

Review

Cerium-Based Catalytic Materials for Industrial Waste-Gas Purification: Current Status, Future Directions, and Mechanistic Insights

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Abstract

Nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO₂), and volatile organic compounds (VOCs) in industrial waste gases pose significant threats to environmental quality and human health. Catalytic purification is recognized as a leading abatement technology, crucial for meeting increasingly stringent emission regulations. Rare-earth (RE) catalytic materials, particularly those based on cerium (Ce), lanthanum (La), praseodymium (Pr), and neodymium (Nd) oxides, have attracted intense research due to their unique electronic configurations, high oxygen storage capacity (OSC), facile reversible redox reactions Ce⁴⁺, Ce³⁺, and exceptional thermal stability. This paper provides a comprehensive and methodical overview of RE catalysts used in industrial waste-gas purification. Initially, the physicochemical characteristics of RE elements and their multifaceted roles as active phases, supports, and promoters are explained. Subsequently, the latest developments in RE-based catalysts for NO_x abatement, CO oxidation, VOC degradation, and the removal of sulfur-bearing gas are critically reviewed. The discussion emphasizes structure–activity relationships, reaction mechanisms, and the synergistic interactions between RE elements and transition metals. Comparative analyses are presented through tables focusing on catalyst composition, reaction conditions, performance parameters, and stability. Special attention is given to the enhanced resistance to water vapor and sulfur poisoning afforded by RE materials. Finally, current challenges and future research prospects, including cost reduction, scalability, and long-term durability, are suggested. This review aims to provide practical guidance for the rational design and industrial translation of next-generation RE catalytic materials for air pollution control.



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1. Introduction

The continuous growth of industrial sectors, including power generation, petrochemical processing, metallurgy, and transportation, leads to the persistent release of toxic waste gases. Major pollutants, including NO_x, CO, SO₂, and VOCs, are responsible for severe environmental issues such as acid rain, atmospheric haze, photochemical smog, and ozone depletion [1–4]. Furthermore, these pollutants pose a significant health risk, contributing

to the development of respiratory and cardiovascular diseases. Consequently, the development of highly efficient and environmentally sustainable technologies for large-scale waste-gas purification has become a paramount goal in environmental engineering and catalysis [4–6].

Heterogeneous catalysis stands out as a preeminent abatement technology due to its high efficiency, operational flexibility, and amenability to industrial processes [7–11]. Traditional catalytic materials, often based on noble metals or transition-metal oxides, are frequently susceptible to deactivation, operate within limited temperature ranges, and are highly sensitive to sulfur and water vapor. In this context, rare-earth (RE) elements have emerged as crucial components in advanced environmental catalysts [5–8].

RE elements are a chemically similar group of metals characterized by semi-filled 4f orbitals. This unique electronic configuration confers distinct physicochemical characteristics, including high oxygen affinity, variable oxidation states ($\text{Ce}^{4+}/\text{Ce}^{3+}$), and high lattice stability [12–14]. Among them, Cerium oxide CeO_2 has been extensively studied due to its exceptional oxygen storage–release capacity (OSC) and rapid oxygen mobility. These properties enable RE catalysts to promote redox reactions, stabilize active metal sites, and inhibit the sintering of the catalyst structure [12–14].

RE elements fulfill multiple roles in industrial waste-gas purification, acting as the primary active substance, structural stabilizer, electronic promoter, or catalyst support [3–6]. Their integration has been demonstrated to significantly enhance low-temperature activity, broaden operating windows, and increase resistance to deactivation by moisture and sulfur compounds. RE-promoted catalysts are now widely utilized in automotive exhaust treatment, stationary power plants, and chemical manufacturing [13–17].

Despite extensive development, the rational design of optimal RE catalytic materials remains a challenge, primarily due to the complex interactions among RE oxides, transition metals, and reaction intermediates [14–19]. A deeper understanding of structure–activity relationships and mechanistic pathways is required for further optimization. This paper aims to comprehensively review recent studies on RE catalytic materials for industrial waste-gas purification, discussing catalyst design principles, performance characteristics, and future trends. While numerous reviews have summarized the catalytic activity of rare-earth-based materials for individual reactions, fewer studies have systematically addressed their long-term durability and deactivation behavior under realistic industrial conditions [14–17]. In practice, industrial waste gases are multicomponent, highly fluctuating, and rich in catalyst poisons, including sulfur compounds, water vapor, chlorine species, alkali metals, and particulates. These factors often dominate catalyst lifetime and determine commercial viability. Distinct from prior reviews, this work emphasizes catalyst deactivation mechanisms, industrial gas complexity, and durability-oriented design principles, providing a translational framework linking laboratory-scale catalyst performance with real industrial deployment. Special attention is devoted to identifying deactivation pathways and mitigation strategies enabled by rare-earth elements, as well as emerging directions for robust catalyst design.

2. Economic Considerations for Rare-Earth Catalysts

While rare-earth elements, particularly cerium, exhibit excellent catalytic properties, their high cost and limited natural reserves remain significant challenges in their widespread use. Cerium, although abundant compared to other rare-earth elements, is still expensive relative to traditional catalytic materials such as transition metals. However, the unique properties of cerium, such as its high oxygen storage capacity, thermal stability, and resistance to catalyst poisoning by sulfur and water, make it an attractive choice for industrial waste-gas purification [18,19]. Additionally, research has demonstrated that

cerium-based catalysts have longer lifetimes and higher resistance to deactivation under harsh operating conditions compared to conventional catalysts. This means that, despite the high initial cost, cerium catalysts can offer significant cost savings over the long term by reducing the need for frequent replacements and maintaining consistent performance. Moreover, the use of cerium in combination with other rare-earth elements or transition metals can reduce the overall amount of cerium required, making catalyst systems more cost-effective. Ultimately, the economic feasibility of using rare-earth-based catalysts hinges on optimizing their efficiency and lifetime to offset the high material costs. The performance comparison of rare-earth catalysts and conventional catalysts in industrial waste-gas purification is detailed in Table 1.

