

Review

Advances in Adsorption, Absorption, and Catalytic Materials for VOCs Generated in Typical Industries

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Abstract: In recent years, atmospheric composite pollution has become increasingly serious, and accelerating VOC governance has become the focus of and difficulty in atmospheric governance. Volatile organic compounds (VOCs) come from a wide range of sources, and industrial sources are the main source of anthropogenic VOC emissions in China. Chemicals, oil refining, and solvents are three typical VOC-emitting industries, and their control is an important part of accelerating and optimizing VOC governance. It can be controlled by source control, process control, and pipe end treatment; among these, pipe end treatment is divided into recovery technology and destruction technology. In pipeline end treatment, with the key materials of adsorption, absorption, catalytic oxidation, and catalytic combustion, the research and development of adsorbents, absorbents and catalysts has become a hot spot in recent years. This paper summarizes the chemical materials used in typical VOC pipe end-treatment technology (including adsorbents used in the adsorption method, absorbents used in the adsorption method, and catalysts used in the catalytic oxidation and catalytic combustion methods), summarizes the advantages and disadvantages of various materials and their application range, and looks forward to the direction of future developments.

Keywords: VOCs; recovery technology; destruction technology; adsorbent; absorbent; catalyst



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1. Introduction

VOCs are important precursors of PM_{2.5} and O₃, which will react chemically with SO₂ and NO_x in the atmosphere and trigger secondary pollution [1–3]. In recent years, with the acceleration of industrialization, the annual emissions of VOCs have increased dramatically, especially in developing countries. Studies have shown that China's anthropogenic VOC generation (2011–2019) is generally on an upward trend, and the VOC emissions in 2019 are still at a high level at about 23.42% [4], and if the existing control level is maintained unchanged, it is expected that the total anthropogenic VOC emissions in China will increase by 22.91% in 2025 compared with 2019 [5]. Therefore, the governance of VOCs is urgent.

The sources of VOCs are extensive and complex and are mainly divided into two categories: natural and anthropogenic sources. In China, industrial sources are the most important source of anthropogenic VOCs, and most of the VOCs come from human industrial development activities. The dominant ones are petrochemical, chemical, and solvent-using industries in China.

According to the Communiqué of the Second National Pollution Source Census of China, the top three industries in terms of VOC emissions are chemical raw materials and the chemical-product manufacturing industry, with 1,075,700 tons; the petroleum, coal, and other fuel-processing industries, with 677,500 tons; and the rubber- and plastic-product industry, with 403,600 tons. The above three industries together accounted for 44.78 percent of the VOC emissions from industrial sources.

The use of volatile chemical products (VCPs)—including pesticides, paints, printing inks, adhesives, detergents, and personal-care products—now accounts for half of the fossil fuel VOC emissions in industrialized cities [6].

China's consumption of LPG plus motor gasoline is the second highest in the world, and China's evaporative emissions in 2010 were as high as 185,000 tons [7]. Vehicle evaporative emissions are the main source of atmospheric VOCs and arise from two main pathways, namely tailpipe emissions and evaporative emissions [8]. Nowadays, tailpipe emissions have been greatly reduced as a result of national policies to control vehicle emissions and technological improvements, but according to statistics, in most parts of the world, except for the United States of America and Canada, VOCs emitted from oil and gas evaporation account for 10.6 percent to 30.0 percent of the total anthropogenic emissions [9–12].

In China, the highest proportion of VOCs from light-duty gasoline vehicles (LDGVs) and gasoline motorbikes are aromatics, and the highest proportion of VOCs from light-duty diesel vehicles (LDDVs) are alkanes [13]. The main VOCs emitted from diesel vehicles are carbonyl compounds, aromatics, and alkanes.

Solvent-using industries mainly include the automobile-production coating process and the furniture manufacturing industry but also includes motorbikes, containers, construction machinery and steel structures, aluminum profiles, wood processing, ships, and other characteristic industries. In 2018, volatile organic compound (VOC) emissions from the industrial-coating field were nearly 3500 kt, which accounted for about a quarter of China's VOC emissions from industrial sources and many of the provinces' (autonomous regions and municipalities directly under the central government) major industrial VOC emission sources.

In the petrochemical industry, the base materials for the aromatic petrochemical industry are compounds such as benzene, toluene, xylene, etc., and the only way to obtain aromatic compounds in this industry is through an aromatic extraction plan. About 98% of industrial ethylbenzene is produced through the alkylation reaction of ethylene and benzene, and the device used in this process is the dry-gas ethylbenzene plant (FCC); according to a survey, more than 20 enterprises in China, such as Dalian, Fushun, etc., are using this device [14,15]. Emissions of VOCs from production processes are frequent and occur in large quantities in the petrochemical industry.

The printing industry, as a national support industry in China, is widely used in the construction, apparel, food, and cosmetic industries, and in the development of the printing industry sector.

The printing industry is one of the most important contributors to industrial VOC emissions in China (nearly 10 percent), with emissions second only to industrial coatings (27 percent) [16]. Printing production generally includes three processes: pre-press, printing, and post-press processing, and the use of a variety of VOC-containing raw and auxiliary materials makes it possible to emit VOCs in each of these printing production processes.

In addition to these industries, there are many other industries where VOCs are designed to be emitted during the production process, such as the rubber industry, and the machinery-coating industry.

Because of the seriousness of the industrial emissions of VOCs, the State has formulated a series of policies and standards for VOC emissions.

Emissions of volatile organic compounds in China are bound by the standard for fugitive emission of volatile organic compounds (State. No: GB 37822-2019 [17]). The standard specifies the requirements for the control of unorganized emissions from the storage of VOC materials, the control of unorganized emissions from the transfer and conveyance of VOC materials, the control of unorganized emissions from process VOCs, the control of leakage of VOCs from equipment and piping components, the control of unorganized emissions of VOCs from the open surface of liquids, the requirements for the system of collecting and treating the unorganized emission of VOCs, and the requirements for pollution monitoring in and around the enterprise's plant.

Of course, there are many standards for VOC emissions in various industries. Typical industry emission standards are shown in Table 1.

Table 1. VOC emission standards for typical industries in China.

Ordinal Number	Standard Caliber	Standard Name	Implementation Date
1	GB 31570—2015 [18]	Emission standard of pollutants for the petroleum refining industry	1 July 2015
2	GB 31571—2015 [19]	Emission standard of pollutants for the petroleum chemistry industry	1 July 2015
3	GB 24409-2020 [20]	Limit of harmful substances from vehicle coatings	1 December 2020
4	GB 30981-2020 [21]	Limit of harmful substances from industrial protective coatings	1 December 2020
5	GB 20951—2020 [22]	Emission standard for air pollutants in petroleum transport	1 April 2021
6	GB 20952—2020 [23]	Emission standard for air pollutants in gasoline filling stations	1 April 2021
7	GB 33372-2020 [24]	Limits for volatile organic compound content in adhesives	1 December 2020
8	GB 38507-2020 [25]	Limits for volatile organic compounds (VOCs) in printing inks	1 April 2021
9	GB/T 38508-2020 [26]	Limits for volatile organic compound content in cleaning agents	1 December 2020
10	GB/T 38597-2020 [27]	Technical requirement for low-volatile-organic-compound-content coating products	1 February 2021

So, relaxing these typical standards will be a powerful blow to accelerating the optimization of China's atmospheric management.

The control and management of VOCs can be realized in three ways: source containment, process control, and end-of-pipe management. Source containment refers to the selection of process routes and raw materials (and as far as possible, the use of VOC-free raw materials) for production; process control refers to the remediation of VOCs generated in the existing production process, with improving the sealing of each link being one of the effective measures; end-of-pipe treatment refers to the use of physical or chemical means for the collection and treatment of VOCs discharged during the production process. End-of-pipe treatment technology is an important part of VOC treatment, and optimizing end-of-pipe treatment is especially important. Among the recovery and destruction technologies for end-of-pipe treatment, adsorption, absorption, catalytic oxidation, and catalytic combustion are several commonly used VOC treatment methods, and adsorbents, absorbents, and catalysts, as the key to these methods, are of great help in studying their development and optimization for the treatment of VOCs.

2. Adsorption Method—Adsorbents

Adsorption is the most common method for treating industrial VOCs, and its equipment has the advantages of simple construction, high adsorption efficiency, and strong adaptability; adsorption can not only effectively enrich and separate VOCs, but the adsorption material can also be reused through thermal desorption or vacuum desorption [28]. Therefore, the adsorption method is a more commonly used approach in the process of VOC treatment. The adsorbent is the key to the adsorption method, and in the actual application process, the adsorbent material directly affects the investment and operation

costs and safety. Therefore, many studies focus on the development and optimization of adsorbents [29]. The following adsorbents are used in the adsorption method.

2.1. Carbon-Based Adsorbent Materials

2.1.1. Activated Carbon

Activated carbon is a widely used adsorbent characterized by an extended surface area, microporous structure, universal adsorption effect, high adsorption capacity, and high surface reactivity. Activated carbon is synthesized from a variety of materials, the most used on a commercial scale being precursors of cellulose, such as peat, coal, lignite, and coconut shells, among other substances [30].

The activated-carbon adsorption method is one of the most-used technologies for the treatment of industrial VOCs, and activated carbon has become one of the most widely used adsorption materials because of its excellent properties such as large specific surface area, rich functional groups, high mechanical strength, and resistance to acids and alkalis [31].

There are two main types of activated carbon: granular activated carbon and activated carbon fiber. Granular activated carbon consists of particles with a rich pore structure and is usually used for gas-phase adsorption and liquid-phase adsorption. It is widely used in air and water purification, vapor recovery, exhaust-gas treatment, and other fields. Activated carbon fiber has a fibrous form and is usually made into plates, and it is widely used in air purification and protective masks. Common methods of preparing activated carbon include physical and chemical methods. Activated carbon prepared by the physical method usually has a uniform pore distribution and a large specific surface area, while activated carbon prepared by the chemical method can increase the selective adsorption capacity for specific substances through surface functional groups.

Studies have shown that activated carbon can adsorb most VOCs such as alkanes, alcohols, aldehydes, ketones, esters, aromatics, etc. However, the adsorption capacity of activated carbon for organic gases such as ketones, ethers, and esters is greatly reduced. This is because acyl contains ketones, ethers, esters, and other organic gases, and acyl in the reaction process will produce an exothermic reaction and make acyl clusters on the carbon surface. If the acyl-containing organic gases are continuously adsorbed, the exothermic polymerization reaction will be intensified and cause the charcoal layer to catch fire. At the same time, due to the ketone polymerization reaction, the activated carbon pores are blocked, leading to activated carbon desorption and the regeneration of the difficulty of the increase in the cost; activated carbon for the adsorption of the higher humidity of the VOCs is not ideal. The theory of Dubinin and Serpinsky shows that water molecules first adsorb onto polar functional groups through hydrogen bonding at low relative pressure and then form water clusters to fill the pores of the activated carbon at high relative pressure, leading to high transport resistance and pore blockage [32]. This phenomenon can be weakened by removing surface oxygen groups and increasing the ratio of sp²/sp³ hybridized carbon atoms for the competitive adsorption of water molecules [32]. During use, there is a risk of spontaneous combustion if the desorption temperature exceeds 120 °C. Meanwhile, when the desorption temperature is lower than 120 °C, the VOC gas cannot be adsorbed within the activated carbon, and the organic matter cannot be completely desorbed. This results in a short service life of the activated carbon and an increase in operating costs.

According to that study, when the humidity rises from 0% to 90%, the adsorption capacity of VOC adsorption using activated carbon alone will drop by 55.9%. Because of this, scholars have used PDMS to cover the modification. After such modification, the adsorption capacity of activated carbon under the same humidity conditions is improved, though only by 19.3%, but the PDMS cost is high, and the regeneration ability is poor under the alternating current environment. To further enhance the adsorption capacity of activated carbon in high humidity, Lu et al. [33] experimented with modified activated carbon through the introduction of nanocarbon nanospheres originating from biomass sugar into the silica gel in a hydrothermal environment to prepare carbon–silica materials. The results showed that the adsorption capacity of VOCs could be maintained regardless of

humidity and that these materials exhibited excellent desorption characteristics. However, the adsorption capacity of these carbon–silica materials was much lower than that of the formal AC.

At the same time, activated carbon after treatment with iron oxide or sodium hydroxide or sampling can usually obtain better adsorption performance. Hydrophobic modification of activated carbon can improve its adsorption selectivity. Li et al. [34] Hydrophobic modification of activated carbon (AC) using tetraethyl orthosilicate (TEOS) and trimethylchlorosilane (TMCS) showed that this modification led to a loss of specific surface area and pore volume as well as poor regeneration performance under dry working conditions, but it resulted in an increase in the relative humidity, improved the hydrophobicity, and facilitated adsorption and the post-regeneration adsorption performance. The resultant data are analyzed in Table 2.

Table 2. Analysis of activated carbon properties before and after TEOS and TMCS modification.

Activated-Carbon Status	Water Contact Angle (>90 Indicates Hydrophobicity)	Adsorption of Toluene (RH: 0%, 60%, 90%) (mg/g) (Breakthrough Adsorption Capacity and Saturation Adsorption Capacity)	Toluene Adsorbed after Regeneration (1st, 2nd, 3rd) (mg/g) (Breakthrough Adsorption Capacity and Saturation Adsorption Capacity)
Bare AC	111.6° ± 1.61°	462.1–564.1	165.4–237.3
		232.5–311.0	120.0–172.4
		170.0–201.3	119.7–160.4
AC/TEOS-30%TMCS-24h	143.6° ± 2.66°	363.4–439.7	247.3–357.2
		352.9–413.3	152.4–229.6
		325.3–397.8	150.9–218.8
C/TEOS-50%TMCS-24h	143.4° ± 1.35°	379.3–444.6	
		366.1–404.9	
		332.1–384.6	

Nowadays, scholars have even found that functional groups (HD/PR/PD) are favorable for the adsorption of VOCs at the edge of activated carbon, so in the future, we can utilize the functional groups to improve their adsorption of VOCs [35]. Green development is closely linked together with the management of VOCs and recycling. Recently, Zhou [33] and other scholars prepared environmentally friendly green activated carbon adsorbent materials with a high specific surface area and high adsorption performance by using fast-growing bamboo as the precursor and water vapor as the high-temperature activator. Through the fiber observation and BET tests, they found that the activated carbon prepared in this way has a high adsorption and cyclic adsorption capacity; this is also true for activated carbon, but this type of adsorption material provides a kind of environmental protection and uses green preparation, which could have future activated-carbon application prospects.

Overall, activated carbon adsorption is suitable for the treatment of industrial organic-waste gases with a large air volume, low concentration, and non-stable emission. When the concentration of waste gas is medium to high, the adsorption saturation cycle is short. It can be improved by regular desorption treatment.

2.1.2. Activated Carbon Fiber

Activated carbon fibers are activated-carbon-containing fibers, which are different from carbon-containing fibers due to the different high-temperature activation of carbonization; Figure 1 shows the activated carbon fiber preparation process. Activated carbon fiber has a high adsorption capacity, pore size, and specific surface area, among other characteristics; its specific surface area ratio is about dozens of particles of activated carbon than the specific surface area of hundreds of times. Activated carbon fiber's fine fiber structure

shows that it has many short and shallow fibers; through this microporous and fibrous structure, it can reduce the adsorption-bed pressure drop and mass transfer resistance, which makes the activated carbon fiber used in the adsorption of VOCs in the adsorption process able to accelerate the rate of mass transfer and increase the adsorption amount [36].

