

Regenerative Oxidation Technology for VOC Treatment: A Review

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Abstract

Regenerative combustion represents an efficient and energy-saving combustion technology that significantly enhances thermal efficiency, reduces energy consumption, and minimizes pollutant emissions by recovering and reusing heat energy. This technology has found extensive applications in traditional industries, such as chemical engineering, coating, and printing, as well as in contemporary fields, including food processing and pharmaceuticals. In recent years, advancements in the optimization of combustion devices and the development of efficient catalysts have successfully reduced the combustion temperature for treating organic waste gases while simultaneously improving pollutant removal efficiency. This paper reviews the current status of regenerative combustion technology, summarizes key achievements, analyzes the challenges faced in industrial applications, and anticipates future research directions.

Keywords: regenerative combustion; combustion technology; environmental protection; catalytic combustion; volatile organic compounds



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1. Introduction

1.1. The Environmental and Human Health Impacts of VOC Emissions

Volatile organic compounds (VOCs) are a significant component of atmospheric pollution [1], as illustrated in Figure 1. With the rapid advancement of industrial activities, substantial amounts of VOCs are released into the atmosphere. Under sunlight, VOCs undergo photochemical reactions with nitrogen oxides (NO_x), resulting in the formation of ozone [2]. Ozone poses considerable risks to both plant life and human health [3]. Elevated concentrations of ozone not only inhibit plant growth and diminish crop yields but also inflict severe damage on forest ecosystems. Furthermore, VOCs contribute to the formation of secondary organic aerosols (SOAs) through chemical reactions, which serve as key precursors to PM_{2.5} [4,5]. When VOCs and their oxidation products deposit onto soil and water bodies, they disrupt the structure of soil microbial communities and disturb the balance of aquatic ecosystems, thereby threatening ecosystem stability and biodiversity [6]. Consequently, enhancing the management of VOC emissions has emerged as a critical priority in contemporary air pollution control initiatives [7].

Exposure to VOCs is closely associated with various health issues [8], particularly concerning lung health. Inhaling high concentrations of VOCs can trigger acute respiratory symptoms, contribute to chronic respiratory diseases, decrease lung function, and even elevate the risk of lung cancer [9,10]. Yoon et al. [11] found that long-term exposure to toluene and xylene increases oxidative stress, which subsequently damages lung function.

Additionally, Armenta-Reséndiz et al. [12] conducted experimental studies demonstrating that VOCs impact the neurobehavioral patterns of rats. A variety of VOCs exist, with the most common types listed in Table 1.

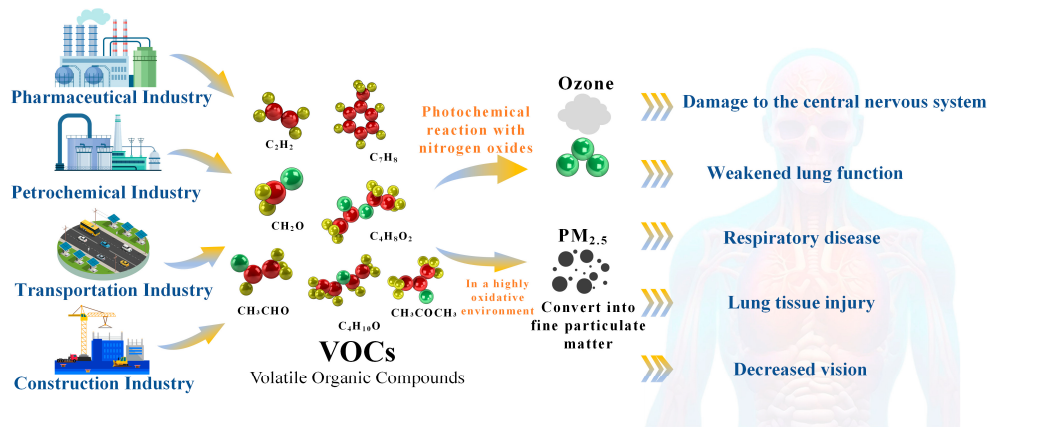


Figure 1. Sources and hazards of VOCs.

Table 1. Common VOC pollutant classifications [13–15].

Types of VOCs	Main Representative Objects
Hydrocarbons	Toluene, N-hexane, benzene, xylene, cyclohexane, etc.
Aldehydes and ketones	Formaldehyde, acetaldehyde, acetone, cyclohexanone, etc.
Ethers	Methyl ether, ethyl ether, dimethyl ether, benzyl ether, benzyl ether, epoxyethane, etc.
Esters	Ethyl acetate, butyl acetate, methyl acetate, ethyl formate, etc.
Cyanide	Hydrogen cyanide, acrylonitrile, acetonitrile, sodium cyanide, potassium cyanide, benzonitrile, etc.
Amide	Dimethylformamide, diethylformamide, methylacetamide, formamide, etc.
Halogenated hydrocarbon	Chloroethylene, dichloromethane, trichloroethylene, bromomethane, freon, etc.

VOCs are primarily generated in industrial sectors such as chemical manufacturing, coating, printing, and pharmaceutical production. The typical components of VOCs include benzene, toluene, ethyl acetate, and formaldehyde. During industrial production processes, VOC emissions are characterized by several features: large exhaust flow rates, typically exceeding 5000 cubic meters per hour, complex gas compositions, and significant fluctuations in pollutant concentrations. Therefore, to achieve the effective control of and reduction in industrial VOC emissions, it is essential to employ treatment technologies that can simultaneously address multiple challenges, including high flow rates, complex components, and variations in concentration.

1.2. VOC Treatment Technologies

Currently, VOC treatment technologies are primarily categorized into two main types: separation and recovery, and decomposition and conversion. Separation and recovery technologies mainly encompass absorption [16], adsorption [14,17], condensation [18], and membrane separation. The absorption method employs solvents to transfer VOCs from the gas phase to the liquid phase, achieving a treatment efficiency of 80% to 90%. However, it necessitates specific absorption liquids for different VOCs [19], which leads to high costs and the potential for secondary pollution. The adsorption method utilizes porous materials, such as carbon-based [20] and oxygen-containing materials, to capture VOC molecules [21]; however, it is challenged by pore blockage. The condensation method separates VOCs by lowering the temperature or increasing the pressure to induce condensation. Meanwhile,

the membrane separation method isolates VOCs from inert gases based on differences in their permeation rates through a polymer membrane, achieving an efficiency exceeding 90%. Nonetheless, this method incurs high equipment and operational costs [22,23].

Decomposition and conversion technologies mainly include a regenerative catalytic oxidizer (RCO) [24,25], regenerative thermal oxidation (RTO) [26,27], photocatalytic oxidation [28], and biodegradation [29]. The catalytic combustion method is suitable for low and medium concentrations of VOCs, with a treatment efficiency of 95–98%, but there are three main problems: First, it requires the use of precious metals (e.g., platinum and palladium) or transition metal oxides as catalysts, resulting in high initial investment and operation and maintenance costs. Second, the catalyst is easily inactivated by the poisoning of sulfur, halogens, and other impurities, not only to reduce the efficiency of the treatment but also to require frequent replacement or regeneration, which increases the operating costs, and the requirements for the feed components are strict; third, the treatment of catalyst deactivation may produce solid waste pollution, and some VOCs may also form harmful intermediate products during the catalytic process, with strict requirements on feed components. Third, the catalyst deactivation treatment may produce solid waste pollution, and some VOCs in the catalytic process may also form harmful intermediate products. In contrast, with the regenerative thermal oxidation method, although the initial equipment investment is larger, without the catalyst, there is no poisoning problem, the RTO system can directly oxidize the VOCs to CO₂ and H₂O at high temperatures, and the decomposition efficiency is more than 99%; while 95% of the heat recovery can significantly reduce the operation of the energy consumption [30], there is no catalyst waste generated, the risk of secondary pollution is low, and the RTO maintains a higher temperature environment. The RTO requires a large amount of fuel supplementation due to the maintenance of a high-temperature environment, and its operating costs are relatively high. Photocatalytic oxidation uses photocatalysts (such as TiO₂) to generate electron–hole pairs under light, which produce highly oxidative hydroxyl radicals and superoxide anions, oxidizing VOCs into CO₂ and H₂O. This technology offers advantages, such as high chemical stability and non-toxicity, but it has high operational costs [31,32]. Biodegradation has a treatment efficiency of 60–90% and is suitable for low-concentration VOCs. However, it is highly affected by environmental conditions such as temperature, humidity, and pH [33]. The characteristics of commonly used VOC treatment methods are summarized in Table 2 below.

Table 2. Common technologies for treating VOCs.

Processing Technology	Processing Methods	Specificities
Separation and recycling technology	Absorption method	Simple equipment, easy to operate, low cost, but low processing efficiency, poor effect on non-polar or insoluble in water exhaust gas [19].
	Adsorption method	High processing efficiency, large equipment volume, no secondary pollution, low cost, easy to clog, and humidity and temperature affect the treatment effect [17].
	Condensing method	Simple process, easy to operate, high energy consumption, large operating costs, high treatment costs [34].
	Membrane separation method	Simple process, high processing efficiency, low energy consumption, no secondary pollution, high cost of membrane material [22], more suitable for high-concentration gas treatment.

Table 2. *Cont.*

Processing Technology	Processing Methods	Specificities
Decomposition and conversion technologies	RCO method	Low energy consumption, high purification efficiency, no secondary pollution, expensive catalyst cost, with a need to be replaced regularly [35].
	RTO method	Large initial investment, large footprint, high removal rate, applicable to various types and concentrations of VOCs [36].
	Photocatalytic method	Photocatalytic device equipment investment is small, simple structure, easy operation and maintenance, high requirements for light source and catalyst, no secondary pollution [37].
	Biodegradation method	Slow reaction speed, large floor space, processing efficiency greatly affected by environmental conditions, low operating costs [38].

RTO technology has been extensively implemented in the field of VOC control [39], owing to its superior performance in treating atmospheric constituents, combined with notable advantages, including low production costs, the ease of installation, and operational reliability. However, the RTO needs to operate at high temperatures above 780 °C, resulting in high fuel consumption and high energy costs. To solve this problem, the regenerative catalytic oxidation (RCO) technology was developed by combining the RTO with catalytic oxidation technology. Matros et al. [40] have shown that RCO systems have multiple advantages over RTO systems: in terms of economics, they can reduce operating costs by about 30%, capital costs by 20%, and fuel consumption is only 1/3 to 1/5 of that of an RTO; in terms of performance, self-heating can be achieved to maintain operation even at very low VOC concentrations, and heat losses are smaller due to lower operating temperatures. In terms of equipment, due to the smaller size of the regeneration bed and reactor, more economical steel and insulation materials can be used, thus realizing significant capital investment savings.

This paper systematically reviews the working principle, reaction mechanism, and the latest progress of the catalyst research of RTO and RCO, aiming to provide a theoretical reference and technical guidance for further research in this field.