Table 1. Performance comparison of rare-earth catalysts and conventional catalysts in industrial waste-gas purification.

Catalyst System	Rare-Earth Content (%)	Reaction Type	Temperature Range (°C)	NO _x Conversion (%) / CO Conversion (%)	VOC Conversion (%)	Stability Feature	References
CeO ₂ /TiO ₂ (Ce/Ti mixed SCR)	~30% CeO ₂	NH ₃ -SCR	200–400	~90–95	—	High thermal & hydrothermal stability	Zhang et al. (report of >90% NO _x conversion at 200–400 °C with CeO ₂ /TiO ₂ -based SCR catalysts) [18]
Cu-CeO ₂	~20% CeO ₂	NO + CO (SCR/NO + CO)	150–300	~95	—	Improved SO ₂ resistance	Mosrati (95% NO _x conversion at ~200 °C with Cu-modified CeO ₂ catalyst) [19]
Fe-CeO ₂	~25% CeO ₂	NH ₃ -SCR	250–450	~90+	—	Improved water/steam tolerance (redox enhancement)	Recent iron-ceria SCR catalysts showing improved redox and surface activity (higher reactive oxygen) [20–22]
Cu-ZnO	~10% Cu, ~5% ZnO	CO Oxidation	250–400	—	~85 (CO)	Lower thermal stability vs. Pt	Cu/ZnO catalysts with ~85% CO conversion at ~450 °C were reported in the literature [21–23]
Pt/CeO ₂	~20% CeO ₂	CO Oxidation	150–300	—	~92 (CO)	Expensive, sensitive to water vapor	Pt/CeO ₂ catalysts with high low-T CO oxidation activity, but stability concerns noted [24–27]

3. Complexity of Industrial Waste Gases and Catalyst Deactivation Risks

Unlike idealized laboratory feed compositions, real industrial waste gases exhibit highly complex and variable chemical environments. In addition to primary pollutants such as NO_x, CO, VOCs, and SO₂, industrial exhaust streams often contain excess oxygen, high concentrations of water vapor, chlorine-containing species, alkali metals, particulate matter, and trace heavy metals. These co-existing components frequently interact with catalysts in unintended ways, inducing rapid or gradual deactivation. Catalyst deactivation mechanisms can be broadly categorized into: (i) sulfur poisoning, involving sulfate forma-

tion on active sites; (ii) hydrothermal degradation, leading to sintering and oxygen-vacancy annihilation; (iii) halogen poisoning, particularly by HCl and chlorinated VOCs; (iv) alkali metal neutralization of surface acidity; and (v) carbon deposition, which blocks active sites and restricts mass transfer. Importantly, catalysts optimized for a single pollutant often experience severe performance degradation when exposed to multicomponent gas mixtures. Therefore, understanding the interaction between rare-earth catalytic materials and complex industrial exhaust compositions is essential for developing catalysts with genuine industrial durability. Table 2 summarizes representative industrial emission characteristics and the corresponding catalyst design requirements.

Table 2. Representative industrial emission characteristics and corresponding catalyst design requirements.

Industry Sector	Typical Gas Composition	Major Deactivation Risks	Catalyst Design Requirements
Steel sintering	NO _x , SO ₂ , CO, dust	Sulfation, fouling	High sulfur tolerance, abrasion resistance
Petrochemical plants	VOCs, H ₂ O, Cl-species	Chlorine poisoning, coking	Strong metal–oxygen bonding, anti-coking
Waste incineration	VOCs, HCl, SO ₂ , alkali metals	Alkali neutralization, Cl poisoning	Acidic surfaces, sacrificial RE phases
Coal-fired power plants	NO _x , SO ₂ , H ₂ O	Sulfation, hydrothermal sintering	Reversible sulfation, thermal robustness

4. Rare-Earth Catalysts for NO_x Removal

Nitrogen oxides (NO_x) and NO₂ are major air pollutants from industrial emissions, contributing significantly to acid rain and photochemical smog. RE catalysts exhibit exceptional performance in NO_x removal, particularly in Selective Catalytic Reduction (SCR) with NH₃ and the reduction of NO using CO or hydrocarbons [20–23]. Their superior performance is attributed to distinct redox properties, high oxygen vacancy concentration, and intense interaction with transition metals.

Cerium-based catalysts are the most explored for NO_x control. The facile reversible redox cycle between Ce⁴⁺ and Ce³⁺ promotes the oxidation of NO to NO₂, which facilitates the fast-SCR pathway at lower temperatures. Furthermore, RE dopants like La and Pr can increase surface acidity and stabilize active metal sites, thereby enhancing NH₃ adsorption and activation, properties essential for high catalytic efficiency in the presence of industrial oxygen [24–28].

Table 3 summarizes the performance of RE-modified catalysts compared to conventional systems, often showing an edge in the following aspects: NO₁ to NO₈ conversion, thermal stability, and sulfur resistance. For example, Cu–CeO₂ and Fe–CeO₂ systems have demonstrated NO conversions exceeding 90% over broad temperature ranges, with enhanced tolerance to SO₂ and H₂O [5–9]. The RE oxides also actively inhibit the sintering of active metals, a frequent cause of catalyst deactivation during long-term operation.