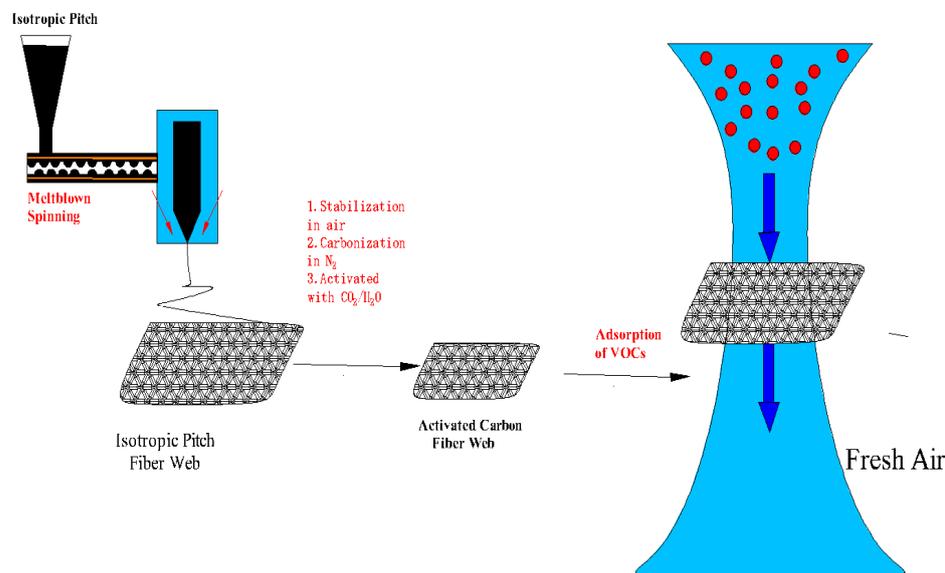


Figure 1. Preparation process of activated-carbon fiber. The red arrow is the fusion spraying process, the blue arrow is the adsorption of VOCs by activated carbon fibres, and the small red circle is the VOCs.

At present, there are four main types of activated carbon fibers that have been industrially produced: (1) polyacrylonitrile-based activated carbon fibers, (2) asphalt-based activated carbon fibers, (3) viscose-based activated carbon fibers, and (4) phenol–formaldehyde-based activated carbon fibers. The earliest industrial application is that of polyacrylonitrile-based activated carbon fiber; however, the most mature process involves asphalt-based activated carbon fiber. However, the most used activated carbon fiber in the industry is the viscose-based activated carbon fiber, because it has the characteristics of being insoluble and non-melting and can be directly carbonized without pre-oxidation during the preparation process, which is a simple and low-cost process; the carbon production rate is high, the emission of hazardous gases is low, the microporous structure is rich, and the specific surface area is large. As for the phenolic-based activated carbon fiber, there are fewer studies at present [37].

It was found that ACFs with more microporous structures had better adsorption of VOCs. Like activated carbon, activated carbon fibers can be modified to increase their adsorption capacity. Acid modification of activated carbon fibers can increase the number of oxygen-containing functional groups, which, in turn, improves the adsorption capacity of polar VOC molecules. Modification of activated carbon fibers using nitric acid was found to increase the adsorption capacity of acetaldehyde from 3.2% (mass fraction) to 9.9%, and modification of activated carbon fibers using metal oxides such as La_2O_3 , CaO , MgO , ZnO , and Al_2O_3 was found to increase the adsorption capacity of acetaldehyde from 3.2% to 20% [38].

Activated carbon fiber (ACF) has also been produced by the reductive carbonization of cellulose fibers over nickel nano-catalysts. Measured by X-ray photoelectron spectroscopy (XPS), 99.5% of the oxygen originally present in the biomass was removed, with more than 63% of the carbon present as reduced material. The reduced ACFs have a high adsorption capacity for non-polar volatile organic compounds (VOCs), and the benzene-uptake capacity of the reduced ACFs is eight times higher than that of conventionally prepared carbon fibers [39]. The surface chemistry of activated carbon fiber (ACF) was

modified with CuSO_4 . Tests yielded a higher adsorption capacity of CuSO_4 -modified ACF for benzene, toluene, methanol, and ethanol vapors compared with untreated ACF [40].

Compared with activated carbon, ACF has excellent adsorption properties, greater adsorption capacity, a faster adsorption rate, and easy regeneration for gas and liquid molecules [41–43].

However, the same activated carbon fibers are prone to saturation, have poor selectivity, are affected by temperature and humidity, are difficult to regenerate, and require complex waste treatment.

2.1.3. Biomass Charcoal

Biomass charcoal is a kind of carbon material made from biomass-based materials by pyrolysis activation and other processes at high temperatures, with a high specific surface area, rich pore structure, and chemically active surfaces, and it has a wide range of applications in the field of environmental pollution control. The sources of biomass carbon materials are relatively abundant and require mild preparation conditions; most of them come from industrial and agricultural wastes—for example, animal waste [44], wood flour [45], banana peels [46], animal bones [47]—and other biomass materials can be made into carbon materials by pyrolysis or carbonization. Current methods for preparing biomass carbon include thermal cracking, hydrothermal carbonization, microwave carbonization, and gasification. The thermal cracking technique is usually used, and the properties of biomass char largely depend on the natural feedstock properties and pyrolysis parameters, especially the control of the pyrolysis temperature [48]. Compared with activated carbon, biochar has several advantages: (1) lower preparation temperature; (2) no activation treatment (or simple activation treatment); and (3) low cost. However, it is also especially disadvantaged as unmodified biochar has a poor adsorption capacity for VOCs, so it is necessary to enhance its adsorption capacity by modifying it. Activation methods are divided into physical modification and chemical modification. The principle of physical activation is to form more micropores and mesopores on biomass charcoal to improve the pore structure and increase the specific surface area. The advantages are the absence of added impurities, the low cost, the introduction of oxygenated functional groups, and that it is clean and easy to control. Physical activation methods include UV irradiation, ball milling, ultrasonic treatment, and gas activation. Chemical activation involves pre-mixing the activator with the precursor raw materials and then activating this under the protection of inert gas at 450–900 °C. The advantages of chemical activation are that the specific surface area is usually higher than that of physical activation, which is as high as 3600 m^2/g , and the yields and adsorption capacities obtained are higher than those of physical activation. The methods include alkali modification, acid modification, grafting of chemical functional groups, and modification with metal salts or metal oxides. The specific modification is shown in Table 3.

HCl, HNO_3 , H_3PO_4 , H_2SO_4 , NaOH, KOH, and ammonia are common acid–base modifiers [49]. In one study, the researcher used cow and sheep bone as raw materials for the preparation of biochar and acetic acid as a modifying reagent. It was found that hydroxyl and carboxyl groups appeared on the surface of modified biochar, and these groups were found to have an adsorption effect on formaldehyde. Activated carbon obtained from corn-kernel waste using ZnCl_2 activation was used to remove toluene from exhaust gas; the corn-kernel biomass charcoal prepared by reacting at 550 °C for 1.0 h with an impregnation ratio of 1.0 showed the best toluene adsorption performance (4.36–4.64 mmol/g), and its cycling ability was good, with the retention of an adsorption capacity of $74\% \pm 3\%$ after five cycles [50]. Waste tree branches were used as the raw material and modified with KOH base; it was found that the biochar so prepared exhibited a high specific area of up to 2150 m^2/g and many micro- and ultra-microporous structures, and the adsorption capacity of the sample was maintained at more than 96% after five adsorption/desorption cycles [51]. Graded porous carbon was prepared from bovine bone as the raw material, and such graded porous carbon was found to have a high specific

surface area, a unique three-dimensional graded porous structure, and a high nitrogen doping content that was 3.56 times higher than that of commercial adsorbents, and it still had excellent recoverable stability with a sample adsorption-capacity retention of more than 98% after five cycles of use [52]. Banana-peel-derived activated carbon was modified, and N-doped activated carbon was prepared by a high-temperature process using two N dopants, i.e., urea and melamine. Urea-doped N had a better effect on the surface excavation of activated carbon. The adsorption capacity of the nitrogen-doped activated carbon for the polar VOC acetone was 44.89 mmol/g at 30 kPa partial pressure of acetone, which was 1.83 times the adsorption capacity of untreated activated carbon (24.57 mmol/g). And it still had good adsorption stability after five adsorption/desorption cycles Yang et al. [53].

Table 3. Methods of biomass modification.

Modification Method	Purpose	Common Reagents
Alkali modification	Increased surface area, oxygenated functional groups	KOH, NaOH, ammonia, etc.
Acid modification	To remove impurities such as metals and to introduce acid functional groups on the surface of the physical carbon	Sulfuric acid, nitric acid, phosphoric acid and citric acid
Grafting of chemical functional groups	Increased adsorption properties, regulated hydrophilic/hydrophobicity, pH, surface charge, etc.	Carboxy, carbonyl, phenolic hydroxyl and lactone groups.
Metal salt or metal oxide modification	To improve the adsorption efficiency toward VOCs, it is necessary to add properties such as catalytic and magnetic properties	MgNO ₃ , MgSO ₄ , MgCl ₂ , CH ₃ COOH.

Studies have shown that biomass charcoal shows high adsorption performance toward common VOCs such as formaldehyde, benzene, toluene, ethylbenzene, etc., and it can be used as an air purification material; it can also be used for the remediation of VOCs in soil and water, and it can be used for industrial-waste gas treatment to remove VOC emissions. Biochar can be used in practice as a sustainable, low-cost, and effective adsorbent for the removal of hazardous VOCs [54]; however, the limited surface area and poor functional groups of biochar severely limit its application. Nonetheless, its textile structure and properties can be upgraded through various activation and/or modification processes to improve the adsorption performance of biochar [55].

2.1.4. Carbon Nanotubes and Graphite

CNTs are engineered carbon nanomaterials with graphene sheets rolled into cylindrical structures that are naturally highly hydrophobic. They are classified into single-walled carbon nanotubes, and multi-walled carbon can be prepared by arc discharge and solid-phase pyrolysis, followed by laser ablation, chemical vapor deposition, solid-phase pyrolysis, and polymerization reaction synthesis. As a new type of nanomaterial, CNTs are characterized by a large specific surface area, a controllable structure, a hydrophobic tube wall, and easy modification. Graphene is a two-dimensional crystal of carbon atoms arranged in a hexagonal arrangement connected by sp² hybridization, which can be prepared by exfoliation, hydrothermal self-assembly, and chemical vapor deposition.

Since the basic structure of carbon nanotubes exhibits a hexagonal array of carbon atoms with strong interaction forces with a wide range of organic compounds, their adsorption capacity is higher than that of activated carbon, and many studies have shown that carbon nanotubes have higher adsorption efficiencies than other carbon materials in the removal of dioxins [56], thiophene [57], 1,2-dichlorobenzene, and polycyclic [58,59].

Carbon nanotubes can be used to adsorb organic vapors, including ethanol, n-hexane, n-nonane, and chlorinated carbonates [60,61]. Jang et al. [62] investigated carbon nanotube (CNT) sponges as a novel adsorbent or to enrich for trace aromatic VOCs. Unlike carbon-based particulate adsorbents, single-walled carbon nanotubes, and multi-walled carbon nanotubes, CNT sponges are usually composed of particles of porous material with a reticulated three-dimensional framework, which is very favorable for trapping organic molecules.

Adsorption of isopropanol with single-walled carbon nanotubes revealed that the functional groups of organic gas molecules and the adsorbent material could undergo a slight chemical reaction, resulting in an adsorption capacity of 82.0 mg/g [63]. Multi-walled carbon nanotubes were used for the adsorption of polar VOCs, and it was found that the polar groups on the surface of the material dramatically altered its adsorption characteristics, extending the penetration time of ethanol on its surface by 65.7% [64].

The adsorption of toluene (VOCs) by reduced graphene oxide was found to be higher than that of graphene oxide under the same experimental conditions. The hydrophobicity enhances the adsorption of non-polar or weakly polar VOCs by graphene oxide, but a severe aggregation effect occurs during its use, which can be improved by making it into a composite material. The hexagonal lattice structure of the graphene layer can also absorb many aromatic VOCs through the effective π - π interactions between graphene and benzene rings [65]. Li et al. [66] prepared a new type of Vaseline-loaded expanded graphite (VEG) composite by the hot-dipping method, and the results showed that VEG was much more hydrophobic than the original expanded graphite and could adsorb more toluene.

Lim et al. [67] used graphene powder with a mesoporous structure to adsorb different concentrations of aromatic compounds (toluene, xylene) and found that compared with graphene oxide, the specific surface area of the thermally expanded graphene powder increased significantly to 542 m²/g. The chemical properties also changed from polar to nonpolar, and the adsorption efficiency for toluene and xylene was high, and the reusability was strong.

Hydrophobic bamboo-derived porous graphitized carbons (BPGCs) were prepared using a co-catalytic graphitization method, and the materials were found to have adsorption capacities for toluene, cyclohexane, and ethanol of 6.7, 3.8, and 2.4 mmol/g, respectively, under dry conditions. Under wet conditions at 80%, their adsorption capacities for toluene and cyclohexane were maintained at 82% and 66% under dry conditions, respectively, whereas the ethanol uptake increased by 33% [68].

Carbon nanotubes (CNTs) are promising adsorbents for carbon-based VOCs but are generally prone to aggregation and can be dispersed by surface activation. Graphene and carbon nanotubes have many potential advantages for adsorption applications due to their special structural and chemical properties. However, carbon nanotubes are toxic, and care should be taken to ensure that they are well packaged when in use. If leaked, they will affect the human body and environment.

2.2. Oxygen-Containing Adsorbent Materials

2.2.1. Metal–Organic Framework (MOF) Materials

MOFs are ordered one-, two-, or three-dimensional skeletons formed by the coordination of metal ions or clusters with organic ligands and are generally obtained by evaporative solvent, diffusion, solvothermal, ultrasonic, or microwave methods [69]. MOF materials can be categorized according to their components and preparation methods: iso-reticulated metal–organic frameworks (IRMOFs), porous coordination networks (PCNs), zeolitic imidazolium skeletons (ZIFs), and institute lava framework materials (MILs).

Among the MOF materials, IRMOF-1 (or MOF-5) is the most representative and has been the most studied. It was originally designed and synthesized by Yaghi's group [70] with the help of the idea of metal carboxylate cluster chemistry. Materials like PCNs are porous materials formed by multiple octahedral cubic solid-pore cages; ZIF materials, which were first proposed by yaghi's group [71], are tetrahedral framework materials syn-

thesized from zeolite-like complexes, with imidazole coordination mainly via the reaction of imidazole ligands (Im)s with Co (II.) or Zn (II.) [72]; and MILs were first synthesized by Ferey at the University of Versailles, France [73]. Some MOF materials have been synthesized with other structures (e.g., UiO and HKUST-1) to make the family larger [74].

Currently, MOF materials for VOC adsorption mainly include the MIL series, IRMOF series, and UiO series. With regard to the adsorption of toluene by different types of MOFs, the size of the adsorption capacity is in the order of UiO-66 > MOF-199 > MIL-101 (Fe) [75]. MOFs are categorized into three types of materials: IRMOF materials, PCN materials, ZIF materials, MIL materials, and others.

The adsorption performance of MIL-101 was found to be superior to that of commercial activated carbon with a similar specific surface area. By modulating the surface functional groups of MOF materials, the hydrophobicity of the materials can be, and specific adsorption can be achieved [76]. A hydrophobic MOF material with naphthalene dicarboxylic acid as a ligand was synthesized, and the adsorption of benzene was 261.7, 229.6, and 205.4 mg/g (20 °C) at 5%, 40%, and 60% relative humidity, respectively [77]. The adsorption effect of the MOF material is better than that of the traditional adsorbent materials such as activated carbon and a zeolite molecular sieve. The adsorption effect of MOFs was better than that of the traditional activated carbon and zeolite molecular sieves, and the selectivity of adsorption and separation could be further improved by designing and regulating the pore structure of MOFs.