2. Regenerative Thermal Oxidation

2.1. Working Principle of RTO

RTO employs high-thermal-conductivity heat storage materials to facilitate heat recycling and waste gas purification. During operation, organic waste gas is directed through the heat storage material for preheating before entering the oxidation chamber, where it is combusted and transformed into carbon dioxide and water. Concurrently, the heat released is absorbed by the heat storage material and utilized to preheat the waste gas in the subsequent cycle. This heat recycling design not only improves combustion efficiency but also decreases energy consumption, rendering it an energy-efficient and environmentally friendly technology for industrial waste gas treatment.

2.2. Types of RTO

2.2.1. Two-Chamber RTO

In the 1970s, the two-chamber RTO was introduced. The two-chamber RTO adopts a dual-bed structure, consisting of two ceramic heat storage beds, an oxidation chamber, four interlocking high-temperature switching valves, and an intelligent control system (as

shown in Figure 2). Its “one-in, one-out” process, combined with switching valves, enables the “heat storage” and “heat release” processes, laying the foundation for subsequent technological developments.

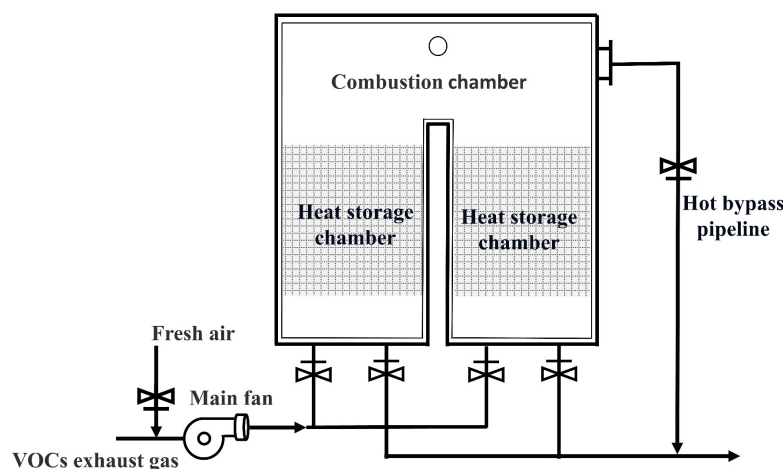


Figure 2. Schematic diagram of the two-chamber RTO.

In the 1970s, the two-chamber RTO was introduced. This system employs a dual-bed structure, comprising two ceramic heat storage beds, an oxidation chamber, four interlocking high-temperature switching valves, and an intelligent control system (as illustrated in Figure 2). The “one-in, one-out” operational process, in conjunction with the switching valves, facilitates the “heat storage” and “heat release” mechanisms, thereby establishing a foundation for subsequent technological advancements.

Chou et al. [41] investigated the exhaust gas removal efficiency and nitrogen oxide formation characteristics of a two-chamber electrically heated RTO. Their findings revealed that at a valve switching time of 1.5 min, a flow velocity of 0.39 m/s, and an oxidation chamber temperature ranging from 750 to 950 °C, the VOC removal efficiency exceeded 96%, with no detectable nitrogen oxide emissions in the exhaust gas.

Iijima et al. [42] investigated the treatment of toluene waste gas utilizing a two-chamber RTO. Their findings revealed that at lower gas flow rates, radiative heat transfer predominated in the preheating process. Specifically, when the mass flow rate of the raw gas was 1810 kg/h and the honeycomb height was 1.5 m, toluene achieved self-ignition without the need for additional heating, resulting in a thermal efficiency of 95%. However, a reduction in honeycomb height to 0.9 m led to an increase in the minimum toluene concentration required for self-ignition from 340 ppm to 530 ppm, thereby indicating that honeycomb height significantly influences treatment efficiency.

Cannon et al. [43] studied the heat recovery of a two-chamber RTO for VOC treatment and found that when the VOC concentration exceeded 3% of the Lower Explosive Limit (LEL), the system could achieve a self-sustaining operation, with a heat recovery efficiency of up to 95%.

Due to the absence of a purge phase in the two-chamber RTO, a portion of the waste gas remains trapped in the heat storage material during each cycle. When the valve switching alters the flow direction of the waste gas, these residual gases are directly routed into the exhaust pipeline and subsequently discharged through the chimney. This process results in the release of partially unoxidized waste gas into the atmosphere, thereby negatively impacting the purification efficiency.

2.2.2. Three-Chamber RTO

In the 1980s, the three-chamber RTO was introduced, incorporating a heat storage chamber in contrast to the two-chamber RTO for the treatment of residual waste gases (as illustrated in Figure 3). The residual waste gases are redirected into the oxidation chamber for secondary oxidation via a purge fan. The implementation of the “purging” function in the three-chamber RTO effectively mitigated the direct emission of residual waste gases during the switching process, thereby significantly enhancing the efficiency of waste gas purification.

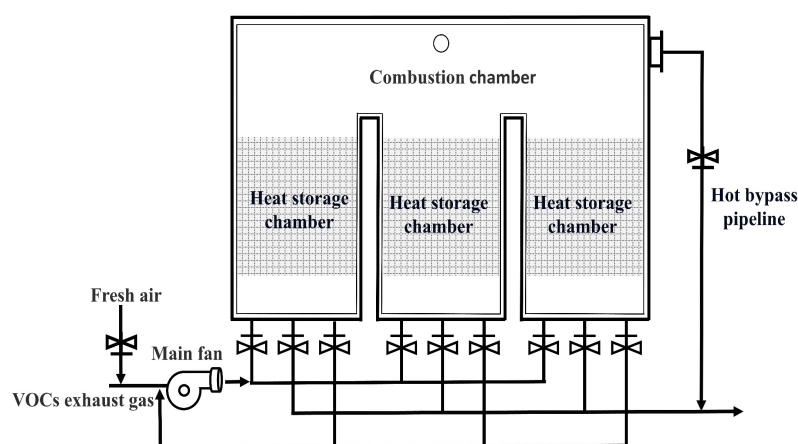


Figure 3. Schematic diagram of the three-chamber RTO.

Currently, experimental research on the three-chamber RTO is limited, with the majority of studies concentrating on numerical simulations. Wang et al. [26] conducted an investigation utilizing a three-chamber RTO model, revealing that the outlet temperature decreases as the apparent velocity of the inlet packing bed increases. Furthermore, an increase in the concentration of VOCs results in elevated temperatures in both the oxidation chamber and the outlet, which in turn leads to increased heat loss and reduced thermal efficiency. Additionally, extending the valve switching time causes the heat storage medium to accumulate heat, resulting in a decrease in the oxidation chamber temperature and an increase in the outlet temperature, further diminishing the system’s thermal efficiency. Extending the valve switching time led to heat accumulation in the heat storage medium, resulting in a decrease in the oxidation chamber temperature and an increase in the outlet temperature, ultimately reducing the system’s thermal efficiency. Lorenzo et al. [44] conducted a numerical flow field simulation study on a 20,000 m³/h three-chamber RTO system and found that the monolithic block structure resulted in uneven airflow distribution. By introducing random packing beneath the structure, they effectively resolved this imbalance. Hao et al. [45] conducted transient simulations to analyze the velocity and temperature distributions in a three-chamber RTO system. Their findings revealed that the unique structure of the ceramic honeycomb heat storage bed effectively ensured even airflow distribution, significantly improving the uniformity of the velocity and temperature. This enhancement played a crucial role in boosting the efficiency and stability of the RTO system. While the three-chamber RTO effectively addresses the issue of direct emissions of residual waste gases during the switching process in two-chamber RTO systems, it also has certain drawbacks, including a higher internal pressure (200–300 Pa) and relatively low space utilization (approximately 66%).

2.2.3. Rotary RTO

In the 1990s, the rotary RTO improved energy efficiency through a multi-chamber design and rotary valve switching. Compared to two-chamber and three-chamber RTO

systems, the rotary RTO offers higher space utilization, smoother airflow switching, and more stable internal pressure (as shown in Figure 4).

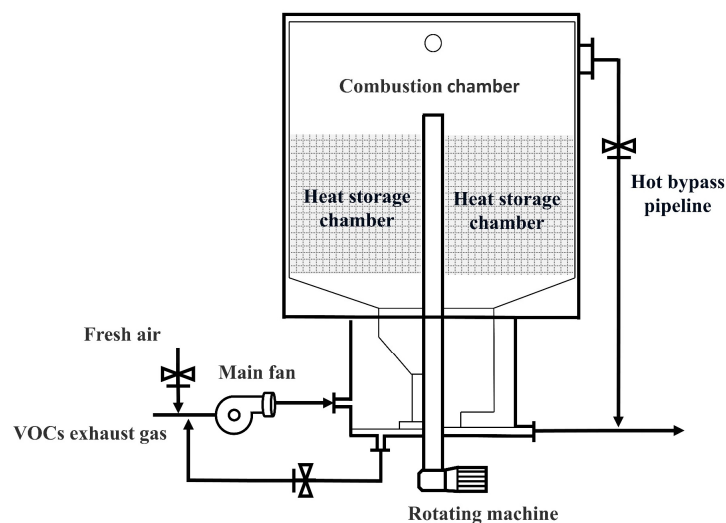


Figure 4. Schematic diagram of the rotary RTO.

The rotary RTO comprises three primary components: a ceramic heat exchange media, an oxidation chamber, and a rotary distribution valve. The furnace assembly is segmented into twelve distinct zones, consisting of five heating zones, five cooling zones, one purging zone, and one dead zone (illustrated in Figure 5). The rotary distribution valve, driven by a motor at a constant speed, facilitates the seamless transition of waste gas streams between zones, thereby minimizing pressure fluctuations and optimizing energy efficiency. The process begins as waste gases are introduced into the RTO via the main fan, where they traverse through the heating zones for thermal preconditioning before entering the oxidation chamber for high-temperature decomposition. Subsequently, the treated gases are temporarily retained in the cooling zones prior to atmospheric discharge. The thermal energy accumulated in the ceramic heat exchange media is utilized for preheating in the subsequent operational cycles, while a dedicated purge fan introduces clean gas to perform chamber cleaning operations, redirecting residual waste gases to the oxidation chamber for complete decomposition.

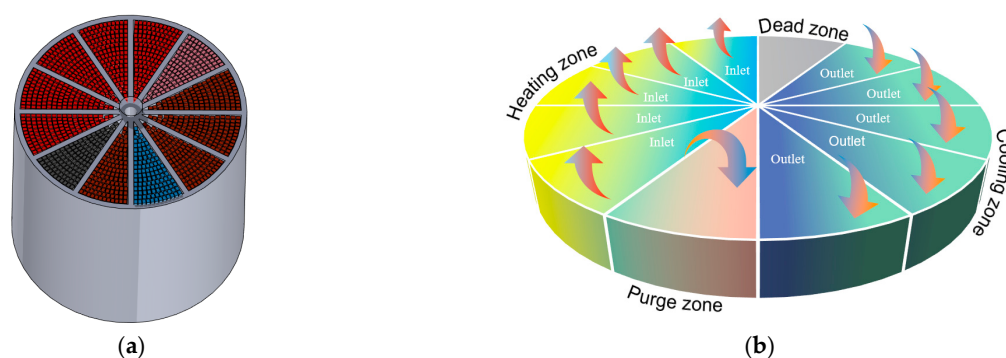


Figure 5. Distribution of the 12 chambers of the rotating RTO furnace (a) and distribution of the four zones of the rotating RTO (b).