Cerium-based catalysts exhibit excellent performance for NO_x removal, especially in selective catalytic reduction (SCR) reactions. Their superior redox properties, facilitated by the Ce⁴⁺/Ce³⁺ redox cycle, enhance NO oxidation and reduction under low-temperature conditions. Studies have shown that cerium-doped catalysts, such as Cu–CeO₂ and Fe–CeO₂, maintain high efficiency in NO_x conversion, even in the presence of industrial poisons like SO₂ and H₂O. These catalysts are particularly valuable in applications such as automotive exhaust treatment, where their ability to withstand water vapor and sulfur contamination is crucial for long-term operation.

Table 3. Rare-earth-based catalysts for NO text removal in industrial waste-gas purification.

Catalyst System	Reaction Type	Temperature Range (°C)	NO _x Conversion (%)	Key Function of Rare Earth	Stability Feature	References
CeO ₂ –TiO ₂	NH ₃ -SCR	200–400	90–95	Oxygen storage, NO oxidation	High thermal stability	[4–7]
Cu–CeO ₂	NO + CO	150–300	95	Redox synergy	SO ₂ resistance	[20–23]
Fe–CeO ₂	NH ₃ -SCR	250–450	92	Enhanced acidity	Water tolerance	[6–11]
Mn–CeO ₂	NH ₃ -SCR	120–250	>90	Low-temperature activity	Anti-sintering	[25–30]
La-V ₂ O ₅ /TiO ₂	NH ₃ -SCR	300–450	88	Structural stabilization	Long-term durability	[23–27]

Oxygen vacancies and lattice oxygen mobility play a central role in Ce-based catalytic NO_x conversions. Mechanistic investigations consistently demonstrate that oxygen vacancies and lattice oxygen mobility play a central role in rare-earth-based NO_x conversion pathways. In Pt/CeO₂ systems, NO oxidation follows a vacancy-mediated mechanism in which lattice oxygen directly participates in NO activation, accompanied by continuous formation and replenishment of oxygen vacancies through the Ce⁴⁺/Ce³⁺ recyclable [20]. Similarly, in Co–CeO_x catalysts, oxygen vacancies serve as preferential adsorption and activation sites that govern the CO-assisted selective catalytic reduction (CO-SCR) of NO_x under oxygen-rich conditions, facilitating efficient electron transfer and intermediate transformation [21]. For Cu-modified CeO₂/TiO₂ catalysts, the synergistic interaction between Cu species and inheritances surface acidity and stabilizes retroactive Ce³⁺ sites, enabling vacancy-driven NO_x adsorption and accelerated SCR reaction pathways [22]. Collectively, these studies highlight that defect engineering and the synergy between rare-earth and transition metals are decisive factors in optimizing NO_x abatement performance across diverse catalytic systems [22]. This vacancy-mediated process is schematically summarized in Figure 1. Despite their excellent intrinsic activity, rare-earth-based NO_x catalysts are vulnerable to deactivation under industrial conditions. Sulfur dioxide readily reacts with surface Ce³⁺ species to form thermodynamic stable cerium sulfates, which suppress oxygen-vacancy regeneration and inhibit the Ce⁴⁺/Ce³⁺ redox cycle essential for NO oxidation. Additionally, prolonged exposure to high water vapor concentrations accelerates hydrothermal sintering, leading to the collapse of surface defect structures. Rare-earth modification provides effective mitigation pathways. La and Pr dopants dilute highly reactive Ce sites and reduce sulfate binding strength, while Ce–Zr solid solutions promote reversible sulfation behavior. These features enable partial recovery of catalytic activity during regeneration and significantly extend catalyst lifetime in sulfur-rich flue gases.

Mechanistic studies indicate that oxygen vacancies and lattice oxygen mobility are central to Ce-based catalytic NO conversion [23–28]. The strong metal–support interactions between RE oxides and transition metals facilitate electron transfer, accelerating the rate of redox cycles. Rational defect engineering and compositional tuning of RE catalysts are promising strategies for developing next-generation NO-abatement technologies [25–29].

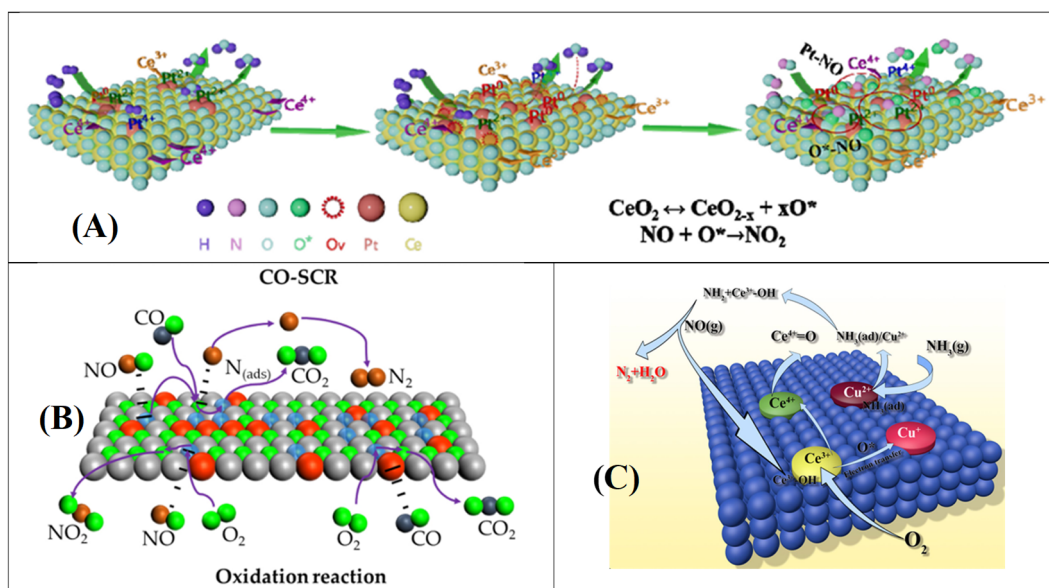


Figure 1. Oxygen-vacancy-driven NO_x conversion mechanisms over Ce-based catalysts: these figures are previous published from (A) [20], (B) [21], and (C) [22].

