

An overview of thermocatalyst technology in air pollution control: (narrative review)

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Abstract:

Air pollution represents a global challenge with significant adverse impacts on human health and the environment. In recent years, modern technologies have received considerable attention for their potential in controlling air pollution. This study provides a comprehensive review of various thermocatalytic technologies employed to mitigate air pollution. Data were collected from a wide range of online scientific literature sources, including databases such as ISI Web of Science, Scopus, Medline (via PubMed), Science Direct, and Google Scholar. Specific keywords related to thermocatalysts, air purification, air pollution, gaseous purification, gaseous pollution, and thermal catalysts were utilized in the search strategy. In thermocatalytic processes, the Mars-van Krevelen (MVK), Eley-Rideal (E-R), and Langmuir-Hinshelwood (L-H) mechanisms play crucial roles. Thermocatalysts demonstrate high efficiency in the removal and reduction of air pollutants. The primary challenges in applying these catalysts include their thermal energy activation and high manufacturing costs. Consequently, ongoing research focuses on reducing energy consumption, lowering production costs, and enhancing catalyst performance in pollutant removal, all of which are conducted at the laboratory scale. To this end, it is recommended that future research prioritize the design and development of optimized thermocatalysts to meet industry needs.

Keywords: Air pollution; Thermocatalys; Thermal catalyst; Temperature; Volatile Organic Compounds (VOCs)

1. Introduction

Pollution is a significant issue that affects various aspects of our environment, including water, air, noise levels, and land. Every individual seeks a healthy life [1]. One of the primary challenges in environmental conservation is the mitigation of atmospheric pollution [2]. Annually, a substantial quantity of harmful substances - including sulfur dioxide, nitrogen oxides, oxides, stable organic compounds, VOCs, acids, particulate matter, and various metallic compounds - are emitted into the atmosphere [2-4]. The primary contributors to air pollution include emissions from vehicular traffic, industries, utilities, construction, and the combustion of fossil fuels [5-7]. It is directly associated with the

prevalence of respiratory disorders and diminished lung function [8]. Several studies have demonstrated that respiratory issues, ranging from short-term allergies to long-term chronic illnesses, are all attributable to contaminated air [9, 10]. Approximately 91% of the global population is exposed to substandard air quality compared to the WHO's recommended guidelines [7]. So, 4.2 million deaths were linked to ambient air pollution in 2018 [1]. It was also noted that approximately 88% of these fatalities occurred in countries with low or moderate income levels [11]. Both indoor and outdoor air pollution are acknowledged for their role in causing significant adverse health effects on people and for influencing social and economic progress [12]. Previous studies have shown that indoor air pollution has

intensified over the past decade, leading to the emergence of the term Sick Building Syndrome (SBS). SBS pertains to the adverse impacts that organisms endure as a result of being exposed to substandard indoor air quality [13]. The US Environmental Protection Agency (US-EPA) has identified indoor air pollution as one of the top five environmental hazards, with significant implications for human health [14, 15]. The detrimental effects of poor indoor air quality encompass a range of health issues, such as respiratory symptoms, allergies, sensory irritation, asthma, SBS, cardiovascular diseases, headaches, and fatigue [15]. Given that people typically spend over 90% of their lives in enclosed spaces with poor air circulation, the development of effective regulatory strategies has become a crucial concern [16]. Advancing techniques and innovations for acquiring materials used in air and gas purification has become a significant priority [2]. In buildings equipped with heating, ventilation, and air conditioning (HVAC) systems, achieving optimal suspended particulate matter levels has traditionally depended on the use of HEPA filters, non-thermal plasma air filters, and polytetrafluoroethylene (PTFE) multi-tube high-efficiency membrane air filters [17, 18]. The adsorption of indoor VOCs has been effectively achieved through the use of activated carbon fiber filters (ACF) and photochemical oxidation methods [19, 20]. Additionally, the removal of inorganic gases has been facilitated by the employment of ionic liquids and porous materials [21]. The materials and methods used for removing toxic and harmful pollutants from water and air include absorption [22–26], biological treatment [24], catalytic and photocatalytic degradation [24], chemical precipitation [24, 25], electrochemical treatment [25], liquid-liquid extraction [24], membrane filtration [24, 25], and ion exchange [24, 25].

The removal of gaseous pollutants can generally be categorized into two distinct processes: adsorption and destruction. Destructive processes, such as oxidation techniques, including electrostatic precipitators, ozone generation, plasma-driven oxidation, and photochemical oxidation (PCO), are recognized for their ability to eliminate pollutants through chemical alteration. Conversely, adsorption involves the capture of pollutants by a sorbent media via physical or chemical binding [15]. Each of these control technologies has inherent limitations but plays a crucial role in mitigating the diverse array of indoor air pollutants [15]. Nano adsorbents demonstrate significant potential as a viable, accessible, and cost-effective solution, with numerous research endeavors exploring various nanomaterials for enhanced pollutant removal due to their high surface area-to-volume ratio and ease of surface functionalization [27]. Recently, advanced oxidation processes (AOPs) have been recognized as effective methods for removing air pollutants [28]. By combining adsorbents with metal oxides as mediators, the adsorption capabilities of the adsorbent can be enhanced by the catalytic properties of the metal oxides, allowing for the effective elimination of pollutants from the fluid flow [29]. In the photocatalytic oxidation method for air purification, semiconductor catalysts are typically combined with ultraviolet or visible light to convert organic compounds in indoor air into harmless and odorless byproducts, such as

water vapor and carbon dioxide [30]. The requirement for ultraviolet (UV) or visible light exposure in the process of photocatalytic degradation (PCD) imposes limitations on the feasibility and environmental benefits of this method when applied on a large industrial scale. Therefore, exploring novel catalysts that can be activated by alternative environmental stimuli, such as temperature, humidity, chemical conditions, or biological processes, holds significant potential [31]. Recent studies have highlighted the degradation of contaminants through thermal catalysis without light exposure due to its benefits, including reduced energy and chemical consumption, as well as simplified operational procedures [32].

Several studies have investigated the effectiveness of thermocatalysts in removing pollutants from air and water. As new and innovative technologies for controlling and reducing air pollution require thorough investigation and analysis, this study examines the various thermocatalyst technologies available in the field of air pollution control. The aim of this study is to identify the most suitable catalyst that offers optimal performance and efficiency, as well as to determine the best materials and operating conditions for pollutant reduction. Overall, this review provides a comprehensive and practical overview of the performance of thermocatalysts and their impact on improving air quality and reducing pollution. Such studies can increase public, scientific, and industrial awareness of the significance and effectiveness of thermocatalytic technologies in combating air pollution. Furthermore, this research could pave the way for the development of catalysts with acceptable performance in both environmental and industrial applications.

2. Material and methods

A narrative review of the scientific literature on the thermocatalyst technology was conducted, focusing on research related to air pollution control. Data were gathered from various online scientific literature sources, including databases such as ISI Web of Science, Scopus, Medline (via PubMed), Science Direct, and Google Scholar. Specific keywords related to the thermocatalyst, air purification, air pollution, gaseous purification, gaseous pollution, and thermal catalyst were utilized in the search strategy. The study's inclusion criteria involved selecting research that contained one or more of these keywords in the article titles, focusing on articles published in English-language journals. Only studies that employed thermocatalyst technology for removing and destroying air pollutants were considered for extraction and evaluation. The research selection process is illustrated in figure 1. In total, 64 articles were identified for screening, and 59 articles that met these criteria were selected for review.