Amelio et al. [46] studied the impact of the switching valve system in RTO on the overall system and found that the switching valve system had a minimal effect on the thermal efficiency. However, the thermal efficiency of systems with valves was slightly lower than that of the valve-less systems. In the rotary RTO system, the energy demand

was not affected by the cycle duration, and the valve speed could be adjusted freely based on actual needs.

2.2.4. Single-Tube Multi-Valve RTO

The single-tube multi-valve RTO represents an innovative integrated system that emerged in the 21st century, offering dual functionality for both pollutant treatment and heat recovery (as illustrated in Figure 6). This advanced configuration employs zero-leakage multi-rotary valve technology coupled with high-precision flow control mechanisms. The system's distinctive feature lies in its ability to dynamically adjust the rotary valves according to the required treatment airflow, enabling the optimal distribution of the flow cross-sectional area ratio. This adaptive capability significantly enhances both the operational flexibility and overall system efficiency. Despite its technological advantages, the single-tube multi-valve RTO remains relatively understudied in the academic literature, with limited published research addressing its design and performance characteristics.

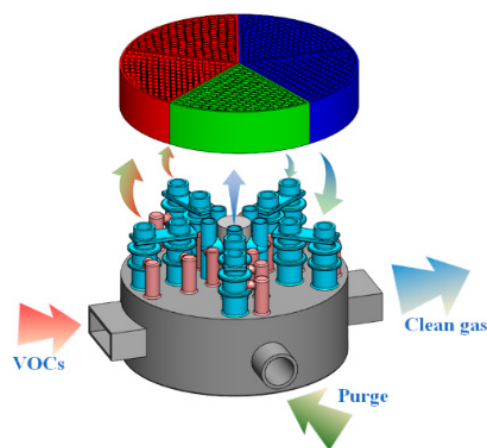


Figure 6. Schematic diagram of a single-cylinder multi-valve RTO.

The RTO technology has undergone four distinct evolutionary stages, each marked by substantial advancements in key performance parameters, including pollutant removal efficiency, thermal efficiency, and operational longevity. Table 3 presents a comprehensive comparative analysis of RTO systems across these developmental phases, highlighting the progressive improvements in their performance metrics. This evolutionary trajectory demonstrates the systematic enhancement of RTO technology through iterative design refinements and technological innovations.

Table 3. Comparison of different RTO performance.

Type	Two-Chamber RTO	Three-Chamber RTO	Rotary RTO	Single-Tube Multi-Valve RTO	Notes
Removal efficiency	95%	99%	99.5%	99.5%	
Thermal efficiency	90%	95%	95%	95%	
Maximum concentration handling	<1 g/m ³	<5 g/m ³	<5 g/m ³	<10 g/m ³	50 mg/m ³ is emission standard
Number of valves	4	9	1	15	
Valve form	Push-down valve/lift valve	Push-down valve/lift valve	Rotary valve	Triple eccentric hard-sealing butterfly valve	
Valve life	1–2 years	1–2 years	0.5–1 years	3–5 years	
Number of heat storage chambers	2	3	12	5	
Land occupation	100%	130%	65%	65%	Using a two-chamber RTO as the baseline

The data from Table 3 shows that RTO technology has undergone multiple generations of iterative optimization, resulting in significant improvements in waste gas treatment capacity and operational efficiency. The valve system has evolved from early push-down valves/lift valves to rotary valves and then to triple eccentric hard-sealing butterfly valves. This evolution has not only enhanced the sealing performance and service life but also optimized the gas flow characteristics. Currently, since the concentration of VOCs is usually highly volatile, when the concentration is at a low level, direct oxidation requires a large amount of additional energy, resulting in a significant increase in fuel costs. In order to solve this problem, the researchers proposed the treatment scheme of “concentration followed by oxidation”. Practice has shown that adsorption rotors and zeolite materials are ideal media for concentrating VOCs. Compared with the single oxidation process, the combined concentration–oxidation process has not only higher economy and treatment efficiency but can also effectively reduce the emissions of secondary pollutants [47].

3. Regenerative Catalytic Oxidizer

The RTO operates in a high-temperature environment of above 760 °C. During the heating phase and steady-state operation, a large amount of fuel is required to maintain the desired temperature, leading to high energy consumption and operational costs.

To effectively reduce energy consumption, researchers developed the RCO by integrating catalyst technology. Compared to the traditional RTO system, the RCO optimizes the heat storage body near the oxidation chamber in the heat storage chamber, replacing it with a material that has catalytic activity (as shown in the three-chamber RCO in Figure 7). This improvement allows the RCO system to operate within a lower temperature range, typically controlled between 250 and 400 °C. After heating to 250–300 °C, VOCs undergo flameless combustion under the action of the catalyst, significantly reducing the demand for fuel and lowering the overall operating costs.

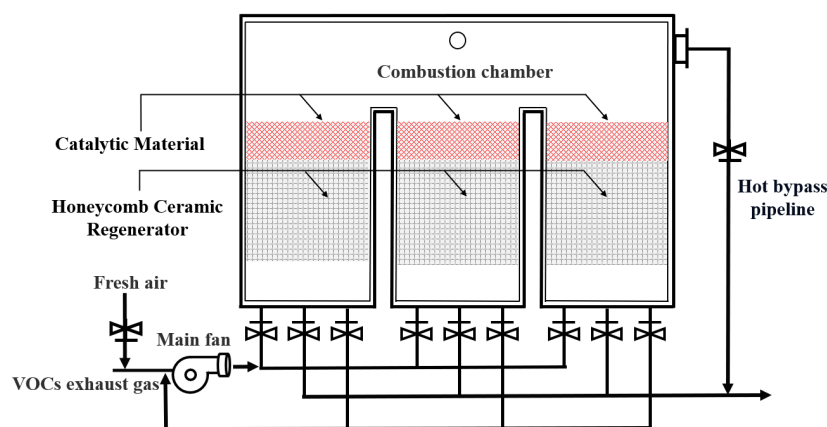


Figure 7. Three-chamber RCO schematic diagram.

3.1. The Working Principle of RCO

RCO combines catalytic oxidation with heat recovery technology, overcoming the limitations of traditional thermal oxidizers by using a catalyst to promote VOC oxidation at lower temperatures. The process is simplified as follows:

(1) Preheating stage: The exhaust gas flows through the heat storage medium for preheating. (2) Catalytic oxidation: The preheated gas passes through the catalytic bed, where the catalyst oxidizes the VOCs into CO₂ and H₂O at temperatures between 250 °C and 400 °C. (3) Heat recovery: High-temperature gases are recovered through heat accumulators and used to preheat cold exhaust gases. (4) Emissions control: The cooled gas is discharged, reducing VOCs and other pollutants.

The complete catalytic oxidation of VOCs is a key reaction in industrial waste gas treatment. The catalyst adsorbs reactant molecules and lowers the activation energy of the reaction, which not only reduces the reaction temperature but also accelerates the reaction rate. The mechanism is typically divided into three main categories (as shown in Figure 8): (1) Eley–Rideal (E-R) [48], (2) Mars–van Krevelen (MVK), and (3) Langmuir–Hinshelwood (L-H) [49].

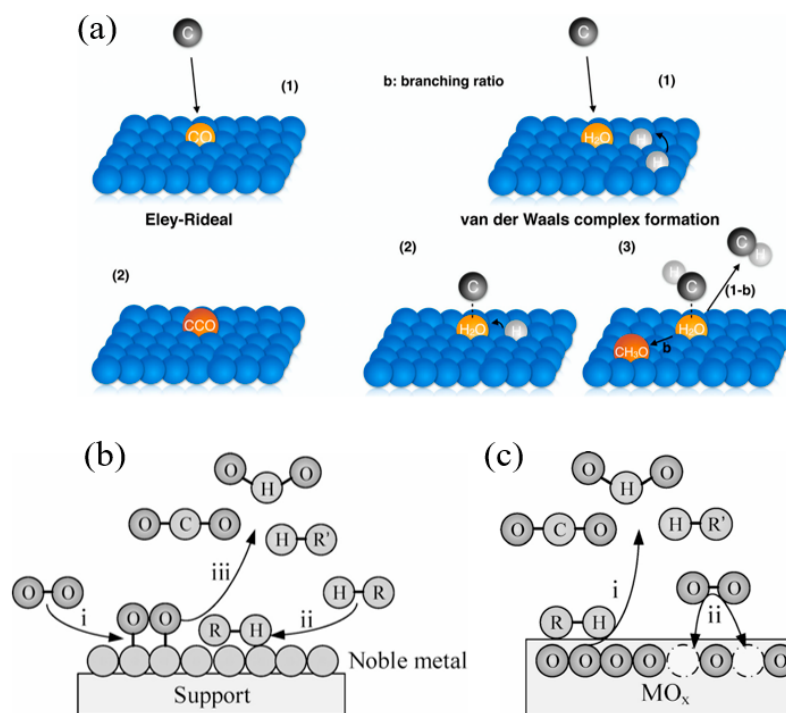


Figure 8. (a) Eley–Rideal, (c) Langmuir–Hinshelwood, and (b) Mars–van Krevelen [48,49].

The E-R model describes the direct reaction process between gas-phase reactants and surface-adsorbed species on the catalyst [50]. This model is particularly suitable for catalytic systems with weak adsorption and fast reactions, showing clear advantages under low-temperature and high-oxygen partial pressure conditions. The MVK model describes the redox cycling mechanism of VOCs with lattice oxygen on the catalyst surface [51]. It is primarily applicable to the catalyst systems of reducible metal oxides, such as cobalt oxide and cerium oxide. The L-H model describes the interaction between adsorbed VOCs and adsorbed oxygen species on the catalyst surface [52]. It can be further subdivided into single-center and dual-center L-H models based on the nature of the adsorption sites for the reactants. These three models describe the mechanism of VOC oxidation from different perspectives.

The nature of catalyst reactions is a redox process, in which reversible redox cycles (e.g., $\text{Ce}^{3+}/\text{Ce}^{4+}$, $\text{Co}^{3+}/\text{Co}^{2+}$) are realized through the electron transfer channels and active sites provided by the catalyst to maintain the long-lasting activity of the catalyst. The performance of combustion catalysts is mainly affected by the synergistic effects of oxygen vacancies, the surface structure, and redox properties: oxygen vacancies enhance the reaction efficiency by promoting oxygen activation, accelerating lattice oxygen migration (e.g., the Mars–van Krevelen mechanism for CeO_2), and modulating the electronic structure; a moderate surface disorder exposes more active sites and enhances the catalyst's contact with the reactants; and the catalysts' reactivity is enhanced through cation doping (e.g., introduction of oxygen vacancies by La^{3+}), the nanostructure design (increasing specific surface area), and the construction of metal–oxide interfaces (e.g., the enhancement of

oxygen overflow by the SMSI effect of Pt/CeO₂), which are some of the strategies that can further optimize the overall performance of the catalysts.