5. Rare-Earth Catalysts for Carbon Monoxide Oxidation

Carbon monoxide CO is a hazardous product of incomplete combustion in many industrial processes. The catalytic oxidation of CO to CO_2 is a critical air purification reaction, where RE catalytic materials have demonstrated exceptional efficacy [30–33]. The primary mechanisms for CO oxidation on RE oxides involve the rapid activation of oxygen and high oxygen turnover at the catalyst surface.

Cerium oxide-based catalysts are widely used due to their powerful OSC, mediated by the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple. The reaction often proceeds via the Mars–van Krevelen (MvK) mechanism, where lattice oxygen directly participates in CO oxidation to CO_2 , creating an oxygen vacancy [29–34]. This vacancy is then quickly refilled by gaseous oxygen, maintaining a continuous catalytic cycle.

In composite ceria-based systems, catalytic CO oxidation is governed by an interfacial oxygen-transfer mechanism involving dynamic redox coupling between adjacent phases. At the $\text{CeO}_2\text{--La}_2\text{O}_2\text{SO}_4$ interface, lattice oxygen from ceria directly participates in CO oxidation to CO_2 , resulting in the formation of oxygen vacancies. These vacancies are rapidly replenished through interfacial oxygen migration from the neighboring oxygen-storage phase, thereby sustaining continuous redox cycling and maintaining high oxidation efficiency under reaction conditions [31]. This oxygen-gateway effect highlights the significance of engineered phase boundaries in promoting oxygen mobility and enhancing catalytic activity (Figure 2).

Table 4 highlights that RE-promoted catalysts achieve significantly lower CO light-off temperatures (T_{50} , the temperature at which 50% conversion occurs) and exhibit superior long-term stability compared to traditional metal oxide catalysts. While noble metal systems, such as Au/CeO_2 and Pt/CeO_2 , offer excellent low-temperature activity, non-noble options, such as CuO-CeO_2 , provide a competitive, lower-cost alternative [32–36]. The strong metal–support interactions (SMSI) between RE oxides and supported metals modify electronic properties, which enhance the adsorption of reactants. This not only boosts catalytic activity but also increases resistance to deactivation by moisture and sulfur—standard components in industrial exhaust streams [13–16].

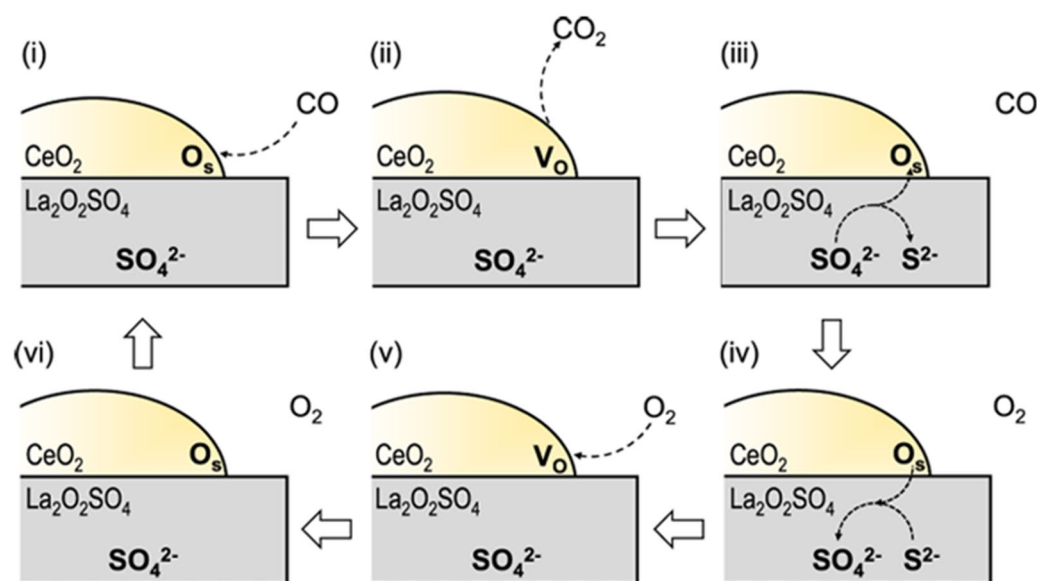


Figure 2. Schematic for (i–iii) oxygen release and (iv–vi) oxygen storage mechanisms at the gas/CeO₂/La₂O₂SO₄ three-phase boundary. Pt is present on the entire solid surface [31].

Table 4. Performance of rare-earth-based catalysts for CO oxidation.