3. Results and discussion

3.1 Functional mechanism of thermocatalyst

Catalytic oxidation has been empirically recognized as one of the most reliable and efficient methods for completely converting contaminants into carbon dioxide and water through thermal catalysis [1, 34]. Thermocatalytic

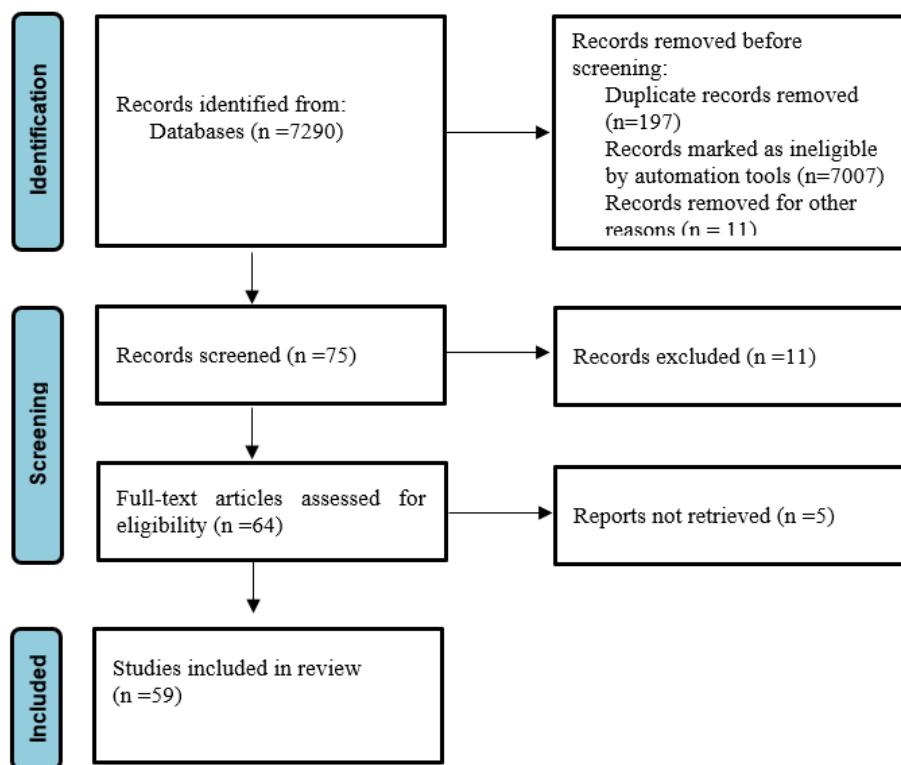


Figure 1. Study selection flowchart.

processes involve breaking existing chemical bonds and forming new ones by providing sufficient thermal energy to overcome the activation energy (E_a). The adsorption of reactants, the state of intermediates, and the release of products are crucial factors in determining the overall catalytic efficiency and specificity [22–24]. The introduction of catalysts into a reaction environment alters the reaction pathway, leading to the formation of a transition state with lower activation energy. Incorporating catalysts into a reaction mechanism alters the pathway, forming a transition state with reduced activation energy [24]. Figure 2 provides a schematic representation of the activation energy and reaction pathway throughout the thermocatalytic process. Thermocatalytic decomposition is a process that utilizes catalysts to reduce the activation energy required, enabling flameless combustion at lower ignition temperatures [35]. The harmful molecules in polluted air adhere to the ac-

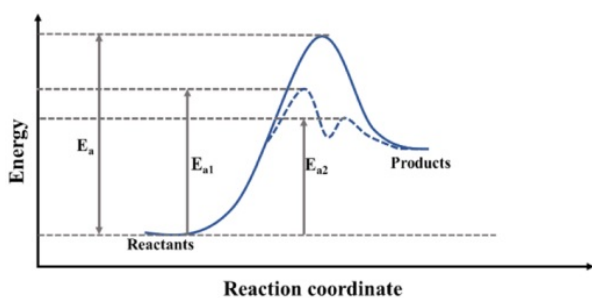


Figure 2. Schematic representation of the activation energy and the pathway of a thermocatalytic reaction throughout the reaction process, reproduced with permission from [24].

tive sites of the catalysts, leading to a series of chemical decomposition reactions that produce simpler molecular compounds such as CO_2 and H_2O . The widespread and effective use of thermocatalytic decomposition suggests that this purification method is poised to replace traditional adsorption techniques [36, 37]. The advancement of innovative thermocatalytic methods that operate under normal conditions has significantly expanded their application in addressing air quality issues [25, 38, 39]. The lack of reliance on costly and often unfeasible light sources provides thermocatalytic technology a competitive advantage over photocatalytic methods, particularly when applied at room temperature [25, 40]. There are several methods for synthesizing thermocatalysts, including sol-gel, precipitation, hydrothermal [36, 41], solvothermal [36, 42], microwave synthesis [38], Pechini method [39], oxalate method [40], wetness impregnation [43], reductive impregnation [44], wet chemical techniques [45], and solution combustion [46]. The choice of method depends on the available equipment, facilities, and specific objectives of the study. Among these, precipitation, saturation [47], hydrothermal [36, 41], and solvothermal [36, 42] methods are most commonly used for catalyst preparation. Following is a brief explanation of three methods: precipitation, hydrothermal, and solvothermal synthesis.

In the precipitation method, active metal nitrate salts, such as copper and zinc, are dissolved in deionized water and vigorously combined with support powders (e.g., Al_2O_3 and SiO_2), with a NaOH solution added incrementally. The resultant product undergoes aging at room temperature, followed by filtration, washing, drying, and calcination prior to catalytic testing, as illustrated in figure 3 [33].

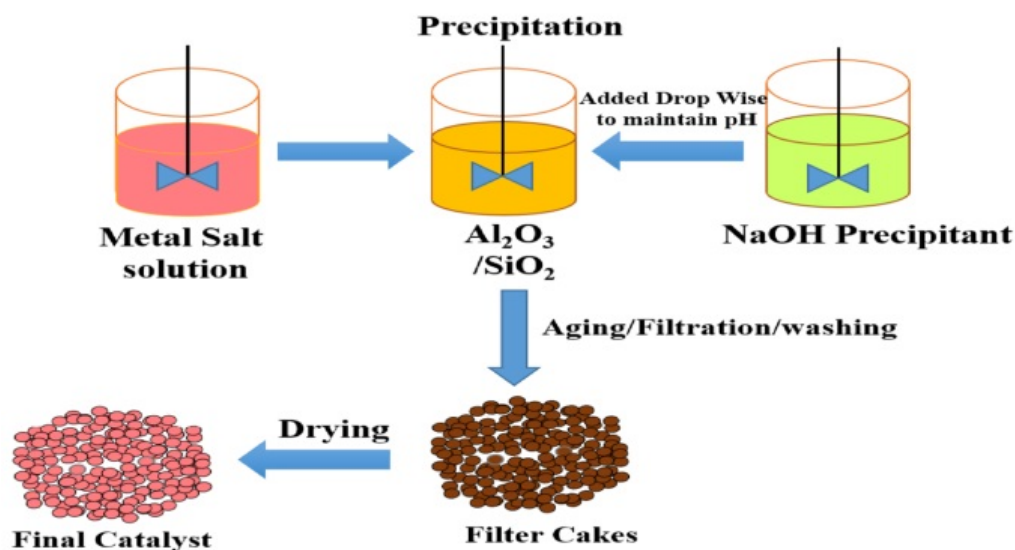


Figure 3. Schematic representation of catalyst synthesis by a precipitation method, reproduced with permission from [33].

Hydrothermal synthesis is an effective method for producing large quantities of high-purity catalysts. It involves dissolving a metal salt in a water/ethylene glycol solution and stirring at elevated temperatures. A precursor solution is prepared and added gradually to the metal salt solution, resulting in a transparent mixture. This is then placed in an autoclave and heated, followed by centrifugation to separate the powder from the solution. Finally, the product is dried in a vacuum oven to yield the desired metal catalyst [33, 49]. Figure 4 depicts the hydrothermal synthesis of copper-based catalysts.