Currently, catalysts used for VOC purification are mainly categorized into three types: precious metal catalysts [53], non-precious metal oxide catalysts [54], and mixed-metal catalysts.

3.2. Precious Metal Catalysts

Precious metal catalysts have attracted significant attention in the field of VOC catalytic oxidation due to their excellent catalytic activity.

Rooke et al. [55] systematically investigated the effects of the pH value and non-ionic surfactants on the morphology of synthesized hierarchically porous Group Vb metal oxides. The study showed that acidic conditions favored the formation of Nb₂O₅ with a larger specific surface area, while Ta₂O₅ achieved the maximum specific surface area under alkaline conditions. Without noble metal loading, niobium oxide supports exhibited higher catalytic activity than tantalum oxide; however, after palladium loading, the tantalum oxide system showed more significant activity enhancement. Among them, supports synthesized at a pH = 6 demonstrated optimal catalytic performance, indicating that synthesis conditions influence catalytic activity by regulating the surface properties of the supports. Group Vb metal oxides show potential as noble metal catalyst supports, but the pH of the reaction medium significantly affects the catalytic performance of the Pd/support systems.

Liu et al. [56] prepared 0.5 wt% Pd/OMS-2 catalysts using the deposition–precipitation method (DP), the pre-incorporation method (PI), and ion-exchange (EX). Figure 9a–d show the TEM images and Pd particle size distributions of the different catalysts. It was found that 0.5 wt% Pd/OMS-2-DP exhibited a greater dispersion of PdO_x particles on the surface. Figure 9c displays the XRD spectra of the different samples. Compared to OMS-2, the peaks at $2\theta = 28.7^\circ$ and 37.4° for 0.5 wt% Pd/OMS-2-PI and 0.5 wt% Pd/OMS-2-EX are narrower and stronger, indicating an improvement in crystallinity. Figure 9f shows the NH₃-TPD spectra of different samples. For OMS-2, the spectrum features a low-temperature peak at 200 °C and high-temperature peaks at 250 °C and 350 °C, reflecting the distribution characteristics of the acidic sites on the catalyst surface. Figure 9g–i show the conversion efficiency of toluene, ethyl acetate, and carbon monoxide for catalysts prepared by different methods. It was found that the OMS-2 catalyst exhibited the lowest activity. The oxidation temperatures for 50% and 90% removal efficiency of toluene were 270 °C and 350 °C, respectively, while those for ethyl acetate were 190 °C and 250 °C, and for carbon monoxide, 128 °C and 140 °C. In comparison, Pd-loaded catalysts significantly reduced the reaction temperature and greatly enhanced the catalytic activity. The catalyst prepared by the DP method exhibited the best performance, attributed to its higher Pd loading, suitable acidity, excellent adsorption capacity, low-temperature reducibility, and high oxygen mobility.

Precious metal catalysts have widespread applications in the catalytic oxidation of VOCs. Among them, noble metals such as Au, Pt, and Pd have garnered significant attention due to their excellent catalytic activity and selectivity. By loading these precious metal active components onto ceramic supports (such as Al₂O₃, CeO₂, TiO₂, etc.) or metal support surfaces, the thermal stability, mechanical strength, and catalytic performance of the catalysts can be significantly enhanced. Based on a review of catalysts for the treatment of VOCs [13], this paper further extends the current progress of precious metal catalyst research results as shown in Table 4.

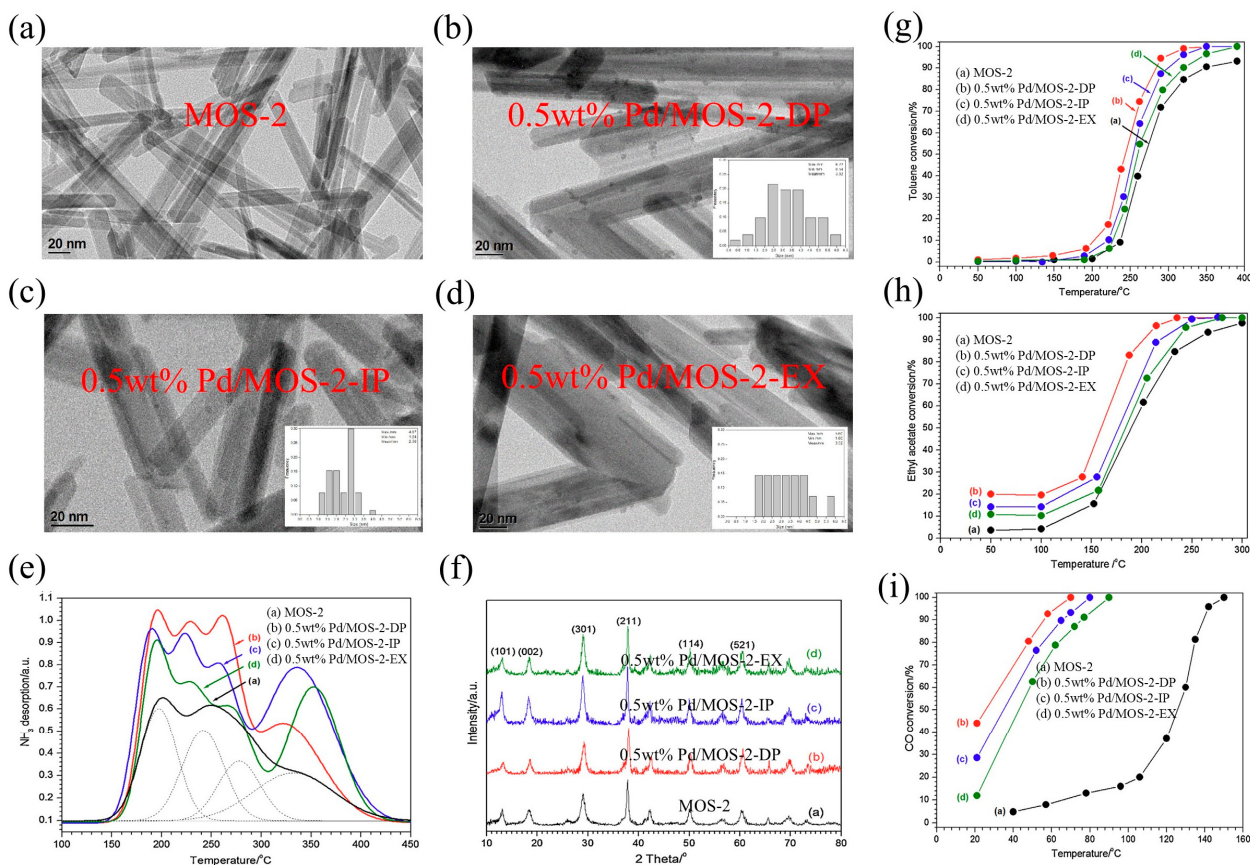


Figure 9. The TEM images and Pd particle size distributions for MOS-2, 0.5 wt% Pd/OMS-2-DP, 0.5 wt% Pd/OMS-2-PI, and 0.5 wt% Pd/OMS-2-EX are shown in Figure (a–d), respectively. Figure (e,f) show the NH_3 -TPD spectra and XRD characterization of the catalysts. Figure (g–i) show the catalytic performance of the catalyst samples for the oxidation of toluene, ethyl acetate, and carbon monoxide, respectively [56].

Table 4. Research findings on noble metal catalysts for VOC treatment.

Catalyst	Support	VOCs	Temperature (°C)	Conversion (%)	Reference
Au	CeZr	Ethanol	222	90	[55]
Au	CeZr	Toluene	322	90	
Au	$\text{Ce}_{0.3}\text{Ti}_{0.7}\text{O}_2$	Propylene	293	100	[57]
Au	$\text{Ce}_{0.1}\text{Ti}_{0.9}\text{O}_2$	Propylene	300	100	
Au	TiO_2	Propylene	400	100	
Au	$\text{CeO}_2/\text{ZrO}_2/\text{TiO}_2$	Propylene	450	95	[58]
Au	CeO_2	Propene	230	100	[59]
Au	$\text{Ce}_{7.5}/\text{Al}_2\text{O}_3$	Propene	250	100	
Au	TiO_2	Propene	320	100	
Au	Al_2O_3	Propene	341	100	
Au	CeO_2	Toluene	293	100	
Au	$\text{Ce}_{7.5}/\text{Al}_2\text{O}_3$	Toluene	330	100	
Au	TiO_2	Toluene	400	100	
Au	Al_2O_3	Toluene	450	100	
Au	$\text{CeO}_2/\text{Fe}_2\text{O}_3$	Benzene	200	100	[60]
Au	Cu:Mn 2:1	Methanol	180	92	[61]
Au	Cu:Mn 2:1	Dimethyl ether	360	95	

Table 4. Cont.

Catalyst	Support	VOCs	Temperature (°C)	Conversion (%)	Reference
Au	CuO	Ethyl acetate	289	100	[62]
Au	Fe ₂ O ₃	Ethyl acetate	354	100	
Au	La ₂ O ₃	Ethyl acetate	325	100	
Au	MgO	Ethyl acetate	290	100	
Au	NiO	Ethyl acetate	345	100	
Au	CuO	Toluene	315	100	
Au	Fe ₂ O ₃	Toluene	345	100	
Au	La ₂ O ₃	Toluene	>400	100	
Au	MgO	Toluene	387	100	
Au	NiO	Toluene	320	100	
Pt	γ-Al ₂ O ₃	Ethyl acetate	310	>90	[63]
Pt	TiO ₂	Ethyl acetate	260	>90	
Pt	TiO ₂ (0.45% W ⁶⁺)	Ethyl acetate	220	>90	
Pt	γ-Al ₂ O ₃	Benzene	180	90	
Pt	TiO ₂	Benzene	170	90	
Pt	TiO ₂ (0.45% W ⁶⁺)	Benzene	160	90	
Pt	Carbon nanotubes	Benzene	112	100	[64]
Pt	Carbon nanotubes	Toluene	109	100	
Pt	Carbon nanotubes	Ethylbenzene	106	100	
Pt	Carbon nanotubes	Meta xylene	104	100	
Pt	MnO _x -T	Toluene	30	98	[65]
Pt	MnO _x -LT	Toluene	70	99	
Pt	MnO _x -B	Toluene	90	99	
Pt	MnO _x -HB	Toluene	90	99	
Pt	CeZr	Ethanol	193	90	[66]
Pt	CeZr	Toluene	207	90	
Pd	Carbon	m-Xylene	170	100	[67]
Pd	UiO-66	Toluene	200	100	[68]
Pd	TiO ₂	Toluene	260	100	[69]
Pd	γ-Al ₂ O ₃	Toluene	200	90	[70]
Pd	Nb ₂ O ₅	Toluene	285	90	[55]
Pd	Ta ₂ O ₅	Toluene	281	90	
Pd	Co ₃ O ₄ (3D)	O-xylene	196	90	[71]
Pd	Co ₃ O ₄ (3DL)	O-xylene	254	90	

Precious metal catalysts exhibit excellent catalytic performance, but their application is limited due to the scarcity of precious metals, high costs, and deactivation issues such as sintering, aggregation, and poisoning during use. Precious metal catalysts are susceptible to chlorine poisoning and loss of activity. For example, Pt-Pd catalysts can suffer from reduced activity in the presence of CVOCs like TCE and trichloromethane, which are more difficult to oxidize than non-chlorinated VOCs. The chlorinated species can also inhibit the oxidation of co-fed non-chlorinated VOCs [72,73].