Catalyst	Support/Composition	T ₅₀ (°C)	T ₉₀ (°C)	Dominant Mechanism	Stability Advantage	References
Au/CeO ₂	—	40	80	Lattice oxygen	Excellent moisture resistance	[21–24]
Pt/CeO ₂	Al ₂ O ₃	90	140	SMSI-enhanced oxidation	Thermal stability	[33–36]
CuO–CeO ₂	Mixed oxide	120	180	Mars–van Krevelen	Low cost, high durability	[10–13]
La-doped CeO ₂	Solid solution	110	170	Vacancy-promoted	Anti-sintering	[14–19]

In industrial exhaust streams, CO oxidation catalysts are frequently exposed to sulfur compounds and moisture, both of which compete with CO for active oxygen sites. Sulfur adsorption can inhibit lattice oxygen mobility, while water vapor may block metal–support inter-facial sites critical for the Mars–van Krevelen mechanism. Rare-earth oxides mitigate these effects by stabilizing surface oxygen species and preferentially adsorbing sulfur away from active metal centers, thereby preserving redox functionality under harsh conditions.

6. Rare-Earth Catalysts in the Oxidation of VOCs

Volatile Organic Compounds (VOCs) are precursors to atmospheric ozone and secondary organic aerosols. Catalytic oxidation is the most efficient technique for VOC removal, and RE-based catalysts are extensively investigated due to their superior oxidation capabilities [33–37]. RE oxides enhance VOC oxidation by promoting oxygen mobility, increasing surface acidity, and improving the adsorption of organic molecules.

CeO₂-based catalysts are highly active against various VOCs, including toluene, benzene, and formaldehyde. The presence of oxygen vacancies facilitates the effective activation of CH and C–C bonds, leading to complete oxidation at relatively low temperatures. When combined with transition metal oxides (e.g., Mn, Co, Cu), RE oxides form highly active mixed-oxide systems with synergistic redox cycles [32–37]. Surface-sensitive spectroscopic studies reveal that rare-earth oxides actively participate in the oxidation of poly-cyclic aromatic hydrocarbons through dynamic redox processes. In Gd₂O₃-based

systems, XPS analyses indicate a pronounced surface chemical evolution during hydrocarbon oxidation, which evidences the direct involvement of lattice oxygen and surface hydroxide species in bond activation and oxidative decomposition pathways [38], as illustrated in Figure 3. These findings confirm that rare-earth oxide surfaces are not merely inert supports but function as redox-active participants capable of sustaining hydrocarbon activation under oxidative environments.

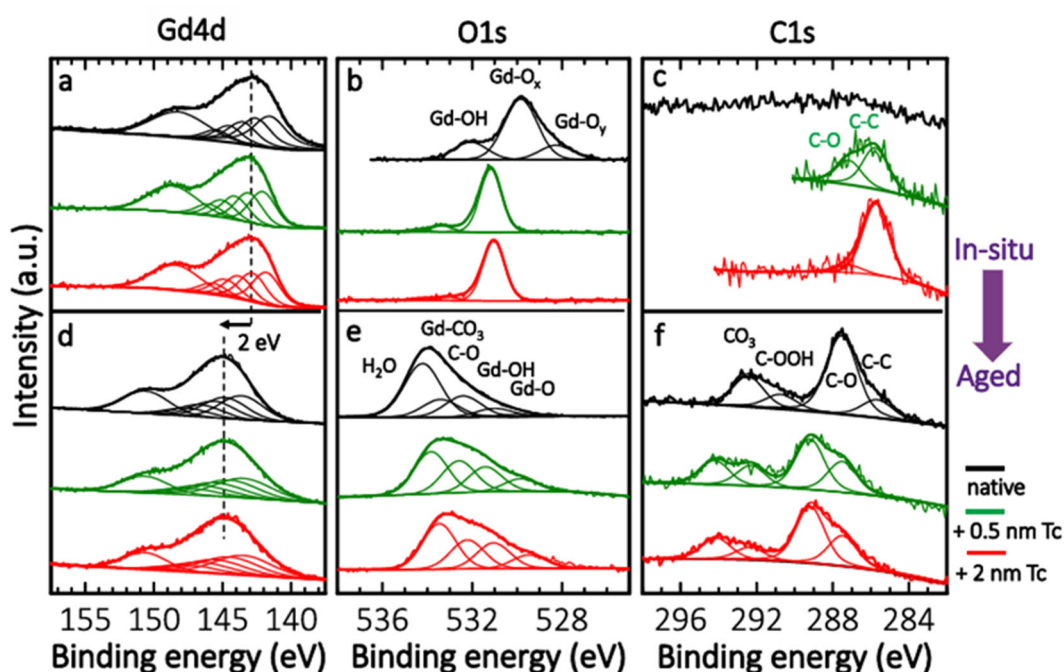


Figure 3. Reactivity of Gd oxide towards Tc and progressive modification of the surface chemical composition in air: XPS analysis [38].

Table 5 details current RE-based catalysts for VOC oxidation, highlighting the target VOCs and the thermal efficiency (T_{90} , the temperature at which 90% conversion is achieved). The data confirms that RE modification lowers the temperature required for complete oxidation and improves catalyst stability under high space velocity conditions [39–42]. Crucially, RE oxides enhance resistance to chlorine and sulfur poisoning, which is vital for treating industrial exhaust streams containing halogenated VOCs [40,43–45]. Mechanistic studies demonstrate that RE elements stabilize surface oxygen species and facilitate rapid electron transfer during VOC oxidation, thereby ensuring an uninterrupted supply of reactive oxygen and promoting the efficient decomposition of complex organics [42–44].

Table 5. Rare-earth-based catalysts for catalytic oxidation of VOCs.