In solvothermal synthesis, the starting materials are typically dissolved in an appropriate solvent. The solution is then heated in a pressurized vessel, usually an autoclave, for a specified duration. This process enables reactions to occur at temperatures and pressures exceeding the boiling point of the solvent, facilitating the formation of specific nanocrystalline structures with unique properties [48, 68]. Figure 5 illustrates the solvothermal synthesis of copper-based nanoparticles, specifically $\text{Cu}_2\text{Ni}_{1+x}\text{Sn}_{1-x}\text{S}_4$ (CNTS). Numerous studies have investigated various types of catalysts, focusing on the significance and impacts of catalyst

preparation, including aspects such as composition, reduction, and calcination. These studies aim to assess and critique the efficacy of catalysts for use in thermocatalytic decomposition [26, 47, 50]. Table 1 presents the review articles referenced in this study, along with the objectives of each article. Table 2 summarizes the research conducted in the field of thermocatalysts, especially focusing on the destruction and removal of air pollutants.

Functionalizing hydrophilic catalytic materials with alkali salts can enhance their ability to remove VOCs by increasing their sorption capacity [51]. The incorporation of nanocatalysts with additional materials has demonstrated a significant impact on the structural characteristics of thermocatalysts [57]. The advancement of thermocatalysis technology, evolving from direct thermal breakdown, represents the most efficient approach to treating VOCs [52]. The degradation of VOCs through thermocatalytic oxidation typically adheres to specific mechanisms [25]. (a) The Mars-van Krevelen (MVK) mechanism is commonly understood as a redox process consisting of two primary steps. First, the reactant interacts with the catalyst lattice oxygen, transforming into harmless H_2O and CO_2 while simulta-

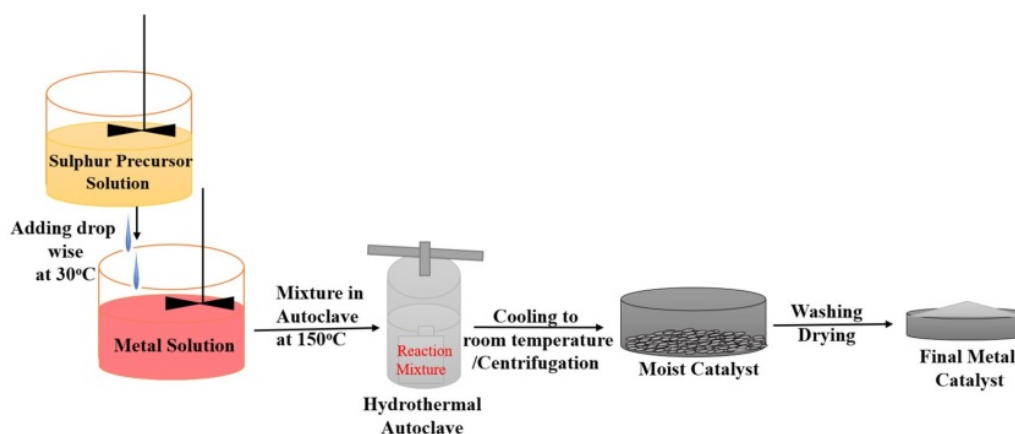


Figure 4. Schematic representation of the hydrothermal synthesis of copper-based catalyst, reproduced with permission from [33].

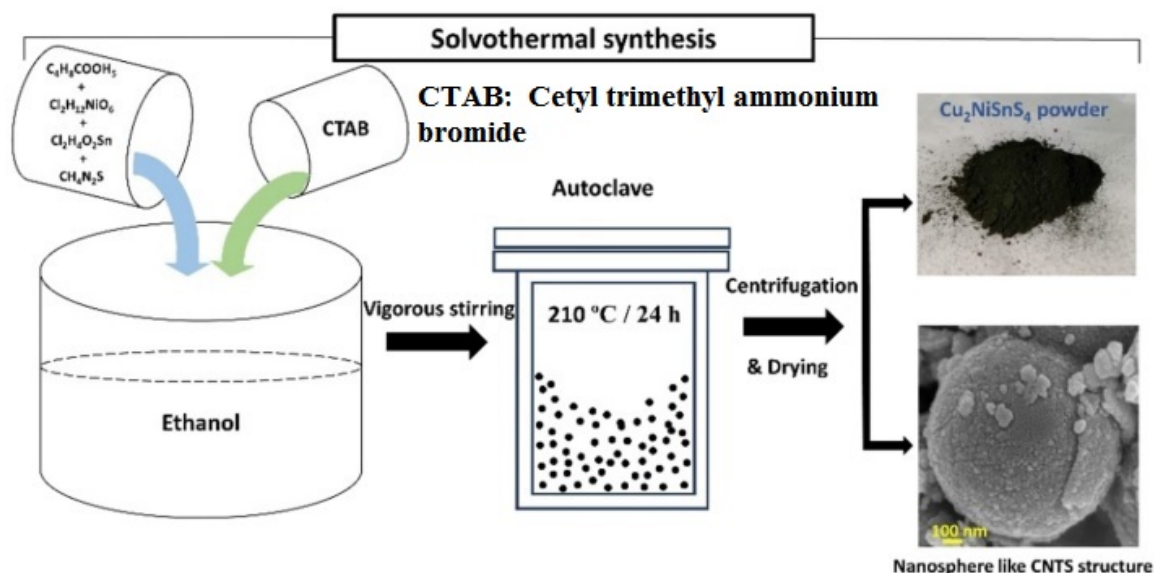


Figure 5. Schematic representation solvothermal synthesis, reproduced with permission from [48].

neously producing oxygen vacancies. Subsequently, the oxygen present in the surrounding air replenishes these vacancies [53, 54]. Oxygen exchange between the catalyst and the pollutant is considered the limiting factor, while the re-oxidation of the reduced catalyst is crucial for catalyst stability within the MVK mechanism, as reduction creates oxygen vacancies that can be replenished by chemisorbed oxygen through electron withdrawal from available donors. Figure 6 presents a schematic MVK mechanism in the thermocatalytic degradation of VOCs [84]. The MVK mechanism changes with temperature. For instance, in the catalytic degradation of formaldehyde, surface hydroxyls on the Ag (111) facets of K-Ag/Co₃O₄ dominate catalytic activity at temperatures below 80 °C. However, above 80 °C, O²⁻ species migrate from Co₃O₄ to replenish the depleted hydroxyl groups [25]. Figure 7 shows the reaction pathway for formaldehyde oxidation over a K-Ag/Co₃O₄ catalyst. (b) The Eley Rideal (E-R) Mechanism involves a reaction that occurs in a single active state. This mechanism can be succinctly described as the interaction between the adsorbed state and the non-adsorbed state. In the degradation of VOCs, subsequent reactions following the E-R mechanism occur between adsorbed pollutants and gaseous oxygen or between adsorbed oxygen species and pollutants in the gas phase [54, 55]. (c) The Langmuir-Hinshelwood (L-H) mechanism pertains to catalytic reactions that primarily occur as surface reactions between two adsorbed molecules located on similar active sites. This phenomenon is commonly observed in the catalytic degradation of VOCs, particularly in reactions involving noble metal-doped manganese oxides [53, 54, 69].

3.2 Thermocatalyst and air pollution

In indoor environments where VOCs concentrations are low, achieving direct thermal degradation is challenging due to the high energy required. Moreover, the thermal degradation process can produce harmful by-products [52]. In contrast, thermocatalytic degradation is considered an

optimal approach for addressing VOCs in indoor settings, offering greater efficiency and lower energy consumption [54]. Various catalysts, such as those based on transition metals and noble metals, have been employed for thermocatalysis [52, 56]. Elevated temperatures in thermocatalytic processes are employed to accelerate reaction rates, achieve the desired outcomes, and overcome kinetic barriers [33, 86]. However, the practical application of thermocatalysts has often been limited by the requirement for high temperatures to ensure effective performance [25]. Efficient thermocatalysts must be capable of achieving nearly complete oxidation of VOCs at relatively low reaction temperatures, ideally below 300 °C, to ensure cost-effectiveness and safe operation [43]. Figure 8 illustrates the temperatures needed for the thermocatalytic degradation of various VOCs.