MOF materials have significant chemical and structural diversity and are superior to conventional porous materials in the adsorption of hazardous gases/vapors due to the ability to fine-tune the pore size and chemistry of MOFs at the molecular level. Furthermore, the average VOC adsorption capacity of MOFs is 1.7 times higher than that of AC, 5.8 times higher than that of zeolites, and 2.1 times higher than that of polymer resins [4,78].

Although MOF materials have many advantages, they still have some disadvantages, such as low mechanical strength, being a powder solid, poor water stability, etc. To improve these shortcomings to meet the needs of practical applications, a series of MOF composites were generated one after another, effectively introducing multifunctionality and synergistic effects, improving the original performance, and extending the functionality, so the MOF composites have a good application in the absorption of VOCs [79].

Qin et al. [80] prepared Co-M-MOFs (M = Cu, Mn, Ni, and Zn) by the ion-assisted solvothermal method. High performance and stability of the composites were achieved. Li et al. [81] synthesized Cu-BTC@GO, and the toluene adsorption capacity of Cu-BTC@GO-5 was much higher than that of conventional activated carbon and zeolite. Cu-BTC, ZSM-5, and Cu-BTC@ZSM-5 were synthesized by a hydrothermal method, and the high specific surface area and hydrophobicity of Cu-BTC@ZSM-5 could enhance the competitive adsorption of toluene to water vapor. Porous crystalline solids comprising metal-organic frameworks (MOFs) have been used for the selective capture of volatile organic compounds (VOCs) containing carboxylic acid functional groups and/or VOCs containing hydroxyl functional groups [82].

In recent years, significant progress has been made in the green synthesis of MOF materials, which has led to the promise of the scaled-up production of MOF materials in a more economical, sustainable, and environmentally friendly manner. Green synthesis can be achieved by the waste synthesis of MOFs, solvent-free synthesis of MOFs, room-temperature synthesis of MOFs, microwave synthesis of MOFs, sequential synthesis of MOFs, and macro synthesis of MOFs [83,84]. MOFs are prime candidates for VOC capture and detection applications due to their high internal surface area (1140–4293 m²) [4].

Compared with other traditional adsorbent materials, MOF materials have the characteristics of having a rich structure and being easy to regulate, and they include a variety of structural compositions and powerful renewable metal active sites as well as the ability to be chemically modified, which show good application prospects in the adsorption and removal of VOCs.

2.2.2. Zeolites (Molecular Sieves)

Zeolites are microporous crystalline silica–aluminates with a highly ordered pore structure, which are widely used in the field of environmental protection due to their adjustable pore size, high hydrophobicity, and easy surface modification [85].

Molecular sieves are categorized into natural and synthetic zeolites. Most of the natural zeolites are formed by the reaction of volcanic tuffs and tuffaceous sedimentary rocks in marine or lacustrine environments. Among the known zeolite ores, the common species include plagioclase zeolite, rhodochrosite, silky zeolite, and hairy zeolite. They are mainly distributed in the United States, Japan, France, and other countries, but China also has many deposits of mercerized zeolite and plagioclase zeolite, while Japan is the country with the largest amount of natural zeolite mining. However, due to resource constraints on natural zeolites, synthetic zeolites have been adopted in large quantities since 1950. Compared with carbon-based materials, zeolite molecular sieves are chemically stable, not easily combustible, and can be used for the adsorption of VOCs at higher temperatures and humidity. By designing the pore structure and silica–aluminum ratio of zeolite materials, their hydrophobicity and surface functional groups can be tuned to achieve the selective adsorption of VOCs.

The ZSM-5 molecular sieve is a zeolite molecular sieve with an MFI structure that was first developed by the Mobil Corporation in the USA; it is cheap and easy to obtain, with an easily tunable silica–aluminum ratio and high-silica three-dimensional cross channels providing active sites for effective adsorption, which can adsorb VOC molecular sieves with different silica–aluminum ratios. ZSM-5 molecular sieves with higher silica–aluminum ratios were found to be better adsorbents than NaY molecular sieves with a lower silica–aluminum ratio. At higher relative levels of coated ZSM-5 on cordierite honeycomb ceramics, metal honeycomb base, and monocrystalline silicon wafers by the fuselage slurry, it was found that the adsorption capacity of formaldehyde became stronger in all of these materials. ZSM-5 molecular-sieve adsorbents prepared using silica sol as a binder were also found to have stronger hydrophobicity and desorption properties than activated carbon with a lower pressure drop and lower resistance [86]. VOC gases are often a mixture of multiple gases, and at higher humidity, this moisture will compete for adsorption with the VOCs and reduce the adsorption capacity of the adsorbent, while Gao et al. found that the strong hydrophobicity of high-silica ZSM-5 molecular sieves made it difficult for water vapor to be adsorbed, and the adsorption performance toward VOCs could be ensured even at a relative humidity of 60%. At an adsorption temperature of 28 °C and a relative humidity of 35%, the adsorption of butyl acetate exhaust gas by AgY molecular sieves with a silica–aluminum ratio of 40 was strongly inhibited, and the adsorption capacity was reduced by 42% compared with that of the dry condition, while the adsorption capacity of AgZSM-5 molecular sieves with a silica–aluminum ratio of 140 was reduced by only 7% [87].

In summary, ZSM-5 molecular sieves with a high silica to aluminum ratio have high adsorption capacity and adaptability to humid environments.

ZSM-5/SBA-15 composite molecular sieves have excellent adaptability to humid environments [88]. The adsorption penetration time of toluene could be maintained at 27.3 min under high humidity. This molecular sieve does not work easily in a high-temperature environment. Recently, a series of modified ZSM-5 molecular sieves was prepared by treating with a mixed alkali solution of sodium hydroxide and tetra-propylammonium hydroxide. The results showed that the alkali-modified molecular sieves increased both the specific surface area and the total pore volume, and their intermediary pore specific surface area and the volume of the pore volume were increased by a factor of 8.6 and a factor of 12.3, respectively. The adsorption capacity of the samples was enhanced [89]. Modification of ZMS-5 molecular sieves with barium ions revealed that the morphology and crystal shape of ZSM-5 molecular sieves were not changed, but their total pore volume and stacked mesopore pore volume increased significantly, and the microporous pore volume decreased; Ba-ZSM-5 molecular sieves had better adsorption performance toward

toluene, n-butanol, and ethyl acetate relative to ZSM-5 molecular sieves [90]. All-silica ZSM5, a high silica–aluminum-ratio Y molecular-sieve raw powder (not high-temperature roasting containing a templating agent), and silica sol were mixed in a mass ratio of 7 to 1:1, and thermo-crystallization was carried out under the condition of 300–500 °C. The silica sol self-assembled and grew around the molecular sieves under the action of the molecular-sieve templating agent, and the hollow-particle molecular sieves with no binder were formed. The prepared hollow particles of molecular sieves do not contain binders and are characterized by high strength, high hydrophobicity, high VOC adsorption capacity, and high-temperature stability. The molecular-sieve adsorbent molded by this preparation method was regenerated about 5000 times or more, and the crystallinity was reduced to 50% (adsorbent failure) [91].

Therefore, the molecular sieves can be modified by suitable modification of the squareness to improve the adsorption capacity.

2.2.3. Silica Gel

Silica gel is one of the alternatives to carbon-based adsorbents because it is cheaper, safer, recyclable, and has a similar adsorption capacity to activated carbon. The preparation of silica gel is divided into three steps: gel preparation, aging, and drying.

The adsorption of three adsorbents, activated carbon, and silica gel on octamethylcyclotetrasiloxane from industrial exhaust at 25 °C was compared, with silica gel having the highest adsorption capacity [92]. The adsorption of toluene by silica gel was investigated at 25 °C, and silica gel was found to have the advantages of a fast adsorption and desorption rate, high adsorption capacity (up to 437.4 mg/g), and long service life [93]. The adsorption capacity of silica gel for toluene was stronger than that of activated carbon, and the desorption amount was much higher than that of activated carbon; the vacuum desorption test showed that the desorption capacity of silica gel for toluene vapor (61.6% desorption rate) was much higher than that of AC desorption (46.22% desorption amount) under ambient temperature conditions. In addition, a significant accumulation of toluene was observed on AC after five cycles of dynamic adsorption/desorption tests. Long-term operational tests showed that more than 75% of the adsorbed toluene could be recovered from the silica gel. Kutluay et al. [94] obtained diacid calix aromatic-tethered silica (DACTS) as an adsorbent by tethering calix aromatic carboxylic acid derivatives to 3-glycidioxypropyl-bonded stationary phases (GBSs), and the results showed that the successfully synthesized DACTS adsorbent exhibited excellent adsorption capacity and reproducibility for VOCs.

In the study by Li et al. [95], hydrophobic mesoporous silica gel was successfully prepared by the co-condensation method using sodium silicate and phenyltriethoxysilane (PTES) as mixed precursors under acidic conditions. The synthesized silica gel adsorbent has a good mesoporous structure (5.1 nm) and hydrophobicity, significantly enhanced moisture resistance, and a high desorption rate (up to 89.7%) when first recovered by vacuum desorption under humid conditions. The adsorption/desorption cycling test demonstrated the stability of the adsorption capacity after five repeated cycles.

Vacuum swing adsorption (VSA) using silica gel (SG) proved to be a promising method for the recovery of volatile organic compounds (VOCs). Sui [96] systematically investigated the removal and recovery of o-xylene, a typical volatile organic compound (VOC), from silica gel by the vacuum swing adsorption (VSA) process. VSA offers greater advantages than conventional thermal treatment and absorption methods because it uses the recovered VOCs as products.

Considering the long-term operation of future applications, silica gel is more suitable for removing and recovering high concentrations of toluene vapors from gas streams using a combined normal adsorption and vacuum desorption process at room temperature [97]. Silica gel can effectively remove aromatic hydrocarbons (toluene, o-xylene) from the gas stream. To explore the adsorption by silica gel of oxygenated VOCs, starting from exploring the principle of the adsorption and desorption of oxygenated VOCs by silica gel, it was found by adaptation that silica gel has a better adsorption of oxygenated VOCs; also, when

the temperature rises by 10–30 °C during desorption, the desorption process is enhanced, which means that the recovery of VOCs is more secure.

Currently, there are fewer studies on silica gel as an adsorbent for VOCs and, like clay materials, the hydrophilic Si-OH on the surface of silica gel makes its adsorption performance poor under high humidity conditions. The use of organic modifiers such as trimethylchlorosilane to coat the surface of the silica gel material can effectively improve its hydrophobicity.

2.2.4. Clay

Natural clays, such as bentonite, are found in large quantities in many soils. Porous clay heterostructures (PCHs) are novel materials with a specific surface area of up to 400–900 m²/g, a unique combination of micropores and mesopores, a high adsorption capacity, and high mass-transfer rates.

Clays are hydrous aluminosilicate minerals that are mainly found in soils, sediments, and weathered/altered rocks; they are layered silicates, consisting of four and six layers of coordinating cations (Si, Al, Mg, etc.) stacked on top of each other. In general, the particle size is small, the surface area is large, and they have good cation-exchange capacity and a negative surface charge. In addition, they are abundantly available in almost all countries at a low cost, 1/20th that of activated carbon. Therefore, a PCH is likely to be an efficient adsorbent to meet the requirements of VOC adsorption/separation technology. The PCH is prepared by using waste or virgin organic clay (e.g., organ-bentonite) as a raw material, and then by inserting a cationic surfactant into the interlayer zone of the bentonite, low-cost and abundant organ-bentonite can be prepared [98]. PCH adsorbent synthesized from organ-bentonite from wastewater treatment was used to adsorb CCl₄, and high adsorption of benzene and CCl₄ by PCHs was observed [99]. A PCH synthesized from cetyltrimethylammonium bromide (CTMAB) and dodecyl ammonium (DDA)-modified bentonite (Bent) was found to have adsorption properties toward six volatile organic compounds (VOCs). In addition to pheromone clay, another clay that researchers are most interested in is kaolin, which is generally adsorbed through hydrogen bonding and has been found to have excellent regenerative ability [100,101] and a good adsorption capacity for phenol and toluene in the air.

Silicones are hydrophobic, organophilic materials that reversibly extract dissolved or dispersed organic compounds with high adsorption capacity and effectively remove butanol, methyl tertiary butyl ether (MTBE), perchloroethylene, trichloroethylene, ethanol, and toluene from freshwater and saltwater [102].

Mobasser et al. [103] used activated carbon, organosilicon, and zeolite for the adsorption of benzene and toluene, and as a result, activated carbon and organosilicon proved to have potential as adsorbents for hydrocarbon VOCs in air purifiers, while zeolite had the least adsorption capacity.

Jarraya et al. [104] modified the clay material by inserting docosyl dimethyl ammonium bromide. The adsorption isotherms showed that the insertion of dimethyl ammonium bromide decoys into the clay material increased its adsorption capacity for toluene, cyclohexane, and chlorobenzene to 2, 2.5, and 3.5 mg/g, respectively.

In the future, its adsorption capacity can be improved by acid modification or alkali modification.

2.3. Other Adsorbent Materials

Adsorption Resin

Adsorption resin is a kind of high polymer that is mainly divided into a gel type and a large-pore type. Currently widely used is the large-pore-type adsorption resin for VOCs with concentration and separation. The ultra-highly crosslinked adsorption resin is also a commonly used adsorbent, with a high specific surface area and richly microporous; compared with activated carbon, it has higher mechanical strength, a more hydrophobic surface, a pore structure that can be adjusted, and other advantages, which

make it a potential alternative to an activated carbon adsorbent. Its main feature is the high hydrophobicity of the surface so that humidity has less influence on the adsorption of VOCs; the polarity can be judged by the water contact angle, as shown in Table 4 below. Compared with activated carbon and activated carbon fiber, the contact angle of the ultra-highly linked adsorbent resin is the largest, as shown in Figure 2, which shows that the hydrophobic ultra-highly cross-linked adsorbent resin is the most hydrophobic.

Table 4. Relationship between water contact angle and polarity.

Water Contact Angle	Polarities
$0^\circ \leq \theta \leq 70^\circ$	Hydrophilic
$70^\circ \leq \theta \leq 110^\circ$	Mesopolar
$110^\circ \leq \theta \leq 180^\circ$	Hydrophobic

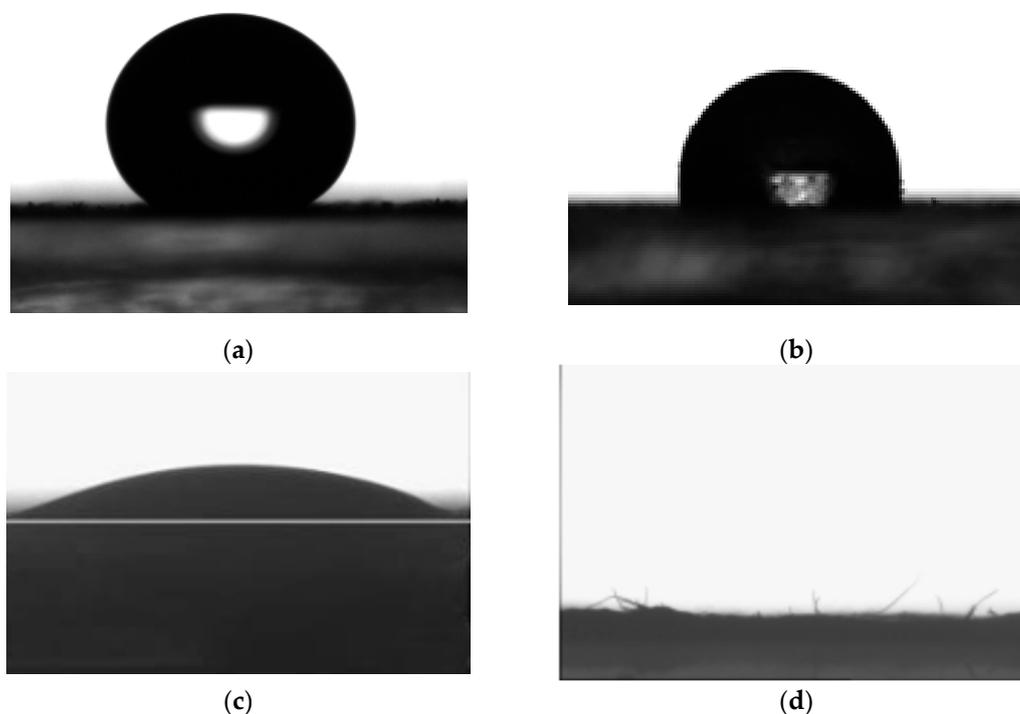


Figure 2. (a) Ultra-highly cross-linked adsorbent resin (contact angle 132°). (b) Activated carbon (contact angle 48°). (c) Commercial ultra-high crosslinking adsorbent resin (contact angle 98°). (d) Activated carbon fiber (contact angle 0°).