Recent studies have shown that non-precious metal-based catalysts not only possess good catalytic performance but also have lower costs, making them ideal alternatives to precious metals.

3.3. Non-Precious Metal Oxide Catalysts

Non-precious metal catalysts perform excellently in VOC oxidation and can be classified into supported and unsupported types. Supported catalysts increase the number of active sites and the contact area by loading the active components onto a support. Among non-precious metal-based catalysts, transition metal and rare-earth metal oxides are ideal alternatives to precious metals due to their high efficiency and low cost. Oxides like CuO and MnO₂, with their unique electronic structures and redox properties, can efficiently catalyze the conversion of VOCs into CO₂ and H₂O.

There is a wealth of research on non-precious metal oxide catalysts. He [74] prepared mesoporous structure ACeO_x (A = Co, Cu, Fe, Mn, Zr) composite catalysts with large surface areas and high porosity using the spontaneous precipitation (IMSP) method. It was found that CuCeO_x achieved a 99% removal rate of chlorobenzene at 328 °C, while other ACeO_x catalysts required temperatures above 405 °C to reach the same level of performance. García et al. [75] investigated the catalytic combustion of naphthalene by metal oxide catalysts (CoO_x, MnO_x, CuO, ZnO, Fe₂O₃, CeO₂, TiO₂, Al₂O₃, and CuZnO), prepared by the precipitation method. The cerium oxide catalysts were found to exhibit stable conversions and high conversion efficiencies at very low temperatures (175 °C), with a conversion efficiency of 90% at 210 °C for the catalytic combustion of naphthalene. Shie et al. [76] used the Pt/γ-Al₂O₃ catalyst for the catalytic oxidative decomposition of PAHS with naphthalene (the simplest and least toxic PAH) as the target compound. It investigated the relationship between conversion, operating parameters, and related factors such as processing temperature, catalyst size, and airspeed. The results showed that the decomposition reaction rate of naphthalene could be accelerated, and the reaction temperature could be reduced by using the Pt/γ-Al₂O₃ catalyst. A high conversion of more than 95% can be achieved at a moderate reaction temperature of 480 K and a space velocity lower than 35,000 h^{−1}. Aparicio et al. [77] investigated the effect of CoO_x/SiO₂ catalysts on the naphthalene combustion reaction. The catalysts were prepared by impregnation with four different concentrations (1, 5, 10, and 15 wt%). It was found that all the loaded cobalt catalysts were found to reduce the combustion temperature of naphthalene during the catalytic combustion of naphthalene. The catalytic activity depended on the metal loading, with the higher loading catalysts being more active. The conversion of CoO_x(15)/SiO₂ to naphthalene was found to reach a conversion efficiency of 50% at a temperature of 228 °C. The conversion efficiency of CoO_x(15)/SiO₂ to naphthalene reached 100% at 270 °C.

Lv et al. [78] synthesized a series of M-Ce_{0.7}Zr_{0.3}O₂ catalysts (M = S, P, Mo) by introducing Lewis and Brønsted acid sites onto the surface of a 3D-ordered macroporous (3DOM) CeO₂ framework. Figure 10 shows the chlorobenzene conversion rate and CO₂ yield curves for Ce_{1-x}Zr_xO₂ (Figure 10a,b) and M-Ce_{0.7}Zr_{0.3}O₂ (Figure 10c,d). It was found that Ce_{0.7}Zr_{0.3}O₂ exhibited the best catalytic activity for the combustion of chlorobenzene.

After modification with acid elements, the activity of Ce_{0.7}Zr_{0.3}O₂ was further improved. Compared with P-Ce_{0.7}Zr_{0.3}O₂, W-Ce_{0.7}Zr_{0.3}O₂, and Mo-Ce_{0.7}Zr_{0.3}O₂, S-Ce_{0.7}Zr_{0.3}O₂ exhibited the best catalytic performance. As shown in Figure 10e, the conversion rate of chlorobenzene over ceria (CeO₂) sharply decreased from 90% to 75% within 24 h of the reaction, whereas Ce_{0.7}Zr_{0.3}O₂ and S-Ce_{0.7}Zr_{0.3}O₂ maintained a chlorobenzene conversion rate of around 90% over the same period, demonstrating excellent resistance to deactivation.

In Figure 10f, the selectivity ratio of the catalyst for chlorine gas is shown. It was found that compared to CeO₂ and Ce_{0.7}Zr_{0.3}O₂, S-Ce_{0.7}Zr_{0.3}O₂ exhibited lower chlorine selectivity, at only 1.2%. The large number of Brønsted acid sites on the catalyst led to the degradation of chlorobenzene mainly through a hydrolysis pathway, significantly reducing the selectivity for chlorine gas.

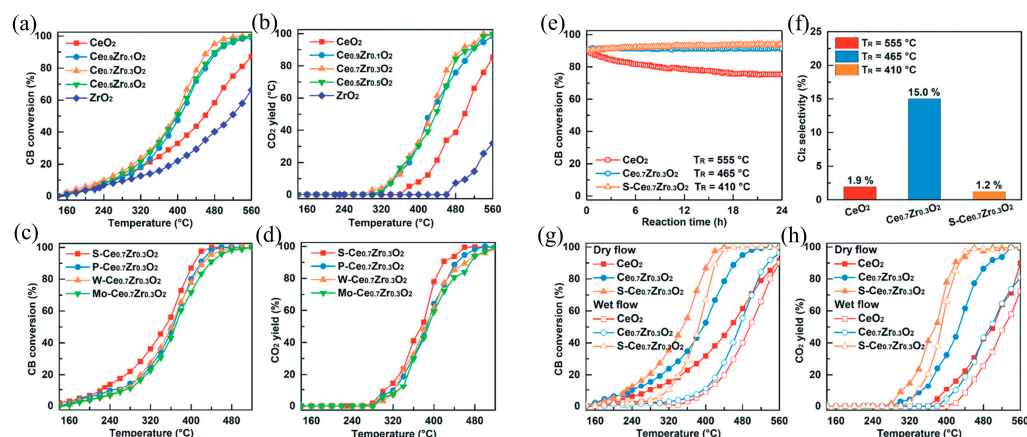


Figure 10. The chlorobenzene conversion rates for $Ce_{1-x}Zr_xO_2$ and $M-Ce_{0.7}Zr_{0.3}O_2$ are shown in Figure (a,c), respectively, while the CO_2 yields are presented in Figure (b,d). Figure (e) illustrates the chlorobenzene conversion rates of the catalyst samples over a 24 h reaction time. Figure (f) compares the selectivity of the catalyst samples for chlorine gas. Figure (g,h) demonstrate the effects of water vapor on the CB degradation catalytic performance and CO_2 yield [78].

Figure 10g,h show the effect of water vapor on the catalytic performance of CB degradation and CO_2 yield. After introducing 5% water vapor, the CB conversion rate and CO_2 yield decreased for all three samples, as H_2O competes with CB or its intermediates for adsorption sites. As the temperature increased, the activity curves for $S-Ce_{0.7}Zr_{0.3}O_2$ became more consistent, indicating that the effect of water vapor diminished. However, for CeO_2 and $Ce_{0.7}Zr_{0.3}O_2$, even at 560 °C, the competitive adsorption effect remained significant.

Figure 11 shows the SEM images of CeO_2 (Figure 11a,b), $Ce_{0.7}Zr_{0.3}O_2$ (Figure 11c,d), and $S-Ce_{0.7}Zr_{0.3}O_2$ (Figure 11e,f), with Figure 11g presenting the EDS image of $S-Ce_{0.7}Zr_{0.3}O_2$. The used samples still maintain a good three-dimensional ordered structure and mechanical stability. CeO_2 and $Ce_{0.7}Zr_{0.3}O_2$ exhibit a large specific surface area, and the EDS analysis indicates that sulfur is evenly dispersed on the surface of the framework. Figure 11h shows the XRD spectra of the three samples, which are similar, with the diffraction peaks weakening and shifting to higher angles after the addition of Zr ions. The HRTEM images (Figure 11i for CeO_2 , (Figure 11j) for $Ce_{0.7}Zr_{0.3}O_2$, and (Figure 11k) for $S-Ce_{0.7}Zr_{0.3}O_2$) display clear lattice fringes, and $Ce_{0.7}Zr_{0.3}O_2$ shows an increase in lattice spacing due to the introduction of Zr ions.

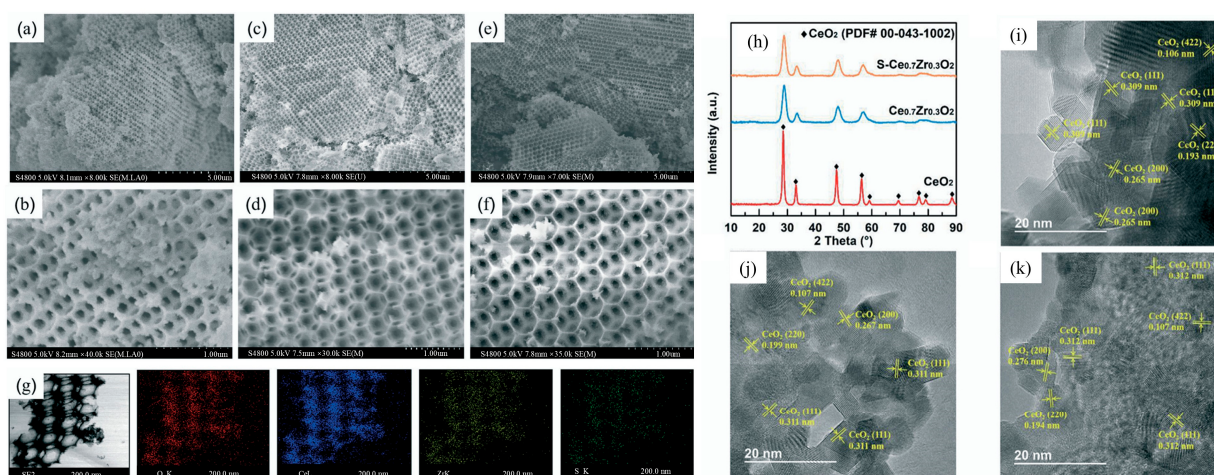


Figure 11. SEM images of CeO_2 (a,b), $Ce_{0.7}Zr_{0.3}O_2$ (c,d), and $S-Ce_{0.7}Zr_{0.3}O_2$ (e,f), and the EDS image of $S-Ce_{0.7}Zr_{0.3}O_2$ (g). (h) shows the XRD characterization of the catalyst samples. (i–k) are HRTEM images of CeO_2 , $Ce_{0.7}Zr_{0.3}O_2$, and $S-Ce_{0.7}Zr_{0.3}O_2$ catalyst samples, respectively [78].