Supported noble metal catalysts (SNMCs) are highly valued due to their numerous advantages, including strong resistance to deactivation, prolonged time-on-stream performance, exceptional catalytic activity, and ease of regeneration. These attributes make them particularly suitable for the oxidation of VOCs in practical applications [43, 58, 59]. The performance and efficiency of SNMCs are typically influenced by the combined effects of particle distribution and the arrangement of catalytic sites (such as Pt centers). These factors are determined by various parameters, such as the type of precursor, synthesis method, particle size, shape, and the physical and chemical characteristics of the supporting material [58]. Kim et al. investigated the efficiency of a platinum (Pt) catalyst supported on titanium dioxide (TiO₂) for the thermocatalytic oxidation of benzene in the presence of air. The enhanced performance of Pt/TiO₂-R (where 'R' denotes the high-temperature hydrogen-based reduction pre-treatment of the catalyst) compared to its non-reduced counterpart was attributed to the increased presence of metallic Pt nanoparticles on the TiO₂ surface as well as the strong metal-support interactions (SMSIs). The interactions at the Pt-TiO₂ interface led to the partial reduction of the metal oxide structure, resulting in the forma-

Table 1. The review articles in the field of thermocatalysts, along with the objectives of each article.

Title	Year	Purpose	Ref.
Review of synergistic photo-thermo-catalysis: Mechanisms, materials, and applications	2020	An analysis of the methods, combined materials, and catalytic properties.	[1]
Plasmonic photothermal catalysis for solar-to-fuel conversion: current status and prospects	2021	A Review of the advantages and difficulties associated with the use of plasmonic photothermal technology.	[22]
Metal-support interaction for heterogeneous catalysis: from nanoparticles to single atoms	2020	Effect of particle size on the metal-support interactions (MSI) on various substrates, the catalytic roles of MSI in chemical reactions, and the changes in MSI under different reaction conditions.	[23]
Research progress on methane conversion coupling photocatalysis and thermocatalysis	2021	Recent research on the photothermal indirect conversion of methane, along with direct conversion methods through photocatalysis and thermocatalysis. The challenges and future prospects of direct methane conversion using single-atom catalysts within a photothermal.	[24]
Advances in thermocatalytic and photocatalytic techniques for the room/low-temperature oxidative removal of formaldehyde in air	2020	The evaluation of the thermocatalytic and photocatalytic effectiveness of created nanomaterials for eliminating gaseous formaldehyde, along with the obstacles and future potential of these technologies.	[25]
An overview of the production of hydrogen and carbon nanomaterials via thermocatalytic decomposition of methane	2023	A review of experimental research on the chemical kinetics of thermocatalytic decomposition (TCD), highlighting current advancements, their significance for reactor design, and future perspectives in TCD development.	[26]
Production of greenhouse gas-free hydrogen by thermocatalytic decomposition of methane-A review	2015	A comprehensive examination of advancements in laboratory-scale TCD.	[47]
Sustainable fuel production by thermocatalytic decomposition of methane-A review	2017	A review of laboratory-scale research on TCD, focusing on recent developments such as the co-feeding effect and catalyst regeneration to improve overall process efficiency.	[50]
Recent advances and future challenges in the catalytic combustion of light hydrocarbon VOCs	2024	Research advancement encompasses the evolution of the catalytic combustion of light hydrocarbons, the strategic development of effective catalyst reaction mechanisms, the enhancement of characterization methodologies, and prospective challenges.	[51]
Manganese-based catalysts for indoor volatile organic compound degradation with low energy consumption and high efficiency	2021	An advancement in manganese-based catalysts involving thermocatalytic, photocatalytic, and photo-thermocatalytic processes for the catalytic degradation of VOCs.	[52]
Recent progress of thermocatalytic and photo/thermocatalytic oxidation for VOCs purification over manganese-based oxide catalysts	2021	A study on the development of different manganese-based oxide catalysts and manganese-based monoliths for effective VOCs removal, catalytic mechanisms, challenges, and future potential.	[53]
A systematic review of intermediates and their characterization methods in VOCs degradation by different catalytic technologies	2023	An investigation of the intermediate products in the process of eliminating various VOCs by different catalytic technologies. Advantages and disadvantages of various catalytic technologies in the control of by-products.	[54]
Simple thermocatalytic oxidation degradation of VOCs	2022	The use of noble metal catalysts and metal oxide catalysts for the thermal catalytic oxidation of VOCs. Challenges in the degradation of VOCs through this method and the potential future developments.	[55]
Noble-metal single-atoms in thermocatalysis, electrocatalysis, and photocatalysis	2021	A review of the recent advancements in noble-metal single-atom catalysts (NMSACs) for catalytic applications, as well as the challenges and future prospects in their design.	[56]

Continue of Table 1.

Title	Year	Purpose	Ref.
Understanding the progress and challenges in the fields of thermo-catalysis and electro-catalysis for the CO ₂ conversion to fuels	2024	Recent advancements in CO ₂ conversion using various catalysts involve examining and contrasting studies focused on the conditions used, as well as the activity and stability of catalysts for both thermocatalytic and electrocatalytic CO ₂ conversions.	[33]
Applications of Al ₂ O ₃ -Based Nano-Catalysts in Thermocatalytic CO ₂ Transformations: Impacts of Surface Acidity and Basicity	2023	An investigation of a range of modification strategies, such as the use of promoters and various synthesis or treatment methods on tuning the surface acidity and basicity of Al ₂ O ₃ -based nano-catalysts.	[57]
Platinized titanium dioxide (Pt/TiO ₂) as a multi-functional catalyst for thermocatalysis, photocatalysis, and photothermal catalysis for removing air pollutants	2021	A review of the effectiveness of multi-functional platforms for the elimination of gaseous pollutants, focusing on the material properties, process factors, and the fundamental mechanisms involved.	[58]
Review on noble metal-based catalysts for formaldehyde oxidation at room temperature	2019	A focus on the relationship between the chemical and structural properties of the catalysts and their formaldehyde oxidation performance, as well as the catalytic reaction mechanisms.	[59]
Thermocatalytic Degradation of Gaseous Formaldehyde Using Transition Metal-Based Catalysts	2023	A review of the exposed crystal facets, alkali metal and nitrogen modification, precursor types, and alkaline or acid treatments in the thermocatalysts activity of transition metal oxide.	[60]
A review of CO ₃ O ₄ -based catalysts for formaldehyde oxidation at low temperature: Effect parameters and reaction mechanism	2020	The advancements in research concerning CO ₃ O ₄ -based catalysts for the oxidation of formaldehyde in recent years.	[61]
Advances on transition metal oxides catalysts for formaldehyde oxidation: A review	2017	An overview of different elements that improve activity at low temperatures, including morphology and tunnel structures, synthesis techniques, specific surface area, the quantity and nature of active surface oxygen species, oxidation state, and the density of active sites.	[62]
Recent progress in materials exploration for thermocatalytic, photocatalytic, and integrated photothermocatalytic CO ₂ -to-fuel conversion	2022	Recent developments in material design for effective CO ₂ conversion via thermocatalysis, photocatalysis, and photothermocatalysis over the last five years highlight the reaction pathways and mechanisms involved in activating the C=O bond and forming intermediates.	[63]
Low-temperature catalytic oxidation of volatile organic compounds: a review	2015	An analysis of various common metals used for the catalytic oxidation of VOCs and the impact of key influencing factors, including the characteristics of the metal and support, dispersion, particle size, and metal morphology.	[64]
Thermocatalytic decomposition of methane: a review on carbon-based catalysts	2023	The effect of the carbon source, particle dimensions, surface area, and active sites on the performance of carbon materials as catalysts and support structures.	[65]
Two-dimensional nanomaterials in thermocatalytic reactions: transition metal dichalcogenides, metal phosphorus trichalcogenides and MXenes	2023	A review of the use of 2D transition metal dichalcogenides (TMDs), metal phosphorus trichalcogenides (MPTs), and MXenes in thermocatalysis.	[66]
Photocatalytic and thermocatalytic conversion of methane	2021	An overview of different techniques and approaches for converting methane (CH ₄) using thermocatalytic and photocatalytic methods, for example, non-oxidative coupling, oxidation, steam reforming of methane (SRM), CO ₂ Reforming of Methane (CRM), and the functionalization of methane.	[67]

tion of Ti³⁺ centers and oxygen vacancies. In-situ analysis using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) revealed that benzene molecules were converted into carbon dioxide through intermediates such as phenolate, benzoquinone, carboxylate, and carbon monoxide [43]. Benzene molecules initially adsorb onto active sites, while O₂ molecules undergo dissociative adsorption on Pt nanoparticles, producing O*. The subsequent reaction of adsorbed benzene with O* generates phenolate species, leading to aromatic ring-opening and oxidation processes that yield intermediates, CO, and eventually CO₂, with O*

replenished through ongoing O₂ dissociation [4, 43, 87]. Figure 9 illustrates a schematic representation of the thermocatalytic reaction pathway for benzene using Pt/TiO₂-R. Vellingiri et al. proposed that an effective strategy to enhance the efficiency of thermocatalytic formaldehyde (FA) removal is to improve the distribution of noble metallic species within the catalyst. This can be achieved by loading individual atoms or nanoparticles of noble metals onto support materials with high specific surface areas [25]. Research has shown that noble metals such as gold (Au), palladium (Pd), and platinum (Pt), when dispersed or immo-