The ultra-highly cross-linked adsorbent resin with rich microporous medium-pore distribution significantly improves the adsorption/desorption performance for medium and high concentrations of VOCs, which can be seen in the pore size distributions of the new resin and the commercial resin; the comparison of adsorption and desorption performances is shown in Figure 3.

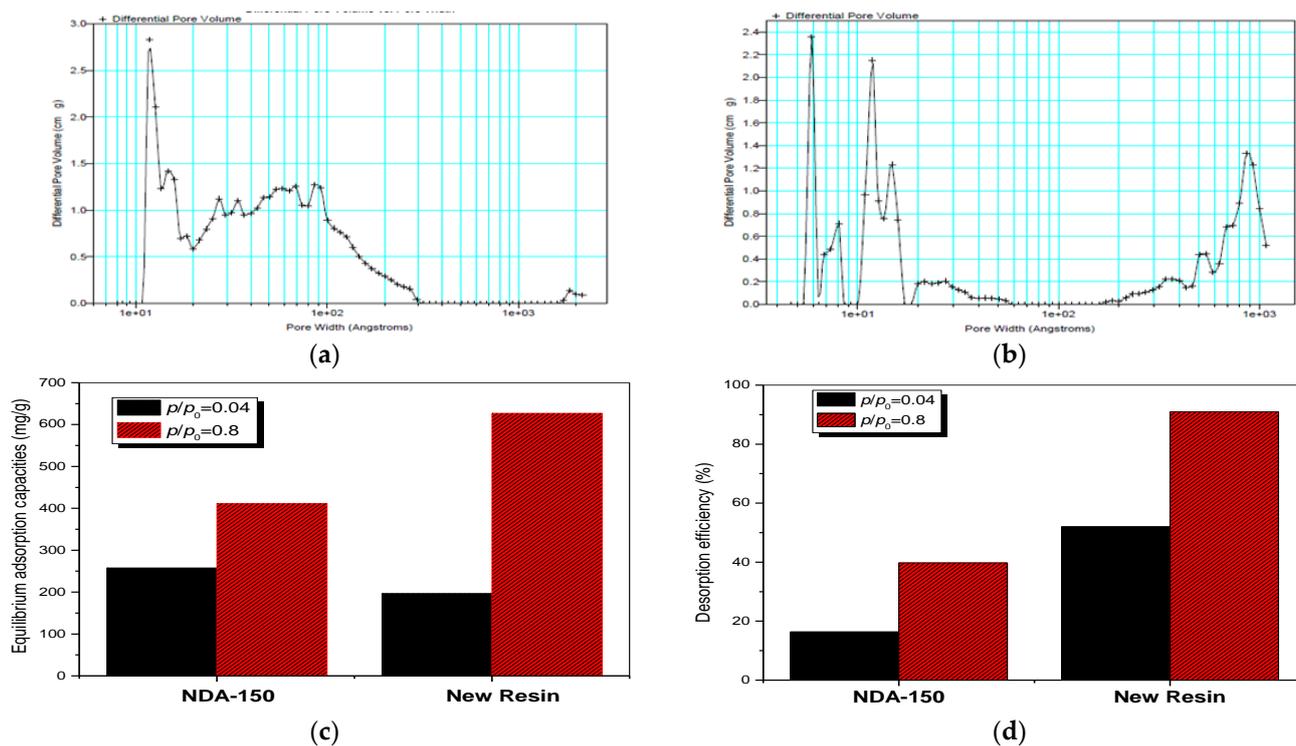


Figure 3. Pore size distribution of the new resin (a). Pore size distribution of the new resin (b). Comparison of adsorption performance between the new resin and NDA-150 resin (c). Comparison of desorption performance between the new resin and the NDA-150 resin (d).

It has a regular spherical appearance, a high specific surface area (generally up to 1000 m²/g or more), and high mechanical strength, and the pore structure of the material can be regulated according to the characteristics of VOCs. It is non-catalytic and has a wide range of adsorption objects; it can be used for the adsorption and recovery of chemically active VOCs, such as ketones, and of chlorinated hydrocarbons, such as methylene chloride, ethylene chloride, trichloroethylene, and other chlorinated hydrocarbons.

The adsorption resin is significantly better than activated carbon and molecular sieves in terms of its hydrophobicity and non-catalytic activity, but its solubilization effect and high wind resistance due to its small size need to be considered in industrial applications.

The adsorbent resins HCR-1, HCR-2, and HCR-3 were prepared by combining the resin powder as the raw material, firstly by dispersion polymerization and then by cross-linking modification, using organic adhesive as a binder [105]. The specific surface area of the three resins is quite large, and their structures include microporous, mesoporous, and microporous structures. HCR-2 has the best performance among the three adsorbent materials after experimental testing.

Compared with HCR-2, HCR-2 has the following advantages: The desorption rate of column-adsorbent HCR-2 for toluene (8000 mg/m³) in exhaust gas reaches more than 98.7% in 0.8s of residence time. When the concentration of toluene is 8000 mg/m³, the dynamic adsorption amount is 148 mg/g. Compared with the traditional adsorption resin ball G-01, the wind resistance is greatly reduced, significantly reducing the energy consumption in industrial use.

A new environmentally friendly hybrid (organic–inorganic) hyper-crosslinked resin has been designed for the removal of acetic acid (AcOH). Based on the combination of a biomass-derived resin matrix and inorganic particles capable of stabilizing and neutralizing AcOH, the new ZnO/COPs are expected to outperform state-of-the-art VOC absorbers [106].

The large specific surface area and hydrophobicity of HCP make it still have a good adsorption effect in high humidity, and future research should be devoted to the functionalization modification of its surface and the optimization of the synthesis process.

The advantages and disadvantages of the adsorption of VOCs by adsorbent materials, as well as the types of applicable VOCs, are summarized in the following Table 5.

Table 5. Advantages and disadvantages of different adsorption materials for VOC adsorption and types of applicable VOCs.

Absorbent Material	Pros	Cons	Applicable VOC Types
raw materials	High adsorption capacity, acid and alkali resistance, low cost	Incomplete desorption/desorption Difficult regeneration due to high-temperature resistance	Small molecular weight, medium to high polarity, gaseous, water-soluble, and aromatic VOCs
activated carbon fiber	Fast adsorption, easy regeneration, large adsorption capacity	Higher cost, easy to saturate, poor specificity	Small molecular weight, low to medium polarity, and aromatic groups containing VOCs.
biochar	Green environmental protection, high-efficiency adsorption, safety	Slow adsorption speed, high cost, poor adsorption selectivity	Large molecular weight, medium to low polarity, and oxygenated compounds
carbon nanotube	Fast adsorption, efficient adsorption, renewability	High preparation cost, poor stability, possible toxicity, and environmental impacts	Adsorption of many types of VOCs, especially small molecular weight, polar, and aromatic hydrocarbon VOCs
graphene	Highly efficient adsorption, high stability, renewability	Slow adsorption speed, easy to saturate, can only be used in specific environments.	Small molecular weight, polar, and aromatic VOCs
MOF	With high adsorption capacity, the special network structure is predictable, versatile, and tunable.	High cost of preparation of precursors, poor thermal stability	A variety of VOCs with different molecular weights, polarities, and chemical properties
zeolite molecular sieve	Highly ordered in molecular size, adjustable pore size, microporous pore, rich skeleton structure, selective adsorption according to the molecular size of VOCs, and molecular sieve thermal stability, easy to regenerate.	The adsorption effect is affected by temperature and humidity	Small molecular weight, low polarity, volatile organic compounds that are stable at moderate to high temperatures.
silica gel	Good stability, high adaptability to humidity, simple operation	Poor hydrothermal stability and mainly microporous structure, not conducive to the adsorption of VOC gas at low concentrations, easily rigid	Small molecules, low to medium polarity, VOCs in humid environments, VOCs that require high reproducibility and stability, and VOCs that are suitable for operation at low temperatures and do not require particularly rapid treatment.

Table 5. Cont.

Absorbent Material	Pros	Cons	Applicable VOC Types
clay	Low cost, environmental protection, stable adsorption effect	Limited capacity, slow adsorption speed, short replacement cycle, greatly affected by humidity	Suitable for the adsorption of polar and small- and medium-sized molecules, humid environments, VOCs requiring rapid adsorption, high renewability requirements, low-cost needs, and the need for flexible control of adsorption performance
adsorption resin	High-efficiency adsorption, easy operation, good selectivity	High cost and limited adsorption capacity	Suitable for the adsorption of high polarity, large molecular weight, liquid phase VOCs requiring selective adsorption, high efficiency adsorption, good regeneration performance, as well as special environmental adaptability.

3. Absorption Method—Absorbents

The absorption method is the use of a non-volatile or low-volatile liquid as an absorbent for a variety of VOC components in tail gas. Using the absorbent solubility differences and a packed tower, a spray tower, and a rotating packed bed as absorption equipment, the VOC components in the tail gas are transferred from the gas phase to the liquid phase, and then the different physical properties of the VOCs and the absorbent are used to achieve the separation of governance. Absorption is widely used because of its simplicity, high efficiency, low operation, low investment cost, and the ability to regenerate the absorbent. However, to achieve high absorption efficiencies while meeting the principles of green chemistry and green engineering, it is necessary to select suitable absorbents.

The absorbent is usually selected with a high boiling point, low volatility, low toxicity, and VOC solubility of oil organic solvents, such as diesel oil, washing oil, etc. Water is the most commonly used type of absorbent, but generally, ammonia, H₂S, and other inorganic gases have a better absorption effect. The absorption of organic gases is not obvious; this is because the majority of the VOCs' water solubility is poor, such as the solubility of benzene in water under the conditions of room temperature, which is only 0.07 g for each 100 g of water. In recent years, the research of hot-spot absorbers has been endless, such as that on surfactant absorbers, microemulsion absorbers, ionic liquid absorbers, etc.

At present, more absorbers have been reported, which can be divided into the following four categories: organic solvents, surfactants, microemulsions, and ionic liquids.

Organic solvent absorbent: The use of this absorbent to treat VOC gases can be traced back to the 1970s. It is used up to a certain boiling point for very heavy oil substances, such as waste motor oil, lubricating oil, washing oil, biodiesel and diesel fuel, and some pure organic solvents.

As an intramolecular material with both hydrophilic and hydrophobic groups, surfactants can spontaneously form a nonpolar micellar microenvironment after reaching a certain concentration in solution, which significantly improves the solubility performance of insoluble or insoluble organics. Researchers used cyclodextrin as an absorbent for the absorption and purification of toluene exhaust gas. The results showed that β -cyclodextrin absorbed toluene the most, about 250 times more than water. Some other surfactants (e.g., anionic sodium dodecyl sulfate, nonionic polyoxymethylene octyl phenol ether, cationic cetyltrimethylammonium bromide, and biosurfactants such as rhamnolipids and lipopeptides) have shown high adsorption effects on VOCs.

A microemulsion is a thermodynamically stabilized system that is generated spontaneously from components such as a co-surfactant, surfactant, water or brine, and oil in appropriate ratios. Due to its strong solubilizing effect on organic pollutants, it has been widely used to absorb and purify VOC exhaust gas in recent years. The researchers constructed a microemulsion system with Tween as a surfactant, n-butanol, n-butyric acid, and n-butylamine as co-surfactants, as well as toluene as the oil phase, and realized the absorption and purification of toluene exhaust gas through a packed tower. The results showed that the absorption efficiency of the Tween-20/n-butylamine/toluene/water microemulsion system for toluene could reach 65%. Although the preparation of the microemulsion absorbent is complicated, and it is not easy to regenerate and reuse after absorption saturation, the use of a microemulsion to purify and treat VOC exhaust gas is technically feasible, and the effect is better than that of a single surfactant. However, industrialized applications are not common at present.

An ionic liquid absorbent means an ionic liquid, which consists of an organic cation and an organic or inorganic anion and that is liquid at or near room temperature. As a green solvent with high designability, ionic liquids can achieve the selective solvation and absorption of specific gases by introducing structure-specific functionalized groups through the fine-tuning of their structure and properties. Researchers investigated the dissolution and absorption of 14 representative VOCs in 135 imidazolium-based ionic liquids, and the results showed that the cations and anions in the ionic liquids play a decisive role in the absorption and purification efficiency of VOCs. By substituting cations and anions in ionic liquids, the interaction between ionic liquids and VOC molecules can be enhanced, thus improving their absorption and purification efficiency.

Zhang et al. [107] prepared a novel complexing absorbent consisting of polyethylene glycol 200 (PEG200) and ionic liquids (ILs) for the absorption of volatile organic compounds (VOCs) such as dichloromethane (DCM) and benzene, and its absorption rate was 85.46% for DCM and 87.15% for benzene in the first 5 min; the regeneration performance was remarkable as the absorption rates of DCM and benzene did not show significant attenuation or obvious decay over five cycles. Gui et al. [108] used 1-ethyl-3-methylimidazole acetate ([EMIM][Ac]) to absorb two common pharmaceutical volatile organic compounds (VOCs), dichloromethane (DCM) and ethanol. The results showed that the removal rates of DCM and ethanol reached 91.82% and 97.01%, respectively.

However, the viscosity of ionic liquids is usually high, which makes the gas–liquid two-phase mass transfer limited; second, the cost of ionic liquids is relatively high, resulting in poor economic feasibility. They have long been considered green solvents; however, recent data suggest that ionic properties do not necessarily infer nontoxic or low-toxicity properties. Several ionic compounds have shown significant toxicity, leading the scientific community to reduce the use of ionic liquids or find other, more environmentally friendly alternatives. The use of renewable, biodegradable, and non-toxic sources, such as amino acids, amino alcohols, or sugars, can improve the green properties of ionic liquids. Novel bio-based ionic liquids obtained from choline chloride and fatty acids can absorb hydrophilic and hydrophobic VOCs and are usually less toxic to various organisms than the usual chlorinated and commercial ionic liquids [109].

Deep eutectic solvents (DESs) have emerged as a more environmentally friendly alternative to ionic liquids. Hydrophobic deep eutectic solvents (DESs) have been developed as a new type of green absorbent for efficient hydrophilic VOC elimination [110].

The most common deep eutectic solvents are usually based on mixtures of ammonium or phosphine salts with hydrogen-bonding donors, which are capable of interconnecting with each other through hydrogen-bonding interactions. This combination forms a liquid with a melting point that is significantly lower than the melting point of each component. Deep eutectic solvents share many of the properties of ionic liquids, but they are cheaper to produce, are often made from naturally occurring chemicals, are less toxic, and are mostly biodegradable. Scholars have studied the absorption of three VOCs by seven deep eutectic solvents at different temperatures and VOC concentrations [111]. Significantly lower gas–

liquid partition coefficients were obtained compared with water. The VOC absorption capacity of the solvents increased linearly with an initial VOC concentration of up to 1000 g/m³. Absorbed VOCs could be easily desorbed by heating, and the solvents showed very good reusability. The high absorption capacity, the ease of the desorption process, and the fact that they are inexpensive, easy to prepare, and have a low environmental impact make deep eutectic solvents excellent candidates for VOC absorption processes [112].