Ismail et al. [79] synthesized three different morphologies of CeO_2 catalysts: shuttle-shaped ($\text{CeO}_2(\text{S})$), nanorods ($\text{CeO}_2(\text{R})$), and nanoparticles ($\text{CeO}_2(\text{P})$). The schematic diagram of the catalyst synthesis process is shown in Figure 12a. The characterization by SEM and TEM (Figure 12b–i) reveals that $\text{CeO}_2(\text{S})$ exhibits a uniform spindle-like morphology, with a large number of crystal defects, distortions, and significant oxygen vacancies on the surface. These oxygen vacancies play a key role in the catalytic reaction. The XRD results in Figure 12j show that $\text{CeO}_2(\text{S})$ has broader and weaker diffraction planes compared to the other two morphologies. Additionally, Figure 12k displays a large number of 2–5 nm nanopores in its structure, indicating a higher surface porosity and surface area. Figure 12l shows that $\text{CeO}_2(\text{S})$ achieves 90% toluene conversion at 225 °C, while $\text{CeO}_2(\text{R})$ reaches 90% conversion at 283 °C, and $\text{CeO}_2(\text{P})$ at 360 °C. $\text{CeO}_2(\text{S})$ exhibits a clear advantage in toluene conversion.

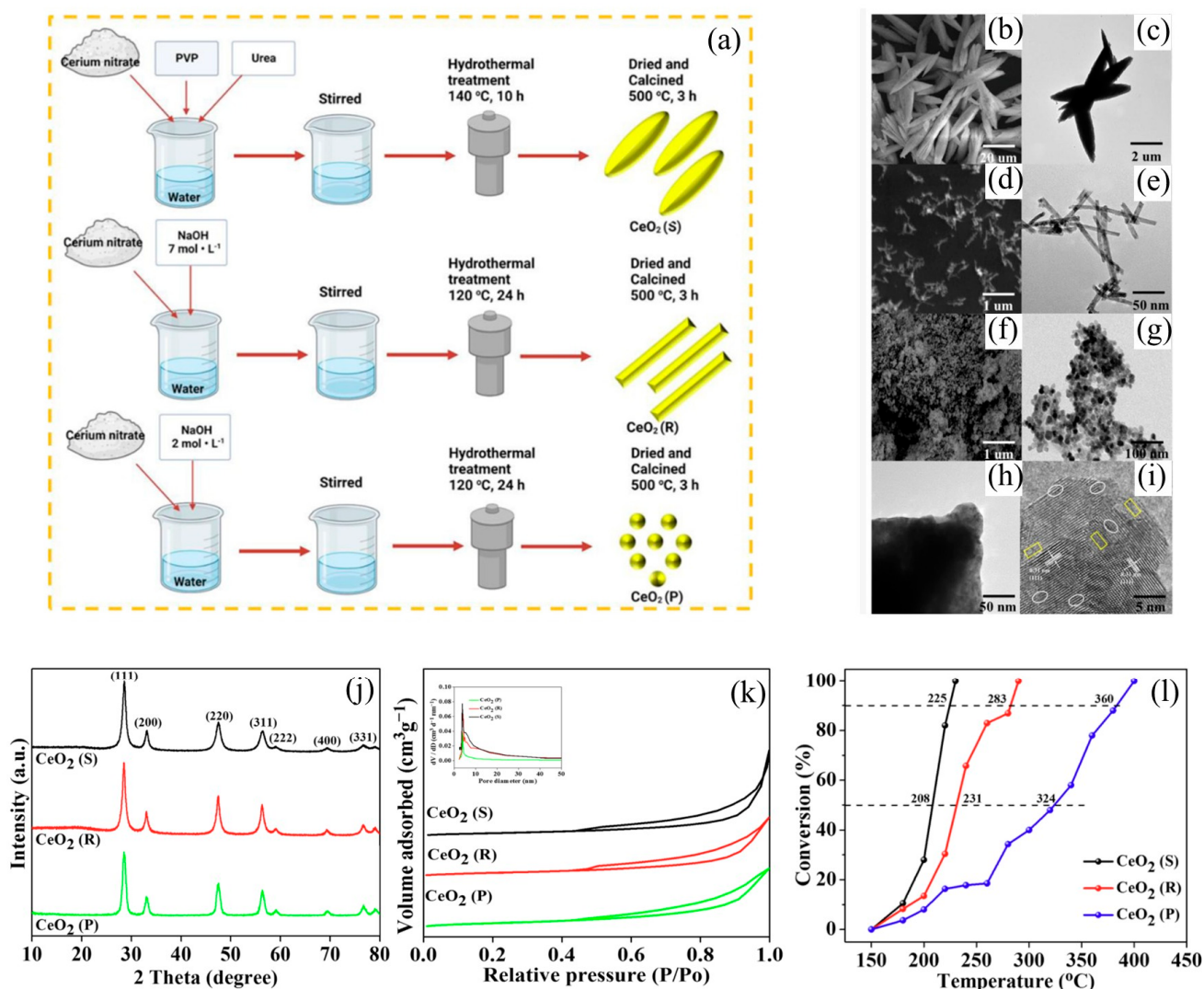


Figure 12. Schematic illustration of the preparation of $\text{CeO}_2(\text{S})$, $\text{CeO}_2(\text{R})$, and $\text{CeO}_2(\text{P})$ (a); SEM and TEM images of $\text{CeO}_2(\text{S})$ (b,c); SEM and TEM images of $\text{CeO}_2(\text{R})$ (d,e); SEM and TEM images of $\text{CeO}_2(\text{P})$ (f,g); HRTEM images of $\text{CeO}_2(\text{S})$ (h,i); XRD characterization patterns (j); N_2 adsorption–desorption isotherms (k); and catalytic performance of the catalysts for toluene conversion (l) [79].

Transition metal oxides have shown excellent catalytic performance in the oxidation of volatile organic compounds (VOCs), and this paper further extends the recent research advances of non-precious metal catalysts in the oxidation of VOCs based on relevant summaries in the literature [13], as shown in Table 5.

Table 5. Research findings on non-precious metal oxides catalysts for VOC treatment.

Catalyst	VOCs	T ₉₀ (°C)	T ₁₀₀ (°C)	Reference
CuO	Ethyl acetate	290	311	[62]
Fe ₂ O ₃	Ethyl acetate	355	370	
La ₂ O ₃	Ethyl acetate	367	384	
MgO	Ethyl acetate	>400	>400	
NiO	Ethyl acetate	344	365	
CuO	Toluene	309	330	
Fe ₂ O ₃	Toluene	394	-	
La ₂ O ₃	Toluene	>400	>400	
MgO	Toluene	>400	>400	
NiO	Toluene	324	330	
Co ₃ O ₄	Acetylene	-	360	[80]
Co ₃ O ₄	Propylene	-	460	
Co ₃ O ₄	1,2-Dichloroethane	-	350	[81]
Co ₃ O ₄	Benzene	263	-	[82]
Nb ₂ O ₅	Toluene	400	-	[55]
Mn ₃ O ₄	Toluene	270	-	[83]
Mn ₂ O ₃	Toluene	295	-	
MnO ₂	Toluene	375	-	
Co ₃ O ₄	Propane	-	250	[84]
CeO ₂	Trichloroethylene	205	-	[85]
Mn ₂ O ₃	Ethylbenzene	374	-	[86]
Mn ₃ O ₄	Toluene	325	100	[87]
CuO	Toluene	-	535	
CeO ₂	O-xylene	240	-	[88]
CeO ₂	Naphthalene	195	-	

Compared to noble metal catalysts, non-noble metal oxides have gained significant attention due to their cost-effectiveness and strong resistance to poisoning. However, relevant studies have shown that constructing multi-component metal oxide composite systems can create synergistic effects at the molecular level, often leading to higher catalytic activity and selectivity than single-component metal oxides, thereby significantly enhancing the catalytic oxidation efficiency of VOCs.

3.4. Mixed-Metal Catalysts

The synergistic effects between metals in mixed-metal catalysts result in catalytic activity and oxidation performance that surpass those of single-metal catalysts. Currently, mixed-metal catalysts have become a research hotspot in the field of VOC treatment.

Wang et al. [89] investigated the effects of different Co loadings (1 wt%, 5 wt%, 10 wt%) on the low-temperature catalytic oxidation performance of CoCe bimetallic catalysts for toluene. Characterization using SEM, TEM, HRTEM, and elemental mapping (as shown in Figure 13a–j) revealed that the Co species in the CoCe-5 catalyst were highly dispersed, and the morphology was similar to that of CeO₂.

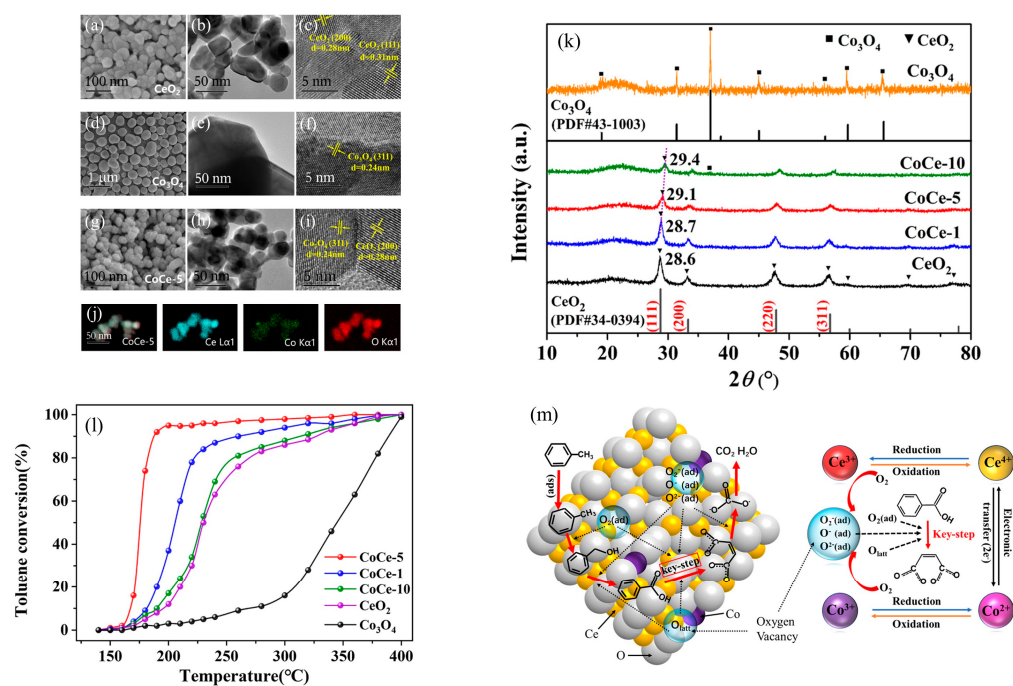


Figure 13. The SEM images of CeO₂, Co₃O₄, and CoCe-5 (a,d,g), TEM images (b,e,h), HRTEM image (c,f,i), the elemental distribution of CoCe-5 (j), the XRD characterization of the sample catalyst (k), the effect of the sample catalyst on the toluene conversion rate (l), and the reaction mechanism of toluene oxidation on the CoCe-5 sample (m) [89].