Table 2. The research was conducted on thermocatalysts in the destruction and removal of air pollutants.

Catalyst	Synthesis method	Pollutant under study	Crystallite or Particle size (nm)/Pore size (nm)	BET (m ² /g)	Ref.	
ZrO ₂	m-ZrO ₂	Dimethyl Methylphosphonate (DMMP)	5/-	88.7	[36]	
	t-ZrO ₂		5/-	66.1		
TiO ₂ /Mg (OH) ₂	Thermal decomposition and precipitation	Chemical warfare agents (DMMP, 2-chloroethyl ethyl sulfide, and 2-chloroethyl phenyl sulfide)	-	223	[37]	
CuBTC	CuBTC CuBTC -P	Microwave	NO	-1.7516 -13.4832	987.16 344.51	[38]
MnCeOx	Pechini	Formaldehyde and ozone	-	-	[39]	
MnOx	Oxalate	Benzene	-1 – 5	385.4	[40]	
CeMnxOy/TiO ₂	Hydrothermal	Benzene	15.5/-	84.5	[41]	
NiCux/CNT	solvothelmal (ST)	Methane	7.3 – 20/-	-	[42]	
Pt/TiO ₂	Incipient wetness impregnation	Benzene	-/51	43	[43]	
Pt/sepiolite	Reductive impregnation	Formaldehyde	2 – 4/31 – 32	51 – 71	[44]	
PtNi(OH) _x /γ-Al ₂ O ₃	Wet chemical	Formaldehyde	γ-Al ₂ O ₃	-/15.5	94	[45]
			Pt/γ-Al ₂ O ₃ (IM)	2.27/15.8	97	
			PtNi/γ-Al ₂ O ₃ (IM)	1.94/14.2	81	
			Pt/γ-Al ₂ O ₃	3.1/14.5	93	
			PtNi/γ-Al ₂ O ₃	2.92/13.6	91	
CeO ₂	Urea solution combustion route	Carbon	20 – 50/-	-	[46]	
Pt/MnO ₂	An in-situ growth method using a hydrothermal	Formaldehyde	Pt/MnO ₂ -CF	-/7.5	64	[69]
			MnO ₂ -CF	-/7	54	
			MnO ₂ -MS	-/17.4	42	
			Pt/MnO ₂ -MS	-/13.7	36	
Pt/NiO	Fast chemical bath deposition	Formaldehyde	Pt/NFO0.5	2-3/5.9	188	[70]
			Pt/NFO1	2-3/7.5	161	
			Pt/NFO3	2-3/7.4	154	
			Pt/NFO5	2-3/7.2	155	
3D-NiCo ₂ O ₄ nanosheets	solvothelmal	Formaldehyde	-	81.54	[71]	
Pd/γ-Al ₂ O ₃	Commercially catalysts	Formaldehyde	2 – 4/5.6	278	[72]	
Fe ₂ O ₃ -MnO ₂			6×12 mesh/9.4	123		
CuO-MnO ₂			4×8 mesh/10.6	120		
CoxMn _{3-x} O ₄	Anodic electrodeposition	Formaldehyde	-/23.96 – 25.46	11.06 – 11.6	[73]	
A glass foam impregnated with ruthenium	-	Ethanol, Acetone, Toluene, Heptane	2 – 5/590000	0.4	[74]	
Fe ⁰ /zeolite (1 – 2 mm)	Plasma	BTX	30 – 60/-	-	[75]	
Cu ₂ O/zeolite (1 – 2 mm)	Chem Inc		30 – 60/-	-		
Pt/NaY zeplite	-	Formaldehyde	2-3/3.17	419	[76]	
K-Pt/NaY-1 zeplite			2 – 3/1.99	398		
K-Pt/NaY-2 zeplite			2 – 3/2	295		
K-Pt/NaY-3 zeplite			2 – 3/2.05	241		
Al ₂ O ₃ /PVC	Wet impregnation	Octahydroquinazolinone	-/3.06 – 6.54	7 – 77	[77]	
Al ₂ O ₃			-/3.82	105		
Co-NPs@NC	Top-down ZIF-67 precursor pyrolysis strategy	Ammonium Perchlorate (AP)	5 – 50/-	56.9 – 241.9	[78]	
VFTC-Trombe wall (such as MnOx-CeO ₂)	VFTC-Trombe wall system with MnOx-CeO ₂ thermocatalytic layer	Formaldehyde	-	-	[79]	
R-MnO ₂ -HS	Facile method	Benzene	188/1000	98	[80]	
NT-purchased	Hydrothermal	Dibenzothiophene	-/3.9	45	[81]	
NT-P25			-/3.7	245		
NT-TBOT			-/3.7	283		
TiO ₂ /SBA-15	Hydrothermal	CO ₂	17.4 – 37.1/2 – 50	440	[82]	
MnOx-ZrO ₂	Chemical precipitation	Toluene, Ethanol	Mn ₃ O ₄	14.5/-	99.6	[83]
			ZrO ₂	8.1/-	26.2	
			MnOx-5% ZrO ₂	17.9/-	85.4	
			MnOx-10% ZrO ₂	18.2/-	86.1	

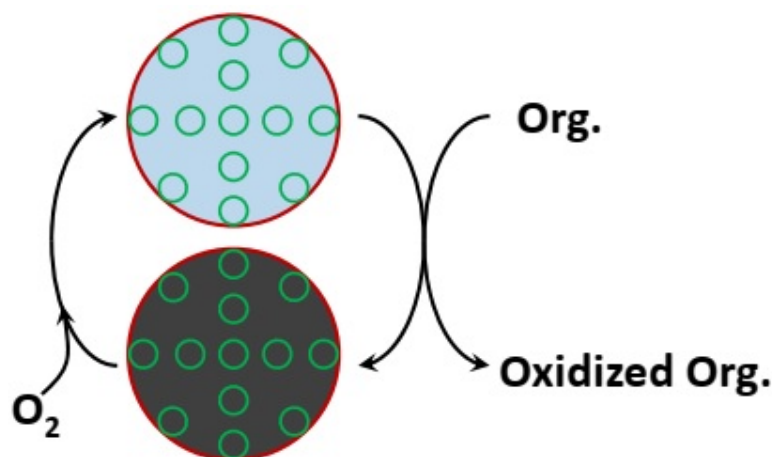


Figure 6. The MVK mechanism in the thermocatalytic degradation of VOCs was reproduced with permission from [84].

bilized on appropriate support materials, exhibit promise in catalytically decomposing gaseous FA at ambient temperatures [44, 59, 70]. However, the practical application of these catalysts is constrained by economic factors and the limited availability of noble metals [45, 56]. Transition metal (TM)-based catalysts have garnered significant interest as alternatives to noble metals due to their notable stability, strong catalytic performance, abundant availability, and cost-effectiveness. These catalysts possess unpaired d electrons or vacant d orbitals, which effectively attract target molecules during the catalytic process. As a result, the degradation of pollutants catalyzed by these transition metals can be enhanced through the formation of chemical bonds and/or the reduction of the reaction's activation energy [88].