A DES based on tetrabutylammonium bromide and decanoic acid showed a high absorption capacity and versatility for different tested VOCs. The maximum absorption enhancement of 1-decene reached 60,000-fold at 303 K compared with water. Regeneration of the absorber was carried out by several absorption/desorption cycles or after water removal without a loss of absorptive capacity [113].

Using a combination of modified CD and acetylpropionic acid, four analogs of DESs, called supramolecular low-melting-point mixtures (LMMs), were formed to study their absorption properties toward five VOCs (acetaldehyde, butanone, methylene chloride, thiophene, and toluene). The gas–liquid partition coefficient of the supramolecular LMMs was reduced by a factor of 250 compared with water; toluene and methylene chloride were absorbed by the supramolecular LMMs at 99% and 95%, respectively (also at higher concentrations). The LMMs also retained their absorption capacity after five absorption/desorption cycles [114].

Each absorber has different advantages and disadvantages when absorbing VOCs and is suitable for different types of VOCs to be absorbed, as shown in the following Table 6.

Table 6. Advantages and disadvantages of different absorbents for absorbing VOCs and applicable types of VOCs.

Absorbent Type	Pros	Cons	Applicable VOC Types
organic solvent	Effective removal, a wide range of applications	Toxic, high energy consumption	Suitable for hydrophobic, polar, and specific compounds;
surfactant	Easy to operate, selective, efficient absorption	Difficult to regenerate, poor regeneration, pollution of water quality	Hydrophobic, polar
microemulsion	Efficient absorption and good stability	Complex operation, high cost, need for waste liquid treatment	Hydrophobic, polar, volatile compounds at high temperatures
ionic liquid	Thermally stable, renewable, highly efficient, relatively environmentally friendly	High cost, toxicity limitations, solubility limitations	Hydrophobic, polar, volatile compounds at high temperatures; unsuitable for high-molecular-weight and toxic compounds
hydrophobic deep eutectic solvents	High absorption efficiency, green, flexible, renewable	High cost	Suitable for low-molecular-weight VOCs

4. Catalytic Oxidation Method and Catalytic Combustion Method—Catalysts

The catalytic oxidation method uses a catalyst to oxidize VOCs at a lower temperature (250~500 °C) into O₂, H₂O, and other relatively less harmful compounds. To achieve this harmless treatment of VOCs, the role of the catalyst is to reduce the reaction activation energy. The catalytic combustion method involves preheating to the ignition temperature of the VOC exhaust gas, with catalyst surface-oxidation decomposition. The key to the catalytic oxidation and catalytic combustion methods is the selection of the catalyst. The design and preparation of new high-efficiency catalysts is an important guarantee for the advancement of this technology. At present, VOC catalysts are mainly classified from the active components, including precious-metal catalysts and non-precious-metal oxide catalysts.

4.1. Precious-Metal Catalysts

Precious metals such as platinum and palladium are the main components that have high catalytic activity, thermal, and resistance to mesotoxicity, but the cost is relatively high. The development of noble-metal catalysts and transition-metal oxides for the catalytic oxidation of VOCs has been widely reported. The oxidation of benzene, butanol, and ethyl acetate by alumina-carrier-loaded group VII metal catalysts was investigated; palladium and cobalt were the most active metals in the oxidation reaction of ethyl acetate; various metals had the highest oxidative activity toward butanol, and the lowest oxidation activity was toward ethyl acetate. Precious-metal catalysts were the earliest catalysts studied in catalytic combustion: mainly Pt, Pd, Rh, Ru, and Au, and so on [115].

Precious-metal catalysts are more mature catalysts with higher activity and selectivity. It was found that the precious-metal-based catalysts loaded with platinum and palladium showed good activity for the complete oxidation of VOCs at low temperatures. Despite the many advantages of precious-metal catalysts, they inherently suffer from the problem of easy sintering at high temperatures. Therefore, it is necessary to load the noble-metal catalysts, where the noble metal is dispersed and loaded onto the carrier; noble-metal catalysts are high-cost, have poor stability, and easily poisoned. Due to the high price and low precious-metal reserves in nature, single-atom catalysts (SACs), especially single-atom precious-metal catalysts, have attracted much attention due to their maximum atomic utilization and dispersion. The emergence of SACs has significantly reduced the number of precious metals and increased the catalytic activity, making the catalytic process progressively more economical and sustainable [116].

Currently, research on SACs is mainly focused on finding suitable carriers for the synthesis of stable single atoms. Depending on the carrier, there are “bottom-up” and “top-down” approaches. The difference between the two is that in the former, the metal precursor is dispersed on the carrier at the atomic scale, while in the latter, metal NPs or bulk metals are used as precursors [117].

The researchers then turned toward the direction of the catalytic activity of highly stable non-metallic catalysts.

4.2. Non-Precious-Metal Catalysts

Non-precious metals are mostly transition metals, containing unsaturated d orbitals, which can easily adsorb and activate reactant molecules and have good catalytic activity. Oxides of transition metals such as Mn, Co, Ce, Cu, etc. have various valence states, and after pretreatment, they will create defects on the catalyst surface and thus enhance the ability for the adsorption and activation of VOCs [118–120].

Compared with noble-metal catalysts, non-precious-metal catalysts have a lower cost, but their catalytic activity and toxicity resistance are relatively weak. Currently, catalysts used for the catalytic oxidation of VOCs mainly include manganese oxide, cerium oxide, cobalt oxide, and copper oxide. Common non-precious-metal catalysts include manganese-based oxide catalysts, cerium-based oxide catalysts, copper-based oxide catalysts, and cobalt-based oxide catalysts. Next, we analyze these non-precious-metal catalysts.

Manganese-based (Mn-based) oxides, as economical and practical environmentally friendly materials, are some of the most competitive and promising candidates for the catalytic degradation of VOCs in thermo-catalytic or photo/thermal catalytic systems [121].

Studies have shown that the activity of MnO_x catalytic oxidation of toluene is in the following order: Mn₃O₄ > Mn₂O₃ > MnO₂ [122]. The grain size, morphology, and crystalline surface of MnO_x catalysts lead to a great difference in the pore properties, specific surface area, and redox capacity [123,124]. Manganese oxides in the form of rods, wires, tubes, and floral spheres, which are prepared by hydrothermal and solution methods, are used for the catalytic oxidation of toluene and of VOCs. For the catalytic oxidation of toluene, the best catalytic performance was obtained for rod-shaped MnO₂; the catalytic performance of core-shell spheres, hollow cubes, and nanorods of Mn₂O₃ prepared by the

sacrificial template method and the hydrothermal method was found to be in the following order: core-shell spheres > hollow cubes > nanorods [125,126].

Increasing the adsorption amount of oxygen and increasing the reaction-specific surface area during preparation can improve the catalytic activity; doping of elements also produces a series of effects—the effect of transition elements, rare earth elements, etc. By introducing doping, it is possible to form composite manganese oxides with spinel-type and chalcocite-type structures, and manganese-based composite oxides show a higher catalytic activity for the oxidation of toluene than a single manganese oxide catalyst. A series of manganese oxides mixed with Zr, Fe, Co, and Cu oxides were reported to be prepared using the reverse microemulsion method for the catalytic combustion of toluene; it was found that the manganese oxides containing the mixed oxides exhibited very good activity for the catalytic combustion of toluene, suggesting that the reverse microemulsion method is an effective way to incorporate highly active substances into combustion catalysts, thus highlighting some potential catalytic combustion active substances. In addition, the catalytic performance of the loaded manganese-based catalysts can be improved by choosing suitable carriers for the preparation of the catalysts [127].

Cerium is a rare-earth element with very abundant reserves. CeO_2 has more Lewis acid sites and abundant oxygen vacancies, which effectively improve the reactive oxygen mobility, enhance the adsorption capacity of reactive oxygen, and show a good ability to store and release oxygen. The catalytic performance of CeO_2 catalysts for VOCs can be effectively improved by adjusting their morphology and exposing the crystalline structure. Morphologies of CeO_2 catalysts (Figure 4), i.e., shuttle (CeO_2 (S)), nanorods (CeO_2 (R)), and nanoparticles (CeO_2 (P)), were used to catalyze the probing reaction of toluene oxidation. The CeO_2 (S) catalysts were found to exhibit the most favorable performance, with a larger surface area and higher surface-oxygen vacancies [128].

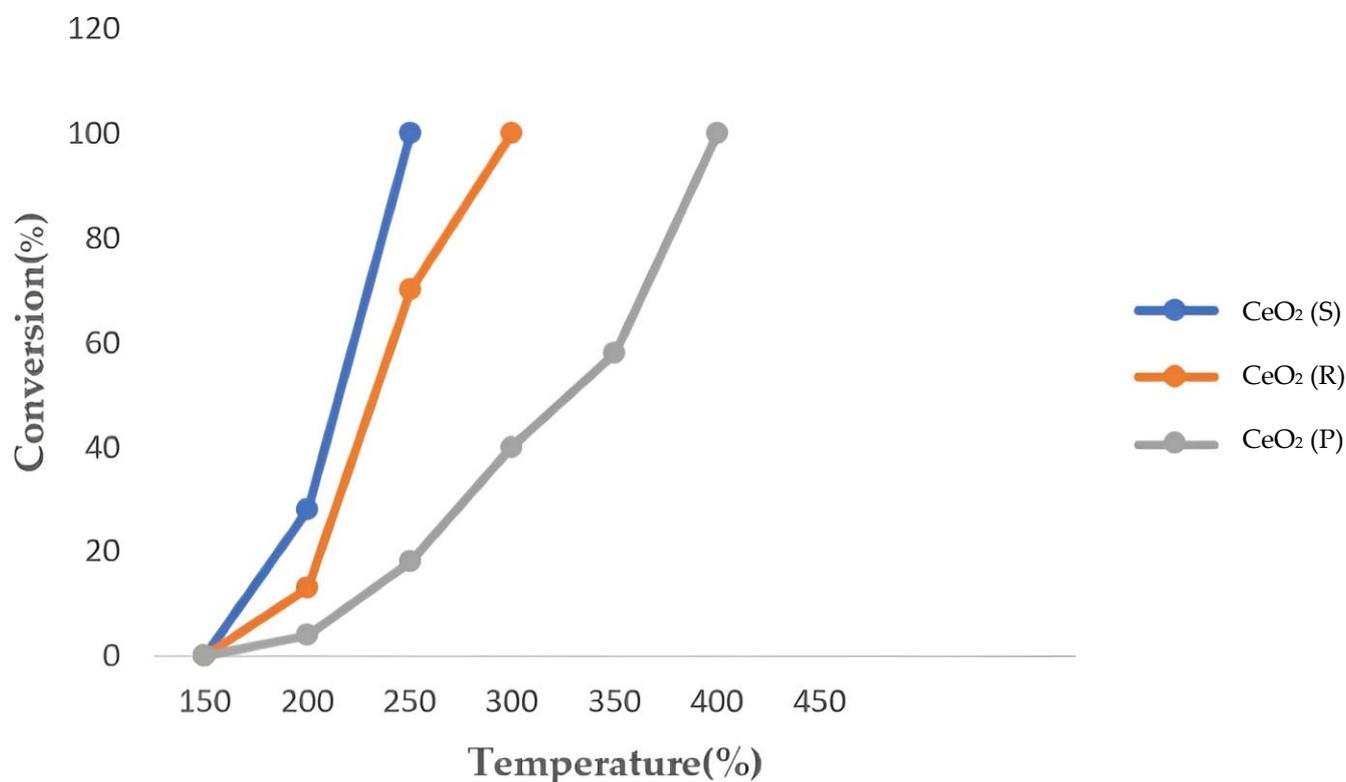


Figure 4. Temperature versus conversion for different shapes of CeO_2 .

Generally speaking, the catalytic activity of Ce-based oxides for VOCs is not high, but due to their low redox potential ($\text{Ce}^{3+}/\text{Ce}^{4+}$), low oxygen-vacancy formation energy, and unique 4f electronic structure, it is easy to form a 4f-d structure with other metals (transition

metals, noble metals) to produce inter-electronic interactions, and they are often used as functional carriers or additives to enhance the catalytic performance of catalysts.

Zhou et al. [129] prepared a series of ceria-based high-entropy oxide catalysts (1:1 ratio of CeO₂ to HEO) by solid-phase reaction, and 100% toluene conversion above 328 °C was achieved for Ce-HEO-T samples. Among all the prepared samples, the medium-content (0.5 wt%) Au/Ce-HEO-500 exhibited the lowest temperature for the complete combustion of toluene (260 °C), which was nearly 70 °C lower compared with the Ce-HEO-500 carrier. In addition, it showed excellent stability for 60 h with 98% toluene conversion. Most importantly, at 5 vol.% H₂O vapor, the toluene conversion remains unchanged or even increases slightly compared with dry air, showing excellent water resistance.

As non-precious-metal catalysts, copper-based catalysts have various valence states (+1, +2, +3), mainly in the form of Cu₂O and CuO. In the process of toluene oxidation, the oxygen-rich vacancies can accelerate the adsorption and activation of gaseous oxygen and improve the catalytic activity of toluene oxidation. However, there are some problems with Cu-based oxide catalysts: if Cu⁺ is the catalytic activity center, due to its unstable nature, it is easy to be oxidized and becomes inactive during the oxidation reaction, so the follow-up research on Cu-based oxide catalysts should focus on enhancing its stability.

Developing an environmentally friendly selective catalytic reduction (SCR) catalyst, one study synthesized a series of new commercial V₂O₅-WO₃/TiO₂ catalysts modified with Cu for the removal of NO and toluene from gas by wet impregnation. The modification of Cu metal resulted in a significant increase in the removal activity of the catalysts, which promoted the redox cycle of the Cu metal and V substances to produce more reactive oxygen species [130].

Cobalt ions usually exist in the form of Co²⁺ and Co³⁺, which have high redox properties and can construct a variety of defects, so the controllability of the material is greatly improved [131]. Co₃O₄ is a very promising transition-metal oxide for the catalytic oxidation of VOCs, which has many advantages such as high low-temperature activity, abundant reserves, and good redox properties, etc. Co₃O₄ has a high activity for the cleavage of C-H bonds with high bond energies, and it is usually used to catalyze the harder balkanization of VOCs [132]. It was found that the doping of small amounts of rare-earth elements (Ce, Pr, Sm, and Nd) could significantly promote the catalytic activity of Co₃O₄. In particular, the Nd-doped Co₃O₄ catalyst exhibited excellent catalytic activity with 90% toluene removal at 162.1 °C, which was even better than that of the Pt-doped Co₃O₄. Nd doping resulted in a higher ratio of Co³⁺/Co²⁺ and more oxygen vacancies compared with the other rare-earth metal dopings [133].

Grape-like GdCoO₃ chalcogenides were synthesized by a simple one-step method. Characterization results showed that abundant reactive oxygen species existed on the surface of GdCoO₃. Most notably, the catalysts prepared in this way exhibited significant catalytic activity for VOC oxidation [134].

However, the catalytic performance of non-precious-metal oxide catalysts with a single active component for the oxidation of VOCs is usually lower than that of precious metals. To enhance the catalytic effect of the catalysts, researchers have developed composite non-precious-metal oxidation catalysts, and the composite metal oxide catalysts are mainly categorized into bimetallic and polymetallic composite oxide catalysts.

