stability of the reaction system.

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