Various monometallic TMO-based thermocatalysts, such as manganese, cobalt, chromium, and cerium oxides, have been developed to promote the breakdown of FA. These thermocatalysts exhibit advantageous pore structure, large surface area, efficient catalytic performance, strong stability, and cost-effectiveness, making them ideal for environmental cleanup [60]. However, despite extensive research on monometallic TMO-based thermocatalysts, they face limitations such as poor O_2 activation capability and insufficient oxygen vacancies, which impact their effectiveness in de-

grading FA [62, 89]. For instance, temperatures exceeding $90^\circ C$ are often necessary to achieve complete FA oxidation [60]. Bi-metal oxide (Bi-TMO) catalysts demonstrate superior catalytic performance in the decomposition of FA compared to single-metal catalysts [60, 71, 72]. The integration of two metal oxides generates a synergistic effect that enhances the catalyst's overall efficiency in degrading FA through thermocatalytic processes. In $CeO_2Co_3O_4$ catalysts, cerium oxide (CeO_2) provides a high oxygen storage capacity, good redox performance, and elevated lattice oxygen activity. Meanwhile, Co_3O_4 contributes to the catalyst's strong oxidation properties and efficient electron transfer capabilities [89]. Similarly, the unique characteristics of manganese oxides, such as variable valence, ease of defect formation, and high catalytic activity, make them highly promising for use in Bi-TM-based catalysts [73, 89]. These attributes are exemplified by their ability to achieve the complete oxidation of FA at relatively low temperatures ($100^\circ C$) [73]. The performance of TMO-based thermocatalysts is influenced by several factors, including crystal structure, catalyst preparation methods (e.g., synthesis techniques and calcination temperature), and physical and chemical properties (e.g., shape, surface area, and particle size). Additional factors include modifications with alkali metals or nitrogen, treatments with alkali or acid, the choice of

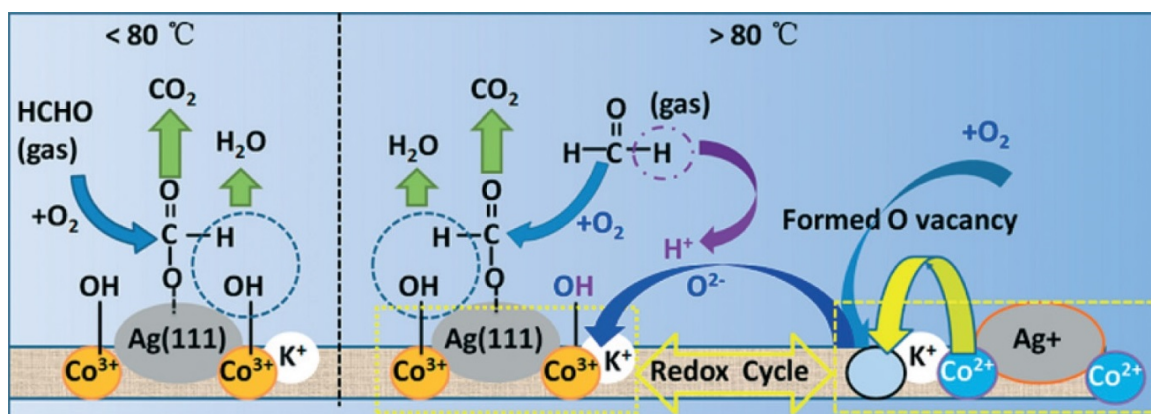


Figure 7. A schematic of the thermocatalytic reaction pathway for formaldehyde oxidation, reproduced with permission from [85].

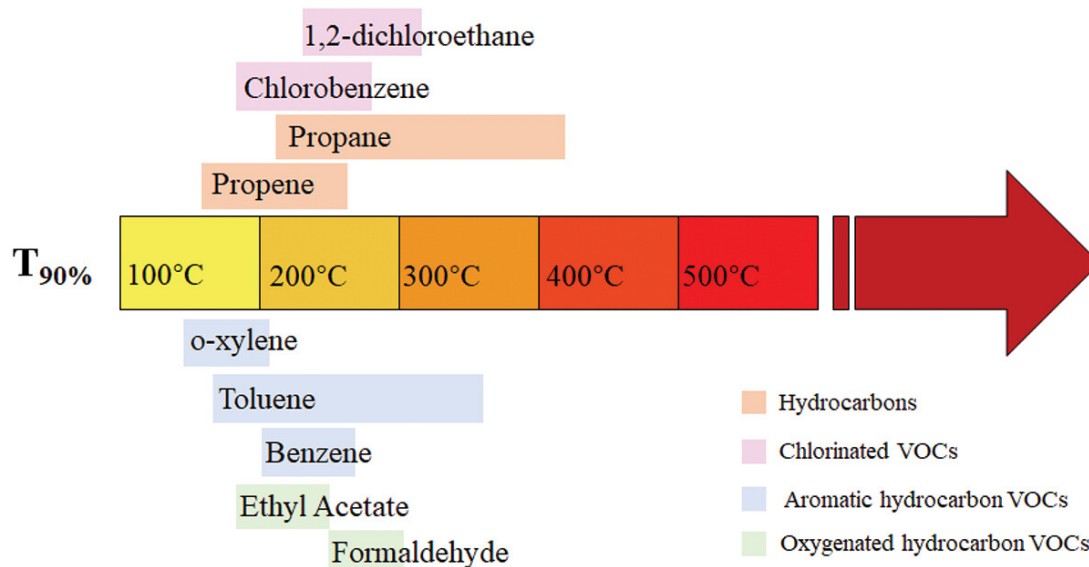


Figure 8. The temperatures needed for the thermocatalytic degradation of various VOCs, reproduced with permission from [86].

precursor, and various experimental operational conditions (e.g., FA supply rate and humidity levels) [60, 62]. Hua et al. conducted a comparative study on TMO-based catalysts for the thermal degradation of gaseous FA, including monometallic, bimetallic, and composite-based TMO thermocatalysts. The catalytic performance was evaluated using the kinetic reaction rate as a metric at varying temperatures. The results indicated that TMO-based composite catalysts exhibited superior performance compared to mono-TMO and bi-TMO catalysts under different temperature conditions, highlighting their greater potential for FA degradation [60]. Lejeune et al. utilized an open-cell foam catalyst composed of a glass foam support impregnated with zerovalent ruthenium nanoparticles. This catalyst effectively

eliminated various VOCs through thermocatalytic oxidation without the need for a wash coating. The researchers successfully achieved complete elimination of the four tested VOCs. The sequence of ease in VOCs reduction with temperature was determined as ethanol > acetone > toluene > heptane. Complete reductions (100%) of ethanol, acetone, toluene, and heptane were achieved at 350 °C with a residence time of 8.8 seconds. Furthermore, efficient elimination of ethanol and acetone was observed at lower temperatures (approximately 250 °C), highlighting the potential of this catalyst as a viable alternative to existing technologies [74]. Rostami and Jonidi Jafari conducted an experiment utilizing a two-stage filtration system within a stainless steel cylindrical reactor. The system involved the