Ag-Mn bimetallic catalysts containing 10 wt.% silver were synthesized by doping, impregnation, and reduction methods and applied to the catalytic oxidation of benzene. It was found that silver loading by the reduction method significantly improved the physicochemical properties of the manganese oxides, exhibiting a larger surface area and pore volume, a higher surface Mn to Mn ratio, stronger reducibility, and stronger surface-oxygen species activity, which are favorable for the catalytic activity of manganese [135].

Cerium–manganese mixed metal oxide catalysts with different Ce/Mn ratios were co-precipitated with sodium carbonate and found to have the highest activity for the Mn-rich sample and the highest activity for Ce_{0.25}Mn_{0.75}O_x [136].

A set of Cu-Mn oxides was prepared by the simple and effective solution-combustion synthesis method of Cocuzza et al. [137]. The prepared catalysts were tested for the complete oxidation of volatile organic compounds (ethylene, propylene, and toluene) and it was found that for total VOC oxidation, optimum performance was achieved with a copper content between 15% and 45%.

Liu et al. [138] synthesized Au@Cu-MnO₂-like core shells and applied them to the catalytic removal of VOCs. They found that H₂-TPR and O₂-TPD showed better reducibility, abundant oxygen uptake, and accelerated the deep oxidation of toluene, which resulted in excellent activity and stability.

Cobalt-zirconium oxide catalysts in unlimited Co/Zr ratios were synthesized for the catalytic combustion of propane using the sol-gel method. The results showed that the catalyst with a Co/Zr ratio of 4 (Co₄Zr₁) not only exhibited a catalytic performance of 90% conversion at 242 °C but also maintained high thermal stability and water resistance. In addition, the introduced Zr resulted in more surface Co³⁺ material and greater surface uptake of oxygen compared with the Co₄Zr₁ catalyst. These results suggest that Co_xZr_y catalysts are promising alternative materials for propane degradation [139].

Wang et al. [140] used potassium manganese oxide x-CeO₂ prepared by a modified co-precipitation method as a catalyst to catalyze formaldehyde, yielding the following Table 7.

Table 7. Catalytic efficiency of formaldehyde over potassium manganese oxide x-CeO₂ catalysts under different conditions.

Temperature	Catalytic Efficiency	Formaldehyde Concentration (ppm)	Catalytic Efficiency	Load Rate (g/m ²)	Catalytic Efficiency
56.7 ± 0.2 °C	76.2%	200	63%	10	62.8%
62.6 ± 0.2 °C	78.3%	500	78.3%	20	78.3%
68.2 ± 0.2 °C	82.1%	1000	70.6%	40	81.1%

These catalysts are mostly loaded catalysts and composite catalysts, and the structural properties, chemical modification, and loading methods of the carriers have an important influence on the stability, structure, and catalytic performance of the catalysts. The common carriers are SiO₂, γ-Al₂O₃, zeolite, carbon materials, and monolithic materials. Some of the carriers have certain catalytic activity, and some of them are inert carriers without catalytic activity. There are fewer reports on loaded catalysts of advanced porous materials and their derivatives. The porous material matrix has several advantages: (1) it can provide more reaction micro spaces for the catalytic oxidation reaction of VOCs and accelerate the mass and heat transfer; (2) it is favorable for the dispersed loading of active components [141].

The porous material matrix includes MOF-based catalytic materials, zeolite molecular-sieve-based materials, and porous carbon-based materials. Non-precious-metal oxides, such as MnO_x, CeO_x, and CoO_x, are rich in reactive oxygen species, oxygen vacancies, and have good redox properties; in this context, the metal oxides obtained by pyrolysis of non-precious-metal-based MOFs can exhibit very good catalytic properties. CeO₂ in air is from the in situ pyrolysis of Ce-MOF. MOF-derived catalysts have shown excellent results in the catalytic combustion of toluene at high temperatures when high humidity is present [142]; among them, UiO-66 is widely used as a carrier for catalysts because of its adjustable pore size and long-term thermal and chemical stability. The advantages and disadvantages of different catalysts and what types of VOCs are suitable for them to catalyze are summarized in the Table 8 below.

Table 8. Advantages and disadvantages of different catalysts and applicable types of VOCs.

Catalysts	Pros	Cons	Applicable VOCs
Precious-metal catalysts	Anti-toxicity, high activity, good stability	High cost, easy to be poisoned, scarce resources	Exhaust gases with highly volatile organic compounds (VOCs), such as benzene compounds, aldehydes, phenols, ketones, and so on. These VOCs are usually highly reactive and more difficult to degrade.
Non-precious-metal catalysts	Inexpensive, resistant to poisoning, resourceful	Poor activity, poor stability	Suitable for treating some common and less difficult-to-degrade VOCs, such as some low-molecular-weight alcohols, ketones, aldehydes, etc.
Manganese oxide catalysts	Low cost, environmentally friendly, high activity	Poor stability, need to be regenerated frequently, general selection.	Manganese-based oxide catalysts are suitable for treating some relatively simple low-molecular-weight VOCs, such as alcohols, aldehydes, ketones, etc.
Cerium-based oxide catalysts	Resistant to toxinization and highly active	Expensive, poor selectivity	Suitable for treating some VOCs containing sulfur, chlorine, etc., which can easily generate toxic intermediates, such as mercaptans and chlorinated alkanes.
Copper-based oxide catalysts	High activity, good stability	Active, poor stability	Suitable for treating some VOCs containing active groups such as hydroxyl and ketone groups, such as alcohols and ketones.
Cobalt-based oxide catalysts	Low cost, high selectivity	High cost, general stability	Suitable for treating some VOCs containing high redox-reaction activity, such as alcohols, aldehydes, and ketones.

Recently, a number of emerging catalysts have emerged, using resins and MOF derivatives as catalysts for VOCs.

A super-crosslinked polymer resin (LXQ-10) was selected as the carrier to synthesize Fe/LXQ-10 catalysts for the removal of gaseous toluene, and the iron loading on the surface of the LXQ-10 resin could improve the toluene removal efficiency compared with the original LXQ-10 resin [143]. A series of Fe-based MOFs with different morphologies were synthesized by pyrolysis for the catalytic oxidation of toluene. The FeOx-100 catalyst was found to have optimal properties, such as a large specific surface area, small microcrystalline size, highly dispersed active sites, and toluene oxidation defects, and FeOx-100 exhibited excellent low-temperature reducibility and good oxidation performance of toluene at low temperatures [144].

5. Conclusions

Existing adsorbent materials include carbon-based adsorbent materials (activated carbon, activated carbon fiber, biochar, graphene, and carbon nanotubes), oxygen-containing adsorbent materials, zeolite (molecular sieve), silica gel, clay, and MOFs. The adsorption

effect of VOCs is mainly related to the structure of the adsorbent material, the surface functional groups, and other factors. Therefore, the selection of adsorption materials needs to comprehensively consider various factors to improve their adsorption capacity in the process of practical application. In the field of adsorption and removal of VOCs, traditional activated carbon and zeolite materials perform well, but their poor water stability affects their industrial application, and their adsorption capacity under high humidity can be improved by adjusting the structural properties and functional groups on the surface of the materials. As a new type of porous material, MOFs have the advantage of a large surface-adjustable adsorption capacity, but their high cost and huge pore space limit their large-scale application. Composites based on MOFs, especially those coated with inexpensive microporous materials such as biochar, clay, zeolite, etc., are promising alternatives to the current traditional VOC-adsorbent materials.

Absorbents include organic solvents, surfactants, microemulsions, and ionic liquids. Organic solvents were the first to be used for the absorption of VOCs; surfactants also have a certain degree of an adsorption effect on VOCs. Microemulsions have a better adsorption effect on the adsorption of VOCs, but their preparation is more complex and difficult; ionic liquids have always been regarded as a green and non-toxic absorbent, but it was found that it is not non-toxic. There is the deep eutectic solvent (DES), which has similar properties to the ionic-liquid-type absorber and has a low cost, low toxicity, and is easy to decompose. In the future, it is likely to become the alternative absorber to ionic-liquid absorbers.

Catalysts are divided into precious-metal and non-precious-metal oxide catalysts and composite metal catalysts. The precious-metal catalyst catalytic activity is high, but it is unstable and easy to poison; the non-precious-metal oxide catalyst catalytic activity is not as high as the precious-metal catalyst activity, so it is necessary to increase research into the composite non-precious-metal oxidation catalysts.

MOF materials have abundant chemical sites that can produce a strong interaction with VOCs to degrade in situ. In the future, because of its superior activity, it will increasingly become a new material for catalyzing VOCs, but its stability is poor, resulting in its limited application in industrial catalysis. Some scholars have improved the stability of MOFs by combining highly dispersed noble metals with a MOF, which is not a promising catalyst. Subsequent research work can focus on the development of new preparation methods, constructing the synergistic effects between metal and metal and metal and carrier in composite metal oxidation, exploring the catalytic mechanism, designing and preparing catalysts rich in multiple defective adsorption sites, anti-poisoning, and the generation of long-life catalysts, which can provide a new way of thinking about the catalytic oxidation of VOCs.

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References

1. Zhang, X.; Gao, B.; Creamer, A.E.; Cao, C.; Li, Y. Adsorption of VOCs onto engineered carbon materials: A review. *J. Hazard. Mater.* **2017**, *338*, 102–123. [[CrossRef](#)] [[PubMed](#)]
2. Pusede, S.E.; Steiner, A.L.; Cohen, R.C. Temperature and recent trends in the chemistry of continental surface ozone. *Chem. Rev.* **2015**, *115*, 3898–3918. [[CrossRef](#)]
3. Pullinen, I.; Schmitt, S.; Kang, S.; Sarrafzadeh, M.; Schlag, P.; Andres, S.; Kleist, E.; Mentel, T.F.; Rohrer, F.; Springer, M.; et al. Impact of NO_x on secondary organic aerosol (SOA) formation from α -pinene and β -pinene photooxidation: The role of highly oxygenated organic nitrates. *Atmos. Chem. Phys.* **2020**, *20*, 10125–10147. [[CrossRef](#)]
4. Li, X.; Zhang, L.; Yang, Z.; Wang, P.; Yan, Y.; Ran, J. Adsorption materials for volatile organic compounds (VOCs) and the key factors for VOCs adsorption process: A review. *Sep. Purif. Technol.* **2020**, *235*, 116213. [[CrossRef](#)]
5. Klett, C.; Duten, X.; Tieng, S.; Touchard, S.; Jestin, P.; Hassouni, K.; Vega-González, A. Acetaldehyde removal using an atmospheric non-thermal plasma combined with a packed bed: Role of the adsorption process. *J. Hazard. Mater.* **2014**, *279*, 356–364. [[CrossRef](#)]
6. McDonald, B.C.; De Gouw, J.A.; Gilman, J.B.; Jathar, S.H.; Akherati, A.; Cappa, C.D.; Jimenez, J.L.; Lee-Taylor, J.; Hayes, P.L.; McKeen, S.A.; et al. Volatile chemical products emerging as largest petrochemical source of urban organic emissions. *Science* **2018**, *359*, 760–764. [[CrossRef](#)] [[PubMed](#)]
7. He, Q.; Yan, Y.; Li, H.; Zhang, Y.; Chen, L.; Wang, Y. Characteristics and reactivity of volatile organic compounds from non-coal emission sources in China. *Atmos. Environ.* **2015**, *115*, 153–162. [[CrossRef](#)]
8. Liu, Y.; Zhong, C.; Peng, J.; Wang, T.; Wu, L.; Chen, Q.; Sun, L.; Sun, S.; Zou, C.; Zhao, J.; et al. Evaporative emission from China 5 and China 6 gasoline vehicles: Emission factors, profiles and future perspective. *J. Clean. Prod.* **2022**, *331*, 129861. [[CrossRef](#)]
9. Gaspar, D.J.; Phillips, S.D.; Polikarpov, E.; Albrecht, K.O.; Jones, S.B.; George, A.; Landera, A.; Santosa, D.M.; Howe, D.T.; Baldwin, A.G.; et al. Measuring and predicting the vapor pressure of gasoline containing oxygenates. *Fuel* **2019**, *243*, 630–644. [[CrossRef](#)]
10. Gu, Y.; Liu, B.; Li, Y.; Zhang, Y.; Bi, X.; Wu, J.; Song, C.; Dai, Q.; Han, Y.; Ren, G.; et al. Multi-scale volatile organic compound (VOC) source apportionment in Tianxi, China, using a receptor model coupled with 1-hr resolution data. *Environ. Pollut.* **2020**, *265*, 115023. [[CrossRef](#)]
11. Guo, H.; Zou, S.C.; Tsai, W.Y.; Chan, L.Y.; Blake, D.R. Emission characteristics of nonmethane hydrocarbons from private cars and taxis at different driving speeds in Hong Kong. *Atmos. Environ.* **2011**, *45*, 2711–2721. [[CrossRef](#)]
12. Hata, H.; Yamada, H.; Kokuryo, K.; Okada, M.; Funakubo, C.; Tonokura, K. Estimation model for evaporative emissions from gasoline vehicles based on thermodynamics. *Sci. Total Environ.* **2018**, *618*, 1685–1691. [[CrossRef](#)] [[PubMed](#)]
13. Ou, J.M.; Feng, X.Q.; Liu, Y.C.; Gao, Z.J.; Yang, Y.; Zhang, Z.; Wang, X.M.; Zheng, J.Y. Source characteristics of VOCs emissions from vehicular exhaust in the Pearl River Delta region. *Acta Sci. Circumstantiae* **2014**, *34*, 826–834.
14. Fang, L.; Hao, R.; Xie, X.; Li, G.; Wang, H. Characteristics of VOCs emissions from circulating water of typical petrochemical enterprises and their impact on surroundings. *Atmosphere* **2022**, *13*, 1985. [[CrossRef](#)]
15. Xie, H.; Gao, W.; Zhao, W.; Han, Y.; Gao, Y.; Liu, B.; Han, Y. Source profile study of VOCs unorganized emissions from typical aromatic devices in petrochemical industry. *Sci. Total Environ.* **2023**, *889*, 164098. [[CrossRef](#)]
16. Liang, X.; Chen, X.; Zhang, J.; Shi, T.; Sun, X.; Fan, L.; Wang, L.; Ye, D. Reactivity-based industrial volatile organic compounds emission inventory and its implications for ozone control strategies in China. *Atmos. Environ.* **2017**, *162*, 115–126. [[CrossRef](#)]
17. GB 37822-2019; Standard for Fugitive Emission of Volatile Organic Compounds. National Standard of the People's Republic of China: Beijing, China, 2019.
18. GB 31570—2015; Emission Standard of Pollutants for Petroleum Refining Industry. China Environmental Science: Beijing, China, 2015.
19. GB 31571—2015; Emission Standard of Pollutants for Petroleum Chemistry Industry. China Environmental Science: Beijing, China, 2015.
20. GB 24409-2020; Limit of Harmful Substances of Vehicle Coatings. State Administration for Market Supervision and Regulation, China National Committee for Standardization: Beijing, China, 2020.
21. GB 30981-2020; Limit of Harmful Substances of Industrial Protective Coatings. State Administration for Market Supervision and Regulation, China National Committee for Standardization: Beijing, China, 2020.
22. GB 20951—2020; Emission Standard of Air Pollutant for Petroleum Transport. Ministry of Ecology and Environment, State Administration for Market Supervision and Administration (SAMSA): Beijing, China, 2020.
23. GB 20952—2020; Emission Standard of Air Pollutant for Gasoline Filling Stations. Ministry of Ecology and Environment, State Administration for Market Supervision and Administration (SAMSA): Beijing, China, 2020.
24. GB 33372-2020; Limit of Volatile Organic Compounds Content in Adhesive. State Administration for Market Supervision and Regulation, China National Committee for Standardization: Beijing, China, 2020.
25. GB 38507-2020; Limits of Volatile Organic Compounds (VOCs) in Printing Ink. State Administration for Market Supervision and Regulation, China National Committee for Standardization: Beijing, China, 2020.
26. GB 38508-2020; Limits for Volatile Organic Compounds Content in Cleaning Agents. State Administration for Market Supervision and Regulation, China National Committee for Standardization: Beijing, China, 2020.
27. GB/T 38597-2020; Technical Requirement for Low-Volatile-Organic-Compound-Content Coatings Product. State Administration for Market Supervision and Regulation, China National Committee for Standardization: Beijing, China, 2020.