Catalyst	Target VOC	T_{90} (°C)	Rare-Earth Role	Resistance Feature	References
Mn–CeO ₂	Toluene	250	Oxygen vacancy generation	Chlorine tolerance	[39–42]
Co–CeO ₂	Benzene	270	Redox enhancement	Thermal stability	[33–36]
Cu–CeO ₂	Formaldehyde	120	Low-T activation	Moisture resistance	[23–27]
La–CeO ₂	Ethanol	230	Structural stabilization	Anti-coking	[40,43–45]

Industrial VOC streams often contain chlorine-bearing compounds and aromatics that induce catalyst poisoning and carbon deposition. Chlorine species can irreversibly block active sites, while polyaromatic intermediates promote coke formation. Rare-earth oxides

enhance resistance to these effects by stabilizing surface oxygen vacancies, facilitating complete oxidation pathways, and suppressing carbon accumulation through enhanced oxygen mobility.

7. Surface Defects and Compositional Tuning

While surface defects and compositional tuning are often cited as promising strategies for optimizing catalytic activity, their practical implementation is still limited. Recent studies on defect engineering have highlighted the role of oxygen vacancies and lattice oxygen mobility in cerium-based catalysts. However, these processes are challenging to characterize and manipulate effectively due to the complexity of catalyst surfaces and the lack of non-invasive characterization methods that can directly probe surface defects without affecting them [15–20]. As such, while the potential for defect engineering exists, current methodologies are limited by the need for more advanced tools and techniques. Consequently, “compositional tuning” refers to the careful selection and combination of rare-earth elements and transition metals to achieve a balance between activity, stability, and resistance to deactivation under industrial conditions.

8. Sulfur-Containing Gas Removal and Poisoning Resistance

Sulfur-containing gases, particularly SO_2 , are among the most problematic components of industrial waste gases due to their corrosiveness and high potential for catalyst poisoning. In stationary catalytic systems, SO_2 readily adsorbs onto active sites, forming stable sulfates that lead to irreversible deactivation [46–48]. RE catalytic materials, however, have demonstrated superior resistance to sulfur poisoning and enhanced regeneration capacity, making them highly attractive for industrial waste-gas purification [49–51].

RE oxides (CeO_2 , La_2O_3 , etc.) possess a high affinity for sulfur-based species. This allows sulfur adsorption to occur preferentially on the RE phase rather than on the transition metals that constitute the main active sites. This sacrificial adsorption helps maintain catalytic activity. Furthermore, some RE sulfates are less thermally stable than their counterparts and can decompose under regeneration conditions, restoring catalyst activity [50–52]. As shown in Table 6, RE-modified catalysts exhibit markedly greater sulfur tolerance than traditional catalysts. The CeO_2 - ZrO_2 solid solution, for example, shows superior reversible sulfation behavior, and La-doped SCR catalysts maintain greater structural stability in the presence of SO_2 and H_2O . These characteristics are vital for long-duration operation in demanding environments such as coal-fired power plants and smelting facilities [40,43–45]. Figure 4 presents in situ IR/DRIFTS evidence showing that SO_2 adsorption on CeO_2 is highly dependent on surface structure, leading to the morphology-specific formation of sulfite and sulfate species. These findings provide direct support for the proposed adsorption–transformation mechanisms and help explain the enhanced sulfur tolerance observed in engineered ceria surfaces within catalytic systems [53].

Table 6. Sulfur resistance of rare-earth-based catalytic materials.

Catalyst System	Sulfur Source	Reaction Environment	Activity Retention (%)	Rare-Earth Function	Regenerability	References
CeO_2 - ZrO_2	SO_2	NH_3 -SCR	>85	Reversible sulfation	High	[11–13]
La-doped $\text{V}_2\text{O}_5/\text{TiO}_2$	$\text{SO}_2 + \text{H}_2\text{O}$	NH_3 -SCR	~80	Structural stabilization	Moderate	[24–27]
Fe- CeO_2	SO_2	NO reduction	>82	Sulfur trapping	High	[40,42–44]
Cu- CeO_2	SO_2	CO oxidation	>88	Active site protection	High	[48–50]

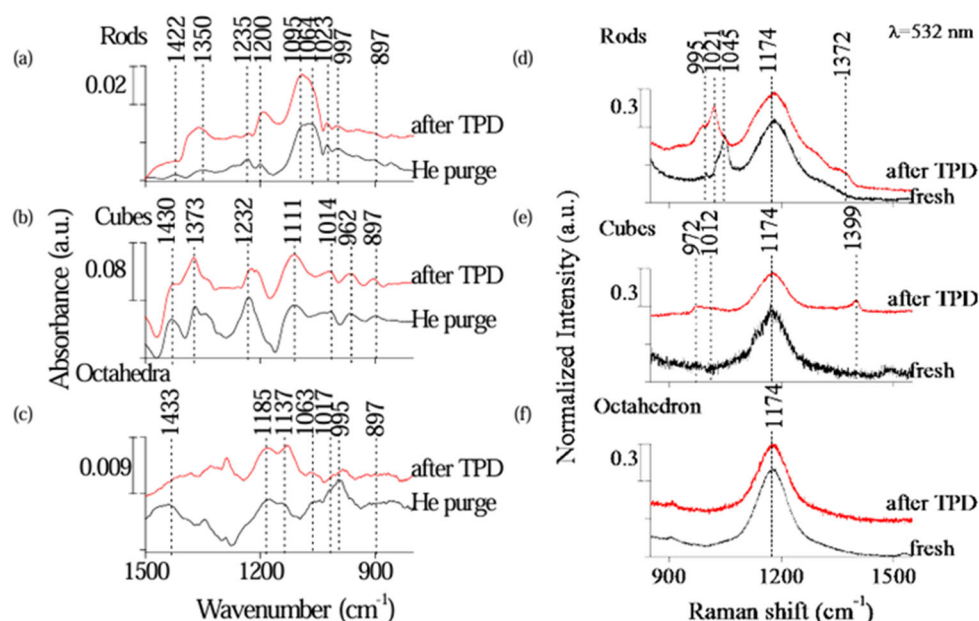


Figure 4. IR spectra of oxidized CeO₂ (a) rods, (b) cubes, (c) octahedra obtained after He purge ($T = 25\text{ }^{\circ}\text{C}$) and after TPD to $400\text{ }^{\circ}\text{C}$ ($T = 25\text{ }^{\circ}\text{C}$). Corresponding Raman spectra of fresh and after TPD for oxidized CeO₂ (d) rods, (e) cubes and (f) octahedra [53].