The Figure 13k XRD analysis shows that as the Co loading increased, the intensity of the CeO₂ characteristic peaks weakened and shifted to higher angles, indicating that Co species were successfully incorporated into the CeO₂ lattice. The introduction of an appropriate amount of Co significantly enhanced the catalyst's activity in the low-temperature oxidation of toluene. The Figure 13l results demonstrate that the CoCe-5 catalyst exhibited the best catalytic performance, achieving a 90% toluene conversion rate at 192 °C. Wang et al. proposed and described the reaction mechanism of toluene oxidation over the CoCe-5 sample (as shown in Figure 13m). The introduction of Co promoted the Co²⁺/Co³⁺ and Ce³⁺/Ce⁴⁺ redox cycles, enhancing the formation of oxygen vacancies. Gas-phase oxygen was activated at oxygen vacancies to form active oxygen species, while the interaction between Co²⁺ and lattice oxygen facilitated the reduction of Ce⁴⁺ to Ce³⁺. Toluene underwent complete oxidation to CO₂ and H₂O through intermediates such as benzyl, benzyl alcohol, and benzoate species, under the synergistic effect of active oxygen and oxygen vacancies. According to the Mars–van Krevelen mechanism, the creation and annihilation of oxygen vacancies were key steps in toluene oxidation, while adsorbed oxygen species participated in the vacancy redox cycle involving the conversion between gaseous oxygen and adsorbed oxygen.

Ali [58] prepared Au/TOS, Mn/TOS, Au-Mn/TOS, and TOS catalysts and compared their propane oxidation performance (as shown in Figure 14a). It was found that Au-Mn/TOS exhibited the best catalytic performance, achieving a conversion rate of 95% at 375 °C and complete conversion at 400 °C. The TEM characterization of the Au-Mn/TOS catalyst (Figure 14b) showed that gold nanoparticles (approximately 5–10 nm) were uniformly dispersed on the surface of TOS, and Au and Mn formed a synergistic region on the surface of CeO₂ and TiO₂. Upon observing the XRD patterns of the catalysts in Figure 14c—(a) Au-Mn/TOS, (b) Au/TOS, (c) Mn/TOS, and (d) TOS—it was found that the XRD diffraction patterns of the Au/TOS and Mn/TOS catalysts were identical to that of TOS. In contrast, the Au-Mn/TOS catalyst exhibited a noticeable change in the 37–39° 2 θ

range, with the combination of Au and Mn generating new diffraction peaks. The enhanced catalytic activity of the Au-Mn catalysts may be related to the presence of $\text{Au}_5\text{Mn}_2/\text{Au}_2\text{Mn}$. The XPS oxygen spectra of the catalyst before and after the catalytic reaction were studied, showing four main oxygen peaks (as shown in Figure 14d, A—after reaction; B—before reaction), corresponding to O_{Ti} (oxygen in TiO_2), O_{Ce} (oxygen in CeO_2), O_{Zr} (oxygen in ZrO_2), and OH^- peaks. It was found that Au and Mn could jointly attract non-stoichiometric oxygen and lattice oxygen belonging to CeO_2 and ZrO_2 , while some free lattice oxygen was attracted by TiO_2 , resulting in an increase in the O_{Ti} peak. Au and Mn jointly attract oxygen in a ratio of 1:6. Compared with monometallic catalysts, Au-Mn catalysts attract a higher total amount of oxygen, showing stronger synergistic effects. These phenomena can be explained by the Mars–Van Krevelen mechanism: after introducing Au into the Mn/TOS catalyst, strong synergistic effects occurred between Au and Mn, forming Au-Mn compounds, which promoted the mobility of non-stoichiometric and lattice oxygen in all the supporting oxides. The highly dispersed Au nanoparticles on the metal oxide support not only increased the migration rate of lattice oxygen but also led to the weakening of the metal–oxide bonds, collectively enhancing the catalytic activity of the Au-Mn/TOS catalyst.

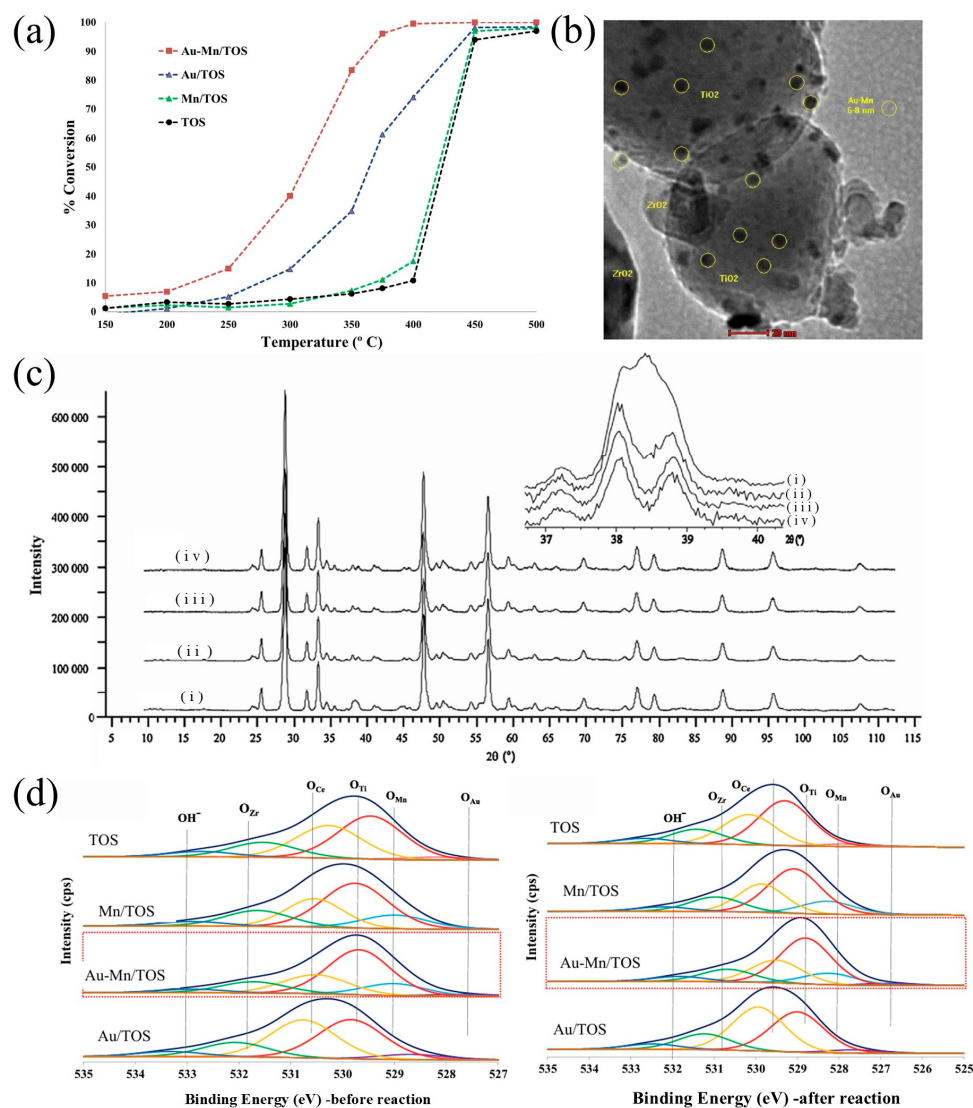


Figure 14. The propane conversion rates of Au/TOS, Mn/TOS, Au-Mn/TOS, and TOS catalysts (a), TEM image of Au-Mn/TOS (b), XRD images of Au/TOS, Mn/TOS, Au-Mn/TOS, and TOS catalysts (c), and XPS oxygen spectra (d) [58].

Carabineiro [90] studied the structures and performances of the Ce-Co and La-Co mixed oxides. Figure 15a–f show the SEM images of the samples Ce-Co 1:2 CX, Ce-Co 1:2 EM, La-Co 1:2 CX, and La-Co 1:2 EM, along with the corresponding EDS spectra labeled as Z1 (Figure 15c), Z2 (Figure 15d), Z1 (Figure 15g), and Z2 (Figure 15h). The Ce-Co 1:2 CX sample displays a uniform dark-bright region structure with a similar composition, while the Ce-Co 1:2 EM sample shows an uneven distribution of cobalt and cerium. The La-Co 1:2 CX surface features a porous structure with some porosity, and the La-Co 1:2 EM sample exhibits an uneven structure and element distribution. NH₃-TPD (Figure 15i) shows that the Ce-Co sample has a higher concentration of acidic sites in the low-temperature region (15.1 $\mu\text{mol/g}$), far exceeding that of the La-Co CX sample (6.1 $\mu\text{mol/g}$). The catalytic performance of the Ce-Co and La-Co samples is shown in Figures 15g and 15k, respectively. The Ce-Co catalyst can completely convert toluene at around 250 °C, whereas the La-Co catalyst exhibits poorer activity. This is due to the strong interaction between Ce and Co, which provides more active sites and higher reducibility.