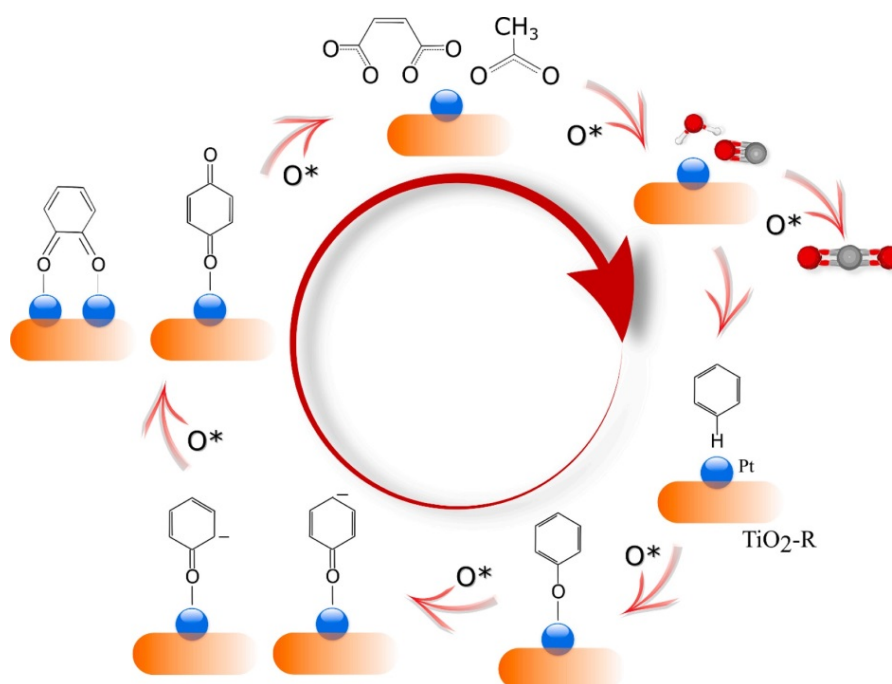


Figure 9. A schematic representation of the thermocatalytic reaction pathway for benzene using Pt/TiO₂-R, reproduced with permission from [43].

application of zero-valent iron and copper oxide nanoparticles onto a natural zeolite bed to evaluate the effectiveness of removing BTX compounds. The results showed that BTX removal rates were 87.47% at 300 °C and 94.03% at 400 °C, corresponding BTX mineralization rates of 37.21% and 90.42%, respectively. Additionally, BTX removal efficiencies of 96.18% and 78.42% were achieved at retention times of 14.1 seconds and 7.05 seconds, respectively. The study suggests that an adsorptive-thermocatalytic process employing Clinoptilolite as an adsorbent bed, combined with FeO and Cu₂O nanoparticles as catalysts, presents a viable and efficient method. This approach demonstrates particular effectiveness under conditions of high flow rates and substantial pollution loads, with an optimal operating temperature of 350 °C [75].

Manganese-based catalysts have generated considerable attention for the catalytic degradation of VOCs owing to their distinct advantages, including high efficiency, cost-effectiveness, and outstanding stability. However, there is still potential for improvement in their catalytic performance [52, 90]. The enhancement of manganese-based catalysts through structural design, surface modification, and defect engineering (e.g., heterojunction engineering) has been discussed [52, 53]. Effective structural design can enhance the specific surface area, increase the number of active sites, and enhance the catalytic efficiency. Surface modification with other metal ions, particularly noble metals, has significantly enhanced catalytic performance. Moreover, defect engineering is recognized as one of the most effective strategies for manipulating the electronic structure of materials, leading to substantial improvement in thermocatalytic performance [52]. Song et al. conducted a study in which they prepared an alkaline K-Pt/NaY nano-catalyst to assess its efficiency in formaldehyde removal under room temperature conditions. They evaluated NaY zeolite composites containing varying amounts of KNO₃ against 300 ppm formaldehyde. The zeolite sample loaded with 15 wt% KNO₃ exhibited slightly better performance (99.3% removal) compared to the sample with 20 wt% KNO₃ (93% removal) [76]. The reduced performance of the latter was attributed to an excessive presence of alkaline components, which decreased the reducibility of Pt. Additionally, the high concentration of surface basic sites resulted in strong adsorption of the generated CO₂ molecules, ultimately obstructing the active catalytic sites [44, 76]. A study discusses the utilization of a nanocomposite consisting of amorphous cerium manganese oxide supported on TiO₂ (CeMnxOy/TiO₂), which exhibits strong absorption across the entire solar spectral range. The nanocomposite efficiently converts absorbed solar energy into thermal energy, resulting in a significant temperature increase. Consequently, it demonstrates solar light-induced thermocatalytic performance, particularly showing high efficacy in benzene oxidation when exposed to the full solar spectrum. The cost-effective CeMnxOy/TiO₂ nanocomposite, with its enhanced thermocatalytic activity, has the potential to serve as a viable alternative to expensive noble metal catalysts for the mitigation of VOCs [91].

Ratnayake et al. employed a simple, one-step method using urea solution combustion to synthesize CeO₂ catalysts.

Initially, CeO₂ nanoparticles were observed combined with graphitic carbon nitride (g-C₃N₄) formed during urea pyrolysis. The enhanced performance was attributed to the unique CeO₂ nanomorphology produced by carbon nitride, which increased the number of reactive sites and facilitated oxygen transfer, leading to a highly effective thermocatalytic process. The researchers proposed that the synthesis of these CeO₂ nanostructures represents a cost-effective and convenient approach for reducing atmospheric pollution by targeting carbon particulates, as opposed to expensive, environmentally harmful noble-metal-based methods [46]. Materials such as layered double hydroxides, graphene, molybdenum sulfide, and others have emerged as prominent areas of study in thermocatalytic research due to their highly advantageous physicochemical properties in catalytic processes [25, 63]. These materials, characterized by small thickness (<5 nm) and large lateral dimensions, are designed to enhance catalytic efficacy by facilitating short diffusion paths, increasing specific surface area, and providing a substantial number of active sites [25, 64]. In one study, six variations of ZrO₂ catalysts, exhibiting nanoparticle, flower-like, and hollow microsphere structures in monoclinic and tetragonal phases, were synthesized, and their effectiveness in the thermocatalytic decomposition of dimethyl methylphosphonate (DMMP) was evaluated. Monoclinic-phase ZrO₂ (m-ZrO₂) catalysts demonstrated superior performance in terms of protection time compared to tetragonal-phase ZrO₂ (t-ZrO₂) catalysts during the thermocatalytic decomposition of DMMP. Within a specific crystal phase, ZrO₂ hollow microspheres outperformed ZrO₂ flower-like structures and nanoparticles. Among the six catalyst variants, m-ZrO₂ hollow microspheres exhibited the highest mass-specific treatment capacity and the longest protection time of 266 minutes at 400 °C, whereas t-ZrO₂ flower-like structures showed the most effective surface-area-specific treatment capacity. The accumulation of phosphorus oxide by-products on the catalyst surface reduced the active sites critical for catalysis [36].

Alharthi et al. proposed a method for the solar-driven thermocatalytic production of octahydroquinazolinone, utilizing aluminum oxide (Al₂O₃) supported on polyvinyl chloride (PVC) as a catalyst under natural sunlight. Their findings indicated that adjusting the molar ratio of the catalyst influenced both the yield and reaction time. Using a 50% Al₂O₃ catalyst under full solar irradiation, they achieved excellent performance with a yield of 98% and a reaction time of 35 minutes. The study introduced an innovative approach for harnessing solar energy in the efficient execution of chemical reactions, employing a cost-effective, recyclable PVC/Al₂O₃ catalyst that is environmentally friendly and provides high product yields [77]. Lin et al. reported that nanometals exhibit a remarkable capability in the thermocatalytic decomposition of ammonium perchlorate (AP) due to their unique electronic properties, including lattice defects and the exothermic enhancement effect of oxidation. Among these nanometals, cobalt nanoparticles show superior catalytic efficacy compared to other nanometals. However, nanometals face challenges such as aggregation and oxidation resulting from their high surface free energy.