Mechanistic studies suggest that RE oxides modify the sulfur adsorption energetic, minimizing the formation of firmly bound metal sulfates. Additionally, vacancies of oxygen in Ce-based systems allow the oxidation of SO₂ to surface sulfate radicals, which are easier to decompose [22–26]. These findings highlight the importance of rationality in selecting rare-earth elements and architecture in catalysts to minimize deactivation caused by sulfur. Generally, rare-earth catalytic materials can be considered a strong option for utilizing sulfur-containing waste gas as an alternative method of purifying the waste gas, offering high catalytic activity and a long working life [33–37,54].

9. Reaction Mechanisms and Structure–Activity Relationships

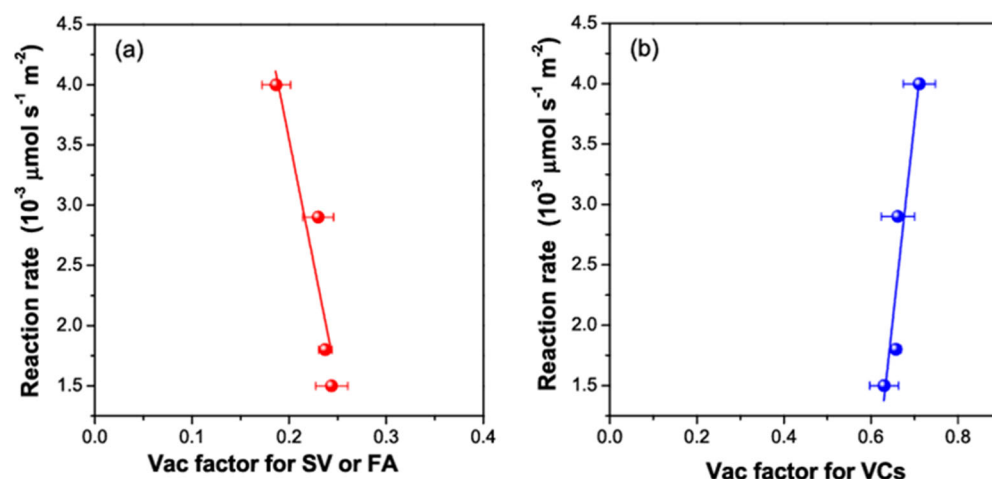
The rational design of high-performance RE catalytic materials hinges on a clear understanding of structure–activity relationships [52,55–57]. The catalytic performance of RE-based systems is determined by key structural parameters, including crystal phase, oxygen vacancy concentration, surface acidity, and the strength of metal–support interaction (MSI).

The facile Ce⁴⁺/Ce³⁺ redox transition enables RE oxides, particularly CeO₂, to maintain a high concentration of oxygen vacancies. These defects serve as active sites for oxygen activation and the adsorption of pollutants [56–59]. The incorporation of transition metals further modifies the electronic structure, enhancing charge transfer processes and lowering the activation barriers for oxidation and reduction reactions.

As summarized in Table 7, catalysts that exhibit superior oxygen mobility and stronger metal–support interactions consistently demonstrate excellent catalytic activity in NO_x reduction, CO oxidation, and VOC degradation. Dopants like La and Pr are used to enhance lattice stability and surface acidity, while Zr incorporation improves thermal resistance and oxygen diffusion. As demonstrated in Figure 5, the formation and surface distribution of oxygen-vacancy clusters on CeO₂ nanocubes directly influence catalytic performance, exhibiting a pronounced linear correlation between the vacancy-cluster factor and the *o*-xylene oxidation rate [57].

Table 7. Structure–activity relationships in rare-earth-based purification catalysts.

Structural Feature	Influenced Property	Affected Reaction	Performance Outcome	Representative Catalyst	References
Oxygen vacancies	Oxygen activation	CO oxidation	Lower light-off temp	CeO ₂	[40,44,45,53]
Metal–support interaction	Electron transfer	NO ₃ reduction	Enhanced conversion	Cu–CeO ₂	[23–25]
Surface acidity	NH adsorption	NH ₃ -SCR	Broader temp window	La–V ₂ O ₅ /TiO ₂	[12–16]
Lattice stability	Thermal resistance	VOC oxidation	Improved durability	Ce–ZrO ₂	[32–35]

**Figure 5.** (a) The relationship between the Vac factor for single oxygen vacancies (SV) or free annihilation of positrons (FA) and reaction rate of o-xylene, and (b) the relationship between the Vac factor for oxygen vacancy clusters (VCs) and reaction rate of o-xylene over ceria nanocubes calcined at different temperatures [57].

Reaction mechanisms over RE catalysts frequently involve Marsvanckel pathways for oxidation reactions and redox-assisted adsorption–desorption cycles for reduction reactions. In SCR systems, RE oxides co-facilitate the adsorption of NH₃ and NO_x, with oxygen vacancies accelerating the transformation of intermediates [58–61]. Spectroscopic analysis confirms that RE elements modulate intermediate stability, minimizing undesirable side reactions. Knowledge of these relationships enables the selective optimization of catalysts through defect engineering, compositional control, and control of nano-structure. Such techniques have become increasingly significant in creating catalysts that can operate effectively in the face of industrial variability [62–65].