28. Kujawa, J.; Zięba, M.; Zięba, W.; Al-Gharabli, S.; Kujawski, W.; Terzyk, A.P. Hedgehog-like structure, PVDF-carbon nanohorn hybrid membranes for improved removal of VOCs from water. *Chem. Eng. J.* **2022**, *438*, 135574. [[CrossRef](#)]
29. Li, D.; Chen, X.; Shu, C.; Huang, Y.; Zhang, P.; Xiao, B.; Zhou, D. Ca-decorated MoBOH as a promising adsorbent for CH₂O, C₆H₆, C₃H₆O, and C₂HCl₃ removal at room temperature: A first-principle study. *Appl. Surf. Sci.* **2021**, *563*, 150233. [[CrossRef](#)]
30. Liang, X.M.; Sun, X.B.; Xu, J.T.; Ye, D.Q. Improved emissions inventory and VOC speciation for industrial OFP estimation in China. *Sci. Total Environ.* **2020**, *745*, 140838. [[CrossRef](#)]
31. Jjia, L.; Shi, J.; Long, C.; Lian, F.; Xing, B. VOCs adsorption on activated carbon with initial water vapor contents: Adsorption mechanism and modified characteristic curves. *Sci. Total Environ.* **2020**, *731*, 139184. [[CrossRef](#)]
32. Rakić, V.; Rac, V.; Krmar, M.; Otman, O.; Auroux, A. The adsorption of pharmaceutically active compounds from aqueous solutions onto activated carbons. *J. Hazard. Mater.* **2015**, *282*, 141–149. [[CrossRef](#)]
33. Lu, X.; He, J.; Xie, J.; Zhou, Y.; Liu, S.; Zhu, Q.; Lu, H. Pree and iparation of hydrophobic hierarchical pore carbon–silica compositts adsorption performance toward volatile organic compounds. *J. Environ. Sci.* **2020**, *87*, 39–48. [[CrossRef](#)] [[PubMed](#)]
34. Li, Z.; Xi, Y.; Chen, T.; Tang, F.; Cai, J.; Ma, J. Trimethylchlorosilane modified activated carbon for the adsorption of VOCs at high humidity. *Sep. Purif. Technol.* **2021**, *272*, 118659. [[CrossRef](#)]
35. Zhang, S.; Chen, Q.; Hao, M.; Zhang, Y.; Ren, X.; Cao, F.; Zhang, L.; Sun, Q.; Wennersten, R. Effect of functional groups on VOCs adsorption by activated carbon: DFT study. *Surf. Sci.* **2023**, *736*, 122352. [[CrossRef](#)]
36. Yue, Z.; Vakili, A.; Wang, J. Activated carbon fibers from meltblown isotropic pitch fiber webs for vapor phase adsorption of volatile organic compounds. *Chem. Eng. J.* **2017**, *330*, 183–190. [[CrossRef](#)]
37. Xu, A.W.; Lan, Y.; Li, Y.R. Characteristics, Development and Application of Activated Carbon Fiber. *Prog. Text. Sci. Technol.* **2023**, *2*, 6–10.
38. Baur, G.B.; Yuranov, I.; Kiwi-Minsker, L. Activated carbon fibers modified by metal oxide as effective structured adsorbents for acetaldehyde. *Catal. Today* **2015**, *249*, 252–258. [[CrossRef](#)]
39. Wang, Y.H.; Bayatpour, S.; Qian, X.; Frigo-Vaz, B.; Wang, P. Activated carbon fibers via reductive carbonization of cellulosic biomass for adsorption of nonpolar volatile organic compounds. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *612*, 125908. [[CrossRef](#)]
40. Park, S.; Yaqub, M.; Lee, S.; Lee, W. Adsorption of acetaldehyde from air by activated carbon and carbon fibers. *Environ. Eng. Res.* **2022**, *27*, 200549. [[CrossRef](#)]
41. Economy, J.; Daley, M.; Mangun, C. *Activated Carbon Fibers-Past, Present and Future*; Preprints of Papers; American Chemical Society, Division of Fuel Chemistry; CONF-960376-; American Chemical Society: Washington, DC, USA, 1996; Volume 41.
42. Mangun, C.L.; Yue, Z.; Economy, J.; Maloney, S.; Kemme, P.; Cropek, D. Adsorption of organic contaminants from water using tailored ACFs. *Chem. Mater.* **2001**, *13*, 2356–2360. [[CrossRef](#)]
43. Yue, Z.; Economy, J. Carbonization and activation for production of activated carbon fibers. In *Activated Carbon Fiber and Textiles*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 61–139.
44. Wu, R.; Bao, A. Preparation of cellulose carbon material from cow dung and its CO₂ adsorption performance. *J. CO₂ Util.* **2023**, *68*, 102377. [[CrossRef](#)]
45. Zhu, L.; Shi, T.; Chen, Y. Preparation and characteristics of graphene oxide from the biomass carbon material using fir powder as precursor. *Fuller. Nanotub. Carbon Nanostructures* **2015**, *23*, 961–967. [[CrossRef](#)]
46. Yang, Y.; Sun, C.; Lin, B.; Huang, Q. Surface modified and activated waste bone char for rapid and efficient VOCs adsorption. *Chemosphere* **2020**, *256*, 127054. [[CrossRef](#)] [[PubMed](#)]
47. Piccoli, I.; Torreggiani, A.; Pituello, C.; Pisi, A.; Morari, F.; Francioso, O. Automated image analysis and hyperspectral imagery with enhanced dark field microscopy applied to biochars produced at different temperatures. *Waste Manag.* **2020**, *105*, 457–466. [[CrossRef](#)] [[PubMed](#)]
48. Rezaee, A.; Rangkooy, H.; Jonidi-Jafari, A.; Khavanin, A. Surface modification of bone char for removal of formaldehyde from air. *Appl. Surf. Sci.* **2013**, *286*, 235–239. [[CrossRef](#)]
49. Wang, W.; Ma, X.; Sun, J.; Chen, J.; Zhang, J.; Wang, Y.; Wang, J.; Zhang, H. Adsorption of enrofloxacin on acid/alkali-modified corn stalk biochar. *Spectrosc. Lett.* **2019**, *52*, 367–375. [[CrossRef](#)]
50. Zhu, J.; Li, Y.; Xu, L.; Liu, Z. Removal of toluene from waste gas by adsorption-desorption process using corncob-based activated carbons as adsorbents. *Ecotoxicol. Environ. Saf.* **2018**, *165*, 115–125. [[CrossRef](#)]
51. Gomez-Delgado, E.; Nunell, G.; Cukierman, A.L.; Bonelli, P. Agroindustrial waste conversion into ultramicroporous activated carbons for greenhouse gases adsorption-based processes. *Bioresour. Technol. Rep.* **2022**, *18*, 101008. [[CrossRef](#)]
52. Yue, X.; Zhao, J.; Shi, H.; Chi, Y.; Salam, M. Preparation of composite adsorbents of activated carbon supported MgO/MnO₂ and adsorption of Rhodamine B. *Water Sci. Technol.* **2020**, *81*, 906–914. [[CrossRef](#)]
53. Yang, F.; Li, W.; Zhang, L.; Tu, W.; Wang, X.; Li, L.; Yu, C.; Gao, Q.; Yuan, A.; Pan, J. Drastically boosting volatile acetone capture enabled by N-doping activated carbon: An interesting deep surface digging effect. *Sep. Purif. Technol.* **2021**, *276*, 119280. [[CrossRef](#)]
54. Hwang, O.; Lee, S.R.; Cho, S.; Ro, K.S.; Spiehs, M.; Woodbury, B.; Silva, P.J.; Han, D.-W.; Choi, H.; Kim, K.-Y.; et al. Efficacy of different biochars in removing odorous volatile organic compounds (VOCs) emitted from swine manure. *ACS Sustain. Chem. Eng.* **2018**, *6*, 14239–14247. [[CrossRef](#)]
55. Shen, Y. Biomass-derived porous carbons for sorption of Volatile organic compounds (VOCs). *Fuel* **2023**, *336*, 126801. [[CrossRef](#)]

56. Long, R.Q.; Yang, R.T. Carbon nanotubes as superior sorbent for dioxin removal. *J. Am. Chem. Soc.* **2001**, *123*, 2058–2059. [[CrossRef](#)] [[PubMed](#)]
57. Crespo, D.; Yang, R.T. Adsorption of organic vapors on single-walled carbon nanotubes. *Ind. Eng. Chem. Res.* **2006**, *45*, 5524–5530. [[CrossRef](#)]
58. Peng, X.; Li, Y.; Luan, Z.; Di, Z.; Wang, H.; Tian, B.; Jia, Z. Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. *Chem. Phys. Lett.* **2003**, *376*, 154–158. [[CrossRef](#)]
59. Yang, K.; Zhu, L.; Xing, B. Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environ. Sci. Technol.* **2006**, *40*, 1855–1861. [[CrossRef](#)] [[PubMed](#)]
60. Kondratyuk, P.; Yates, J.T., Jr. Desorption kinetic detection of different adsorption sites on opened carbon single walled nanotubes: The adsorption of n-nonane and CCl₄. *Chem. Phys. Lett.* **2005**, *410*, 324–329. [[CrossRef](#)]
61. Zhang, J.; Lee, J.K.; Wu, Y.; Murray, R.W. Photoluminescence and electronic interaction of anthracene derivatives adsorbed on sidewalls of single-walled carbon nanotubes. *Nano Lett.* **2003**, *3*, 403–407. [[CrossRef](#)]
62. Jang, Y.; Bang, J.; Seon, Y.S.; You, D.W.; Oh, J.S.; Jung, K.W. Carbon nanotube sponges as an enrichment material for aromatic volatile organic compounds. *J. Chromatogr. A* **2020**, *1617*, 460840. [[CrossRef](#)]
63. Hsu, S.C.; Lu, C. Adsorption kinetic, thermodynamic, and desorption studies of isopropyl alcohol vapor by oxidized single-walled carbon nanotubes. *J. Air Waste Manag. Assoc.* **2009**, *59*, 990–997. [[CrossRef](#)]
64. Hussain, C.M.; Saridara, C.; Mitra, S. Modifying the sorption properties of multi-walled carbon nanotubes via covalent functionalization. *Analyst* **2009**, *134*, 1928–1933. [[CrossRef](#)]
65. Valcárcel, M.; Cárdenas, S.; Simonet, B.M.; Moliner-Martínez, Y.; Lucena, R. Carbon nanostructures as sorbent materials in analytical processes. *TrAC Trends Anal. Chem.* **2008**, *27*, 34–43. [[CrossRef](#)]
66. Li, S.; Tian, S.; Du, C.; He, C.; Cen, C.; Xiong, Y. Vaseline-loaded expanded graphite as a new adsorbent for toluene. *Chem. Eng. J.* **2010**, *162*, 546–551. [[CrossRef](#)]
67. Lim, S.T.; Kim, J.H.; Lee, C.Y.; Koo, S.; Jerng, D.W.; Wongwises, S.; Ahn, H.S. Mesoporous graphene adsorbents for the removal of toluene and xylene at various concentrations and its reusability. *Sci. Rep.* **2019**, *9*, 10922. [[CrossRef](#)] [[PubMed](#)]
68. Rong, Y.; Pan, C.; Song, K.; Nam, J.C.; Wu, F.; You, Z.; Hao, Z.; Li, J.; Zhang, Z. Bamboo-derived hydrophobic porous graphitized carbon for adsorption of volatile organic compounds. *Chem. Eng. J.* **2023**, *461*, 141979. [[CrossRef](#)]
69. Zhang, H.; Li, G.L.; Zhang, K.G. Advances of Metal-Organic Frameworks in Adsorption and Separation Applications, China. *Acta Chim. Sin.* **2017**, *75*, 841–859. [[CrossRef](#)]
70. Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O.M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276–279. [[CrossRef](#)]
71. Jhinjer, H.S.; Singh, A.; Bhattacharya, S.; Jassal, M.; Agrawal, A.K. Metal-organic frameworks functionalized smart textiles for adsorptive removal of hazardous aromatic pollutants from ambient air. *J. Hazard. Mater.* **2021**, *411*, 125056. [[CrossRef](#)]
72. Park, K.S.; Ni, Z.; Côté, A.P.; Choi, J.Y.; Huang, R.; Uribe-Romo, F.J.; Chae, H.K.; O’Keeffe, M.; Yaghi, O.M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186–10191. [[CrossRef](#)]
73. Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. A chromium terephthalate-based solid with unusually large pore volumes and surface area. *Science* **2005**, *309*, 2040–2042. [[CrossRef](#)]
74. Vikrant, K.; Kim, K.H.; Kumar, V.; Giannakoudakis, D.A.; Boukhvalov, D.W. Adsorptive removal of an eight-component volatile organic compound mixture by Cu-, Co-, and Zr-metal-organic frameworks: Experimental and theoretical studies. *Chem. Eng. J.* **2020**, *397*, 125391. [[CrossRef](#)]
75. Vellingiri, K.; Kumar, P.; Deep, A.; Kim, K.H. Metal-organic frameworks for the adsorption of gaseous toluene under ambient temperature and pressure. *Chem. Eng. J.* **2017**, *307*, 1116–1126. [[CrossRef](#)]
76. Huang, C.Y.; Song, M.; Gu, Z.Y.; Wang, H.F.; Yan, X.P. Probing the adsorption characteristic of metal-organic framework MIL-101 for volatile organic compounds by quartz crystal microbalance. *Environ. Sci. Technol.* **2011**, *45*, 4490–4496. [[CrossRef](#)] [[PubMed](#)]
77. Zhu, M.; Hu, P.; Tong, Z.; Zhao, Z.; Zhao, Z. Enhanced hydrophobic MIL (Cr) metal-organic framework with high capacity and selectivity for benzene VOCs capture from high humid air. *Chem. Eng. J.* **2017**, *313*, 1122–1131. [[CrossRef](#)]
78. Tanabe, K.K.; Cohen, S.M. Postsynthetic modification of metal-organic frameworks—A progress report. *Chem. Soc. Rev.* **2011**, *40*, 498–519. [[CrossRef](#)]
79. Duan, C.; Yu, Y.; Xiao, J.; Zhang, X.; Li, L.; Yang, P.; Wu, J.; Xi, H. Water-based routes for synthesis of metal-organic frameworks: A review. *Sci. China Mater.* **2020**, *63*, 667–685. [[CrossRef](#)]
80. Qin, C.; Wang, B.; Wu, N.; Han, C.; Wang, Y. General strategy to fabricate porous Co-based bimetallic metal oxide nanosheets for high-performance CO sensing. *ACS Appl. Mater. Interfaces* **2021**, *13*, 26318–26329. [[CrossRef](#)] [[PubMed](#)]
81. Li, M.; Li, Y.; Li, W.; Liu, F.; Qi, X.; Xue, M.; Wang, Y.; Zhao, C. Synthesis and application of Cu-BTC@ ZSM-5 composites as effective adsorbents for removal of toluene gas under moist ambience: Kinetics, thermodynamics, and mechanism studies. *Environ. Sci. Pollut. Res.* **2020**, *27*, 6052–6065. [[CrossRef](#)] [[PubMed](#)]
82. Centre National de la Recherche Scientifique; Ecole Normale Supérieure; Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris; Instituto Superior Técnico. Metal Organic Frameworks for the Selective Capture of Volatil Organic Compounds Comprising Carboxylic Acid Functional Group(s) and/or Volatile Alcohols. WO2023104665A1, 15 June 2023.
83. Zheng, Z.; Nguyen, H.L.; Hanikel, N.; Li, K.K.Y.; Zhou, Z.; Ma, T.; Yaghi, O.M. High-yield, green and scalable methods for producing MOF-303 for water harvesting from desert air. *Nat. Protoc.* **2023**, *18*, 136–156. [[CrossRef](#)]