These issues can lead to a decrease in catalytic efficiency and may even result in spontaneous combustion or explosions. To address these issues, a common approach is to stabilize the nanoparticles on support materials, which serves as an effective strategy [78]. Hadian et al. noted that a variety of catalysts have been developed for the thermocatalytic decomposition of methane, which can be classified into metal-based and carbon-based catalysts. Carbon-based catalysts offer advantages such as availability, low cost, and the elimination of the need for product separation from the catalyst [26]. In contrast, metal-based catalysts have demonstrated superior performance and activity. The most commonly used materials for metal-based catalysts include nickel, iron, and copper, supported on alumina or silica in both single and bimetallic configurations [47, 50, 92]. Hamdani et al. described thermocatalytic methane decomposition as a promising method for producing CO_x-free and sustainable hydrogen while reducing methane levels in the atmosphere. Noble metals-based catalysts are costly, while iron-based catalysts exhibit enhanced conversion rates at elevated temperatures. In contrast, Ni-based catalysts demonstrate reduced catalytic efficiency under similar conditions. Several carbon-based materials, including activated carbon and carbon black, have shown consistent methane conversion and the production of valuable nanocarbons. The incorporation of transition metal catalysts has substantially improved methane conversion rates on carbon-based catalysts [65]. Li et al. discussed a method for methane decomposition involving the use of thermocatalysis technology at elevated temperatures. This method is associated with several drawbacks, including high energy consumption, stringent equipment requirements, and elevated reaction temperatures, which lead to a reduced catalyst lifespan. Therefore, there is a need to develop novel technologies capable of efficiently harnessing and converting methane under mild conditions to achieve the desired end products [67]. Xu et al. demonstrated that a 10 wt% Ni/carbon nanotube (CNT) thermocatalyst was activated for methane decomposition at 550 °C, but its activity diminished after 1 hour of reaction at temperatures exceeding 600 °C. The introduction of Cu enhanced its stability, with only catalysts containing Cu loadings above 10 wt% remaining both active and stable at temperatures exceeding 650 °C. Analysis of the catalyst revealed that variations in the i) Ni/Cu ratio, ii) size of metal particles, and iii) operating temperature were crucial factors influencing the thermocatalytic decomposition performance, stability, and morphology of carbon byproducts [42]. Shirvani et al. conducted a review on the utilization of two-dimensional (2D) nanomaterials in thermocatalytic reactions, highlighting that reducing the catalyst thickness to a single layer or a few atomic layers enhances product selectivity and reaction rates. However, challenges remain due to the limited thermal and chemical stability of 2D nanostructures, their susceptibility to surface poisoning, rapid loss of activity, and complex synthesis methods causing issues with reproducibility and scale-up. Additionally, identified knowledge gaps emphasize the need for further research to fully explore the potential of these promising thermocatalysts [66]. Wu et al. introduced a

novel passive solar vertical-finned thermocatalytic Trombe wall system that integrates thermocatalytic oxidation with finned heat transfer technologies. They observed that both purification and overall efficiency improved as the height of the fins increased. Additionally, increasing the spacing between the fins resulted in maximum values for thermal, purification, and overall efficiencies, demonstrating a significant enhancement in purification efficiency without compromising thermal performance through the incorporation of vertical fins in the channel. The influence of vertical fins on purification performance was found to be greater than their effect on thermal performance, while ambient temperature had a more pronounced impact on thermal performance than on purification performance [79]. In a study, hollow spheres composed of ramsdellite MnO₂ (R-MnO₂-HS) demonstrated highly effective thermocatalytic capabilities for air purification, particularly benzene, when exposed to full solar spectrum irradiation. Yang et al. observed that the presence of solar light significantly enhanced the oxygen activity within the lattice of R-MnO₂-HS, resulting in a significant enhancement of its thermocatalytic efficiency. These findings present an innovative nanostructured material and strategy for efficiently harnessing sustainable solar energy for environmental remediation and the production of high-quality chemicals [80]. In a separate investigation, titanium nanotubes were synthesized through a hydrothermal two-step process to facilitate oxidative desulfurization. The thermocatalytic process demonstrated exceptional efficiency, achieving near-complete elimination of dibenzothiophene within 10 minutes under optimal conditions [81]. According to the research conducted, no single physicochemical technology can effectively remove all air pollutants or address the challenges associated with indoor air purification [93]. For instance, adsorption is considered one of the most cost-effective treatment methods due to its affordability, simplicity in operation and design, high efficiency for a wide range of pollutants, and ease of use [94]. However, this method has limitations, including low adsorption capacity and restricted sensitivity and selectivity [95]. Biologically based purification systems present promising solutions to overcome challenges such as the diversity and hydrophobicity of pollutants and varying concentrations. Nonetheless, these systems also have drawbacks, including limited efficiency, the requirement for specific conditions, high startup and maintenance costs, and a time-consuming purification process [93]. Wang et al. conducted an extensive review of contemporary advanced oxidation technologies for gas removal, highlighting non-thermal plasma, chlorine- and sulfur-based methods, and O₃ oxidation absorption, with a particular emphasis on the promising application potential of non-thermal plasma. They noted that while O₃ and chlorine-/sulfur-based methods effectively eliminate gaseous pollutants, challenges such as high energy requirements for O₃ generation and health hazards associated with chlorine and sulfur oxidants remain [96]. According to studies, thermocatalyst technology, like other air purification methods, presents both advantages and disadvantages, making its application challenging and prompting ongoing research in this field. The primary advantage of this

technology is its effectiveness in reducing gaseous pollutants, particularly at high temperatures. However, its major drawbacks include high construction and maintenance costs, as well as a reduced lifespan due to the demands of operating at elevated temperatures [97–99].

In addition to researching and developing thermocatalysts for air pollution control, photothermocatalyst technology—a combination of photocatalysts and thermocatalysts for pollution removal—has garnered significant attention from researchers. This approach has proven some effectiveness in enhancing pollutant removal efficiency and improving catalyst stability [82, 83]. However, since the investigation of photothermal catalysts was not the focus of this study, it has not been explored in detail here. To meet the growing demands of the industry, particularly in air purification and pollution control, it is recommended that future research be directed toward this area.

Conclusion

Thermocatalysts utilize both temperature and catalysts to accelerate chemical reactions. The development of thermocatalytic technology is essential for optimizing processes and reducing pollutant emissions. Operating at elevated temperatures, these catalysts convert air pollutants into harmless products. Thermocatalysts function by adjusting the temperature and creating optimal thermal conditions to supply the necessary energy for activating chemical reactions. This capability is particularly crucial in situations where temperature alone is insufficient or where chemical reactions are not easily influenced by heat. In essence, thermocatalysts facilitate thermal and catalytic processes within a chemical reaction. By establishing a synergy between heat and chemical reactions, these catalysts enhance reaction rates and improve overall efficiency. As a technology, thermocatalysts offer substantial potential for transformation across various sectors and improving environmental conditions. According to studies, thermocatalysts are an effective method for removing or controlling air pollution on a laboratory scale. These thermocatalysts can eliminate a wide range of air pollutants, including VOCs, nitrogen oxides, sulfur oxides, and others, while also being environmentally friendly. In thermocatalytic processes, pollutants are initially adsorbed onto the surface of the catalyst. Once adsorbed, thermal energy is applied to break the chemical bonds in the harmful compounds, leading to the formation of new bonds with harmless substances. The primary mechanisms involved in thermocatalytic oxidation include 1) Mars-van Krevelen (MVK), 2) Eley-Rideal (E-R), and 3) Langmuir-Hinshelwood (L-H). These mechanisms play a role in the removal and reduction of pollutants. However, the high costs, stability issues, and energy consumption associated with some catalysts have limited their practical applications. To improve the performance of thermocatalysts while reducing the costs related to their design, development, and operation, the following research areas are recommended:

- Fabrication of thermocatalysts using abundant, available, and stable metal oxides, selected based on criteria such as non-toxicity and reactivity.

- Development of multifunctional thermocatalysts designed to remove and reduce various types of pollutants.
- Creation of thermocatalysts with low activation energy, particularly effective at room temperature, to minimize energy consumption.
- Investigating the performance of thermocatalysts in vehicle exhaust systems for the removal of emitted pollutants.

Additionally, since all of these studies have been conducted in laboratory settings, future research should focus on the design of optimal thermocatalysts with enhanced performance tailored to industrial applications. This approach will facilitate the adoption of this technology as a sustainable solution for controlling air pollution. Increased awareness and investment in thermocatalytic technology could contribute to achieving greater sustainability and efficiency goals.

Authors contributions

Authors have contributed equally in preparing and writing the manuscript.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests

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

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