10. Catalyst Deactivation Mechanisms

Catalytic degradation remains a major challenge in the industrial application of rare-earth catalysts. Common deactivation mechanisms include:

Sulfur Poisoning: SO₂ reacts with cerium oxide (CeO₂) to form thermodynamically stable cerium sulfates. This inhibits the redox cycles of Ce⁴⁺/Ce³⁺, reducing the catalyst's oxygen storage capacity and overall performance. The formation of sulfate species can also block active sites, causing irreversible deactivation.

Hydrothermal Degradation: Prolonged exposure to water vapor leads to the sintering of CeO₂ particles, which reduces the surface area and oxygen vacancy concentration. The thermal stability of the catalyst is compromised, leading to diminished catalytic activity.

Coking: In VOC oxidation reactions, carbon deposition can occur, especially in the presence of aromatic compounds. The carbonaceous deposits block active sites and hinder

mass transfer, decreasing the catalyst's efficiency. However, rare-earth catalysts are often more resistant to coking compared to traditional catalysts due to their ability to stabilize oxygen vacancies and enhance surface mobility.

11. Challenges and Future Development Directions

Despite promising laboratory and pilot-scale results, several challenges must be addressed for the widespread industrial implementation of RE catalytic materials [40,43–45,53]. A primary concern is the potential supply shortage and escalating cost of certain RE elements, particularly Ce and La, which could restrict large-scale adoption. Catalyst deactivation remains a critical industrial issue; the complex composition of industrial waste gases (including SO₂, H₂O, particulates, and hydrogenated compounds) can gradually diminish catalyst activity over extended periods, even with RE modification [64–67]. Furthermore, maintaining consistent catalyst quality during large-scale synthesis is non-trivial and requires rigorous control over structure and composition.

Table 8 summarizes key industrial challenges and outlines active research strategies to mitigate these limitations. Future research should focus on “low loading” designs through enhanced RE dispersion, the exploration of mixed RE systems, and the investigation of viable non-critical RE substitutes. Advanced preparation techniques, such as atomic-layer deposition and scalable sol–gel synthesis, can offer paths toward enhanced catalyst uniformity [65–69]. Future catalyst development must prioritize long-term durability tests under realistic industrial conditions, life cycle assessment, and economic viability. The integration of computational modeling and machine learning is poised to accelerate the discovery of optimized RE catalysts while minimizing material usage. Future development of rare-earth catalytic materials must shift from activity-centered optimization toward durability-by-design strategies. One critical research frontier involves coupling oxygen-vacancy engineering with poison adsorption energetic to selectively trap deactivating species without compromising redox functionality. Multi-rare-earth solid solutions, such as Ce–La–Pr–Zr systems, offer promising routes to simultaneously enhance sulfur resistance, hydrothermal stability, and oxygen mobility. Another emerging direction is the integration of data-driven approaches. Machine learning models trained on structural descriptors, defect densities, and aging datasets can accelerate the discovery of robust catalyst formulations tailored for complex gas environments. In parallel, standardized industrial aging protocols incorporating sulfur, water vapor, chlorine, and thermal cycling must be adopted to bridge the gap between laboratory performance and field durability. Ultimately, the commercial success of rare-earth catalysts will depend not on peak activity but on sustained performance under realistic operating conditions over extended service lifetimes.

Table 8. Challenges and future strategies for rare-earth catalytic materials.

Challenge	Impact on Industry	Proposed Solution	Research Status	References
High rare-earth cost	Increased catalyst price	Low-loading design	Active	[52,55–58]
Sulfur poisoning	Activity loss	Advanced dopants	Demonstrated	[59–65]
Scale-up issues	Performance deviation	Controlled synthesis	Emerging	[34–37,54]
Long-term stability	Short catalyst lifetime	Regeneration strategies	Developing	[4–8]

12. Conclusions

Rare-earth catalytic materials represent one of the most significant developments in industrial waste-gas purification technology. Their unique electronic properties, potent redox activity, high oxygen transport capability, and excellent thermal stability enable superior performance across a wide range of pollution abatement reactions, including NO_x elimination, CO oxidation, VOC degradation, and the removal of sulfur-containing gases.

This systematic review has demonstrated that RE elements function not only as active phases but also as critical promoters and structural stabilizers. Comparative data consistently show that RE-modified catalysts surpass conventional systems in terms of activity, selectivity, and durability, often exhibiting enhanced conversion efficiency, a broader operating temperature window, and improved resistance to sulfur and water poisoning.

Despite these clear advantages, persistent challenges related to RE material cost, resource availability, and long-term industrial durability must be overcome. Addressing these issues will require interdisciplinary approaches spanning catalyst engineering, materials science, and process optimization. The most promising future directions involve minimizing RE usage through better dispersion, designing novel mixed RE oxides, and implementing advanced, scalable synthesis techniques.

In summary, RE catalytic materials are pivotal to the future of industrial air pollution control. Continued research, focused on deepening mechanistic understanding and developing scalable design principles, will accelerate the transition of these high-performance materials from the laboratory to widespread industrial applications. By explicitly addressing catalyst deactivation mechanisms and the complexity of industry-specific emissions, this review provides practical guidance for translating rare-earth catalytic materials from laboratory research to industrial implementation. The insights summarized herein aim to support the rational design of next-generation catalysts capable of long-term operation in real waste-gas environments.

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