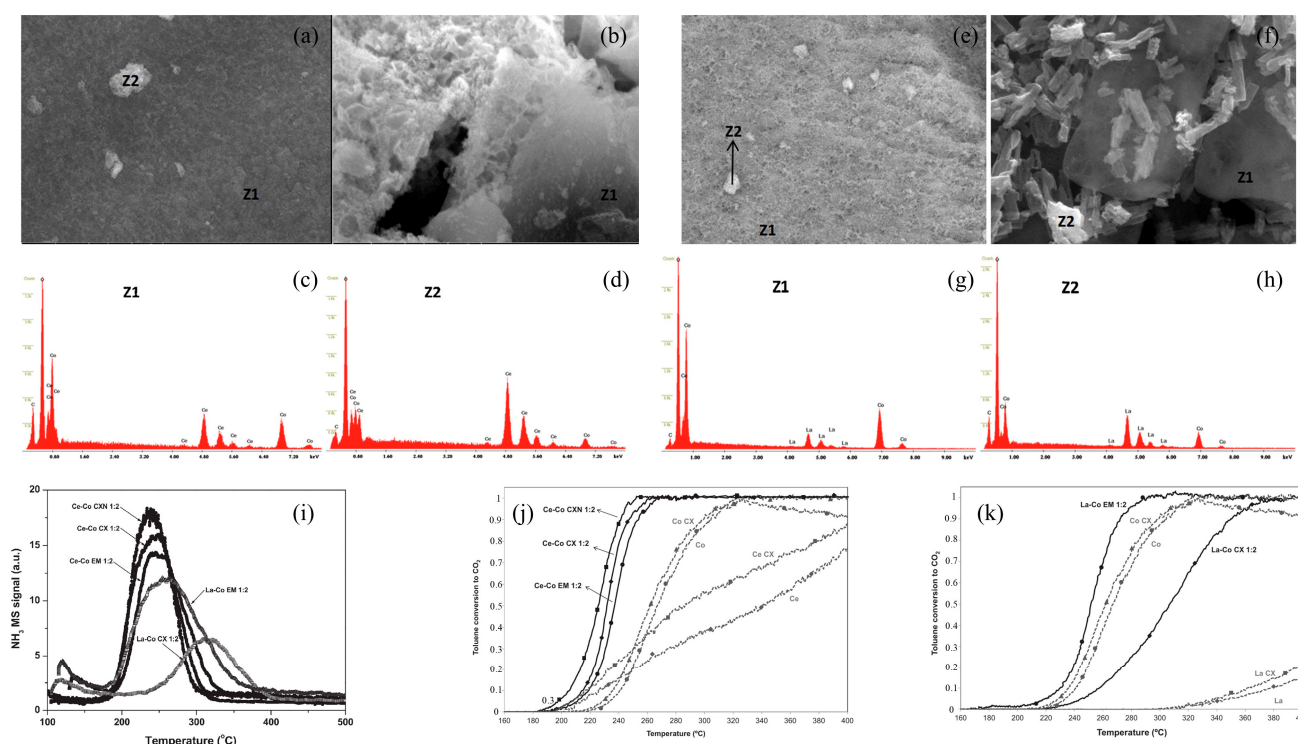


Figure 15. The SEM images of the samples Ce-Co 1:2 CX (a), Ce-Co 1:2 EM (b), La-Co 1:2 CX (e), and La-Co 1:2 EM (f); the corresponding EDS spectra marked as Z1 (c), Z2 (d), Z1 (g), and Z2 (h); and the NH₃-TPD profiles (i), as well as the toluene conversion efficiency of the Ce-Co and La-Co samples (j,k) [90].

TANG et al. [91] prepared a porous-layered Mn-Ce composite oxide catalyst with a specific surface area of 176.2 m²/g using a simple precipitation/decomposition method. Due to the presence of a large amount of Mn⁴⁺ and Ce³⁺, as well as abundant surface adsorbed oxygen, the catalyst demonstrated excellent catalytic performance in VOC oxidation. The catalyst achieved 90% conversion efficiency for benzene, toluene, and ethyl acetate at temperatures of 260 °C, 245 °C, and 180 °C, respectively.

Based on the review of the existing catalysts for VOCs [13], this paper further summarizes the latest research progress of mixed-metal catalysts in the oxidation of VOCs, and the related research results are shown in Table 6.

Table 6. Research findings on mixed metal catalysts for VOC treatment.

Catalyst	VOCs	Temperature (°C)	Conversion (%)	Reference
Au-Pd	Toluene	168	90	[92]
Au-Co	Toluene	300	100	[93]
Au-Ir	Toluene	250	100	[94]
Mn-Ti	Chlorobenzene	177	90	[95]
Sn-Mn-Ti	Chlorobenzene	225	97	
Cu-Co	Benzene	290	90	[96]
Co-Ce (6:1)	Benzene	295	100	[97]
Co-Ce (12:1)	Benzene	285	100	
Co-Ce (18:1)	Benzene	268	100	
Co-Ce (24:1)	Benzene	310	100	
Ce-Zr	1–2 Dichloroethane	120	90	[98]
Mn-Co	toluene	250	98.7	[99]
Mn-Co	Ethyl acetate	194	90	[100]
Mn-Co	n-hexane	210	90	
Mn-Ce	Benzene	260	90	[91]
Mn-Ce	Toluene	245	90	
Mn-Ce	Ethyl acetate	180	90	
La-Cu (1:1 CX)	Ethyl acetate	310	100	
La-Cu (1:2 CX)	Ethyl acetate	309	100	[101]
La-Cu (1:1 EM)	Ethyl acetate	319	100	
La-Cu (1:2 EM)	Ethyl acetate	304	100	
La-Co (1:1 CX)	Ethyl acetate	245	100	
La-Co (1:2 CX)	Ethyl acetate	243	100	
La-Co (1:1 EM)	Ethyl acetate	242	100	
La-Co (1:2 EM)	Ethyl acetate	239	100	
Cu-Ce	Chlorobenzene	328	99	[74]
Mn-Al	Toluene	260	100	[102]
Co-Al	Toluene	310	100	
Cu-Al	Toluene	345	100	
Fe-Al	Toluene	385	100	
Ni-Al	Toluene	380	100	[103]
Pd-Pt	Toluene	160	98	
Cu-Mn (8:2)	Toluene	377	100	[87]
Cu-Mn (86:14)	Toluene	390	100	
Cu-Mn (94:6)	Toluene	380	100	
Cu-Mn (98:2)	Toluene	389	100	

In the field of mixed-metal catalyst research, researchers construct bimetallic or multi-metallic catalysts by introducing different metal elements (such as Co, Ce, Mn, Au, etc.) to fully utilize the synergistic effects between metals. Numerous studies have shown that by optimizing the composition and structure of such catalysts, their catalytic performance can be significantly enhanced, achieving the complete combustion of single-component VOCs at relatively low temperatures (400 °C).

In recent years, regarding chalcogenide-based catalysts during the reaction process, Liu et al. [104] found that the denitrification performance of MnFeTiO_x catalysts significantly decreased after sulfidation treatment, which was mainly attributed to two aspects. Firstly, the presence of SO₂ inhibited the adsorption of NH₃ on the Lewis acid sites, which led to a reduction in the nitrate species on the surface of the catalysts, which in turn impeded the redox reaction between NH₃ and its intermediates and the NO_x redox reaction between NH₃ and its intermediates and NO_x, which ultimately reduced the NO_x conversion. Secondly, SO₂ reacts with NH₃ adsorbed on the catalyst surface to generate sulfur-containing compounds such as NH₄HSO₄ or (NH₄)₂SO₄, which are deposited on

the catalyst surface and cover the active sites, further reducing the catalytic activity. The catalyst deactivation poisoning mechanism mainly includes four aspects. First, harmful substances (e.g., sulfur, chlorine, etc.) react with the active components of the catalyst to generate stable compounds, resulting in the irreversible deactivation of the active sites. Second, impurities or reaction by-products (e.g., ammonium sulfate, chloride, etc.) are deposited on the surface of the catalyst as crystals, which cover the active sites and impede the contact of the reactants [105]. Third, the poisonous substance destroys the pore structure of the catalyst or causes sintering, resulting in a lower specific surface area and fewer active sites [106]. Finally, toxicant molecules compete with reactants for adsorption on the active sites and occupy the catalytic reaction sites [107]. These mechanisms can act individually or synergistically, ultimately leading to a significant degradation in catalyst performance.

In recent years, perovskite-based catalysts have gradually attracted the attention of researchers as a new type of catalytic material. Although its research in the field of VOC degradation is still in its infancy, it has been demonstrated that this type of catalyst has unique advantages and broad application prospects in VOC pollution control.

Liu et al. [108] investigated the performance of hollow spherical LaCoO_3 catalysts in toluene oxidation. They found that the LaCoO_3 catalyst exhibited excellent low-temperature activity, achieving 50% toluene conversion at 220 °C and 90% conversion at 237 °C. This superior performance was attributed to its large specific surface area, which provided abundant active sites and favorable oxygen adsorption and reduction capabilities. Rezlescu et al. [109] conducted a comparative study between iron spinel (CuFe_2O_4 , MgFe_2O_4 , $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$) and perovskite-type (SrMnO_3 , FeMnO_3 , $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$) catalysts. The results showed that perovskite-type SrMnO_3 and $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$ demonstrated superior performance in acetone oxidation (>95% conversion at 300 °C), significantly outperforming iron spinel catalysts, which achieved approximately 70% conversion. The excellent performance of perovskite-type catalysts was primarily attributed to their higher concentration of oxygen vacancies. These oxygen vacancies could accommodate more adsorbed oxygen species (O^- , O_2^- , O^{2-}), thereby enhancing the oxidation efficiency of VOCs. Tarjomannejad et al. [110] examined the catalytic performance of various perovskite-type catalysts $\text{LaMn}_{1-x}\text{B}_x\text{O}_3$ ($\text{B} = \text{Cu}, \text{Fe}$; $x = 0, 0.3, 0.7$) and $\text{La}_{0.8}\text{A}_{0.2}\text{Mn}_{0.3}\text{B}_{0.7}\text{O}_3$ ($\text{A} = \text{Sr}, \text{Ce}$; $\text{B} = \text{Cu}, \text{Fe}$) in toluene oxidation reactions. They discovered that Fe doping was more effective than Cu doping in $\text{LaMn}_{1-x}\text{B}_x\text{O}_3$ perovskite-type catalysts, and the introduction of Sr or Ce at the A site further enhanced the catalytic activity. Among these, $\text{La}_{0.8}\text{Ce}_{0.2}\text{Mn}_{0.3}\text{Fe}_{0.7}\text{O}_3$ exhibited the best performance, achieving complete toluene conversion at 200 °C.

4. Summary and Outlook

RTO technology is a mainstream method for treating VOCs, offering high removal efficiency and stable operation. However, its high-temperature operation results in increased fuel reheating costs. To reduce energy consumption, catalytic combustion technology was introduced, enabling the efficient oxidation of VOCs into water and carbon dioxide at temperatures between 250 and 400 °C. This approach lowers reheating demands, reduces operating costs, and effectively suppresses the formation of harmful by-products such as dioxins.

Catalysts used in catalytic combustion include precious metals, non-precious metal oxides, and mixed-metal oxides. Precious metal catalysts exhibit high efficiency but are expensive and susceptible to sintering and poisoning. Non-precious metal oxide catalysts are cost-effective, resistant to poisoning, and have long lifespans, but their efficiency is relatively lower. Mixed-metal oxide catalysts offer superior activity and stability. However,

all catalysts tend to deactivate over time due to carbon deposition, poisoning, sintering, and water vapor adsorption.

In current VOC catalytic oxidation research, catalysts for single-component VOCs have received significant attention. However, industrial emissions typically consist of complex mixtures of multiple VOCs. Therefore, research should expand into the area of mixed VOC catalytic oxidation, focusing on the development of efficient catalysts and the optimization of multi-site active designs to enhance treatment efficiency and adaptability for complex waste gases. Moreover, the preparation methods of catalysts and the selection of support materials are crucial. Optimizing preparation processes, reducing costs, and improving catalyst performance—particularly through doping techniques to increase the specific surface area and expose more active sites—can further enhance catalytic efficiency and stability. Lastly, improving catalyst thermal stability is also a key focus for future research. By designing new active components or introducing promoters, thermal stability can be enhanced, catalyst deactivation can be reduced, and economic benefits can be improved. In conclusion, future research should focus on the in-depth studies of multi-component VOC catalytic oxidation, combining advanced catalyst design, preparation process optimization, and enhanced thermal stability to provide more efficient, economical, and sustainable solutions for industrial waste gas treatment.

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