84. Zuliani, A.; Castillejos, M.C.; Khiar, N. Continuous flow synthesis of PCN-222 (MOF-545) with controlled size and morphology: A sustainable approach for efficient production. *Green Chem.* **2023**, *25*, 10596–10610. [[CrossRef](#)]
85. Chiang, Y.C.; Chiang, P.C.; Huang, C.P. Effects of pore structure and temperature on VOC adsorption on activated carbon. *Carbon* **2001**, *39*, 523–534. [[CrossRef](#)]
86. Kang, S.; Ma, J.; Wu, Q.; Deng, H. Adsorptive removal of dichloromethane vapor on FAU and MFI zeolites: Si/Al ratio effect and mechanism. *J. Chem. Eng. Data* **2018**, *63*, 2211–2218. [[CrossRef](#)]
87. Gao, J.A.; Wang, W.; Zhang, J. The Study of Surface Coating of ZSM-5 Zeolites and Adsorption of Toluene, China. *Mod. Chem. Res.* **2019**, *11*, 110–113.
88. Gao, J.A.; Li, X.; Shi, D.J. Honeycomb molding process of ZSM-5 molecular sieves and adsorption to toluene, China. *Mod. Chem. Ind.* **2020**, *40*, 123–127.
89. Bhatia, S.; Abdullah, A.Z.; Wong, C.T. Adsorption of butyl acetate in air over silver-loaded Y and ZSM-5 zeolites: Experimental and modelling studies. *J. Hazard. Mater.* **2009**, *163*, 73–81. [[CrossRef](#)] [[PubMed](#)]
90. Niu, C.; Zhao, Y.; Qian, C. Effect of Pore Structure of Alkali Modified ZSM-5 Zeolite on Its VOCs Adsorption Performance, China. *Acta Pet. Sin. Pet. Process.* **2024**, *40*, 37.
91. Shandong Rongchuang Catalytic New Material Co., Ltd.; Beijing University of Chemical Technology. A Recyclable Regenerative VOCs Adsorbent and Its Preparation Method and Application. Chinese Patent CN112516959B, 18 April 2023.
92. Chen, W.; Wang, P.F. VOCs removal performance of barium-modified ZSM-5 molecular sieve and its adsorption mechanism, China. *Shanghai Chem. Ind.* **2023**, *48*, 9–17.
93. Sigot, L.; Ducom, G.; Germain, P. Adsorption of octamethylcyclotetrasiloxane (D4) on silica gel (SG): Retention mechanism. *Microporous Mesoporous Mater.* **2015**, *213*, 118–124. [[CrossRef](#)]
94. Kutluay, S.; Temel, F. Silica gel based new adsorbent having enhanced VOC dynamic adsorption/desorption performance. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *609*, 125848. [[CrossRef](#)]
95. Li, J.; Cai, J.; Liu, X.; Guo, Y.; Sui, H.; He, L. Design and Synthesis of a Water-Resistant Mesoporous Silica Gel for the VOC Adsorption–Desorption Treatment. *Ind. Eng. Chem. Res.* **2023**, *62*, 20833–20843. [[CrossRef](#)]
96. Sui, H.; An, P.; Li, X.; Cong, S.; He, L. Removal and recovery of o-xylene by silica gel using vacuum swing adsorption. *Chem. Eng. J.* **2017**, *316*, 232–242. [[CrossRef](#)]
97. Sui, H.; Liu, H.; An, P.; He, L.; Li, X.; Cong, S. Application of silica gel in removing high concentrations toluene vapor by adsorption and desorption process. *J. Taiwan Inst. Chem. Eng.* **2017**, *74*, 218–224. [[CrossRef](#)]
98. Farjadian, F.; Hosseini, M.; Ghasemi, S.; Tamami, B. Phosphinite-functionalized silica and hexagonal mesoporous silica containing palladium nanoparticles in Heck coupling reaction: Synthesis, characterization, and catalytic activity. *RSC Adv.* **2015**, *5*, 79976–79987. [[CrossRef](#)]
99. Qu, F.; Zhu, L.; Yang, K. Adsorption behaviors of volatile organic compounds (VOCs) on porous clay heterostructures (PCH). *J. Hazard. Mater.* **2009**, *170*, 7–12. [[CrossRef](#)] [[PubMed](#)]
100. Zhu, L.; Tian, S.; Shi, Y. Adsorption of volatile organic compounds onto porous clay heterostructures based on spent organobentonites. *Clays Clay Miner.* **2005**, *53*, 123–136. [[CrossRef](#)]
101. Karaoglu, M.H.; Dogan, M.; Alkan, M. Removal of reactive blue 221 by kaolinite from aqueous solutions. *Ind. Eng. Chem. Res.* **2010**, *49*, 1534–1540. [[CrossRef](#)]
102. Edmiston, P.L.; Osborne, C.; Reinbold, K.P.; Pickett, D.C.; Underwood, L.A. Pilot scale testing composite swellable organosilica nanoscale zero-valent iron—Iron-Osorb[®]—For in situ remediation of trichloroethylene. *Remediat. J.* **2011**, *22*, 105–123. [[CrossRef](#)]
103. Mobasser, S.; Wager, Y.; Dittrich, T.M. Indoor air purification of volatile organic compounds (VOCs) using activated carbon, zeolite, and organosilica sorbents. *Ind. Eng. Chem. Res.* **2022**, *61*, 6791–6801. [[CrossRef](#)]
104. Jarraya, I.; Fourmentin, S.; Benzina, M.; Bouaziz, S. VOC adsorption on raw and modified clay materials. *Chem. Geol.* **2010**, *275*, 1–8. [[CrossRef](#)]
105. Gong, S.F.; Long, C.T.; Liu, Y.W. Synthesis of highly crosslinked cylindrical polystyrene adsorbents for efficient adsorption of toluene, China. *Ion Exch. Adsorpt.* **2012**, *37*, 244–252.
106. Zuliani, A.; Chelazzi, D.; Mastrangelo, R.; Giorgi, R.; Baglioni, P. Adsorption kinetics of acetic acid into ZnO/castor oil-derived polyurethanes. *J. Colloid Interface Sci.* **2023**, *632*, 74–86. [[CrossRef](#)] [[PubMed](#)]
107. Zhang, W.; Luo, J.; Sun, T.; Yu, F.; Li, C. The absorption performance of ionic liquids–PEG200 complex absorbent for VOCs. *Energies* **2021**, *14*, 3592. [[CrossRef](#)]
108. Gui, C.; Li, G.; Zhu, R.; Lei, Z.; Dong, Y. Capturing VOCs in the pharmaceutical industry with ionic liquids. *Chem. Eng. Sci.* **2022**, *252*, 117504. [[CrossRef](#)]
109. Fahri, F.; Bacha, K.; Chiki, F.F.; Mbakidi, J.P.; Panda, S.; Bouquillon, S.; Fourmentin, S. Air pollution: New bio-based ionic liquids absorb both hydrophobic and hydrophilic volatile organic compounds with high efficiency. *Environ. Chem. Lett.* **2020**, *18*, 1403–1411. [[CrossRef](#)]
110. Chen, C.C.; Huang, Y.H.; Fang, J.Y. Hydrophobic deep eutectic solvents as green absorbents for hydrophilic VOC elimination. *J. Hazard. Mater.* **2022**, *424*, 127366. [[CrossRef](#)] [[PubMed](#)]
111. Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R.L.; Duarte, A.R.C. Natural deep eutectic solvents—solvents for the 21st century. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1063–1071. [[CrossRef](#)]

112. Moura, L.; Moufawad, T.; Ferreira, M.; Bricout, H.; Tilloy, S.; Monflier, E.; Gomes, M.F.C.; Landy, D.; Fourmentin, S. Deep eutectic solvents as green absorbents of volatile organic pollutants. *Environ. Chem. Lett.* **2017**, *15*, 747–753. [[CrossRef](#)]
113. Moufawad, T.; Gomes, M.C.; Fourmentin, S. Deep eutectic solvents as absorbents for VOC and VOC mixtures in static and dynamic processes. *Chem. Eng. J.* **2022**, *448*, 137619. [[CrossRef](#)]
114. Panda, S.; Fourmentin, S. Cyclodextrin-based supramolecular low melting mixtures: Efficient absorbents for volatile organic compounds abatement. *Environ. Sci. Pollut. Res.* **2022**, *29*, 264–270. [[CrossRef](#)]
115. Carpentier, J.; Lamonier, J.F.; Siffert, S.; Zhilinskaya, E.A.; Aboukais, A. Characterisation of Mg/Al hydrotalcite with interlayer palladium complex for catalytic oxidation of toluene. *Appl. Catal. A Gen.* **2002**, *234*, 91–101. [[CrossRef](#)]
116. Yu, X.; Deng, J.; Liu, Y.; Jing, L.; Hou, Z.; Pei, W.; Dai, H. Single-Atom Catalysts: Preparation and Applications in Environmental Catalysis. *Catalysts* **2022**, *12*, 1239. [[CrossRef](#)]
117. Ji, S.; Chen, Y.; Wang, X.; Zhang, Z.; Wang, D.; Li, Y. Chemical synthesis of single atomic site catalysts. *Chem. Rev.* **2020**, *120*, 11900–11955. [[CrossRef](#)] [[PubMed](#)]
118. Zhang, J.R.; Li, J.W. Preparation of Cu-Mn-Zr composite catalyst and performance for catalytic oxidation of ethyl acetate. *China Environ. Sci.* **2018**, *38*, 2927–2933.
119. Ying, K.; Chen, R.Y.; Liu, Z.M. Catalytic Removal of Toluene Over Manganese-Based Oxide Catalysts, China. *Mater. Rep.* **2020**, *34*, 23051–23056.
120. Mu, X.; Ding, H.; Pan, W.; Zhou, Q.; Du, W.; Qiu, K.; Ma, J.; Zhang, K. Research progress in catalytic oxidation of volatile organic compound acetone. *J. Environ. Chem. Eng.* **2021**, *9*, 105650. [[CrossRef](#)]
121. Fan, J.; Ren, Q.; Mo, S.; Sun, Y.; Fu, M.; Wu, J.; Chen, L.; Chen, P.; Ye, D. Transient in-situ DRIFTS Investigation of Catalytic Oxidation of Toluene over α -, γ - and β -MnO₂. *ChemCatChem* **2020**, *12*, 1046–1054. [[CrossRef](#)]
122. Kim, S.C.; Shim, W.G. Catalytic combustion of VOCs over a series of manganese oxide catalysts. *Appl. Catal. B Environ.* **2010**, *98*, 180–185. [[CrossRef](#)]
123. Li, R.; Zhang, L.; Zhu, S.; Fu, S.; Dong, X.; Ida, S.; Zhang, L.; Guo, L. Layered δ -MnO₂ as an active catalyst for toluene catalytic combustion. *Appl. Catal. A Gen.* **2020**, *602*, 117715. [[CrossRef](#)]
124. Yang, W.; Su, Z.A.; Xu, Z.; Yang, W.; Peng, Y.; Li, J. Comparative study of α -, β -, γ - and δ -MnO₂ on toluene oxidation: Oxygen vacancies and reaction intermediates. *Appl. Catal. B Environ.* **2020**, *260*, 118150. [[CrossRef](#)]
125. Wang, F.; Dai, H.; Deng, J.; Bai, G.; Ji, K.; Liu, Y. Manganese oxides with rod-, wire-, tube-, and flower-like morphologies: Highly effective catalysts for the removal of toluene. *Environ. Sci. Technol.* **2012**, *46*, 4034–4041. [[CrossRef](#)]
126. Song, C.; Yi, Q.R.; Li, J.W. Preparation of Mn₂O₃ with different morphologies and their catalytic performance for chlorobenzene, China. *J. Funct. Mater.* **2014**, *45*, 13050–13055.
127. Li, W.; Bollecker, S.S.; Schofield, J.D. Glutathione and related thiol compounds. I. Glutathione and related thiol compounds in flour. *J. Cereal Sci.* **2004**, *39*, 205–212. [[CrossRef](#)]
128. Ismail, A.; Zahid, M.; Hu, B.; Khan, A.; Ali, N.; Zhu, Y. Effect of morphology-dependent oxygen vacancies of CeO₂ on the catalytic oxidation of toluene. *Catalysts* **2022**, *12*, 1034. [[CrossRef](#)]
129. Zhou, J.; Zheng, Y.; Zhang, G.; Zeng, X.; Xu, G.; Cui, Y. Toluene catalytic oxidation over gold catalysts supported on cerium-based high-entropy oxides. *Environ. Technol.* **2023**, 1–13. [[CrossRef](#)]
130. Du, Z.; Zhou, C.; Zhang, W.; Song, Y.; Liu, B.; Wu, H.; Zhang, Z.; Yang, H. Commercial SCR catalyst modified with Cu metal to simultaneously efficiently remove NO and toluene in the fuel gas. *Environ. Sci. Pollut. Res.* **2023**, *30*, 96543–96553. [[CrossRef](#)] [[PubMed](#)]
131. Zhang, W.; Valverde, J.L.; Giroir-Fendler, A. Co₃O₄-based catalysts for propane total oxidation: A state-of-the-art minireview. *Appl. Catal. B Environ.* **2023**, *337*, 122908. [[CrossRef](#)]
132. Sun, L.; Liang, X.; Liu, H.; Cao, H.; Liu, X.; Jin, Y.; Li, X.; Chen, S.; Wu, X. Activation of Co-O bond in (110) facet exposed Co₃O₄ by Cu doping for the boost of propane catalytic oxidation. *J. Hazard. Mater.* **2023**, *452*, 131319. [[CrossRef](#)]
133. Hu, Y.; Zhang, L.; Zhang, J.; Liu, Y. High catalytic performance of neodymium modified Co₃O₄ for toluene oxidation. *J. Rare Earths* **2022**, *42*, 94–101. [[CrossRef](#)]
134. Liu, J.; Liu, Y.; Zhang, W.; Liu, L.; Ju, J. Efficient VOC removal over grape-like GdCoO₃ perovskite prepared from the viscous mixture. *Mater. Lett.* **2024**, *357*, 135796. [[CrossRef](#)]
135. Hu, W.; Guo, T.; Ma, K.; Li, X.; Luo, W.; Wu, M.; Guo, H.; Zhang, Y.; Shanguan, W. Promoted catalytic performance of Ag-Mn bimetal catalysts synthesized through reduction route. *J. Environ. Sci.* **2024**, *137*, 358–369. [[CrossRef](#)]
136. Shah, P.M.; Bailey, L.A.; Taylor, S.H. The influence of cerium to manganese ratio and preparation method on the activity of ceria-manganese mixed metal oxide catalysts for VOC total oxidation. *Catalysts* **2023**, *13*, 114. [[CrossRef](#)]
137. Cocuzza, C.; Sartoretto, E.; Novara, C.; Giorgis, F.; Bensaid, S.; Russo, N.; Russo, N.; Fino, D.; Piumetti, M. Copper-manganese oxide catalysts prepared by solution combustion synthesis for total oxidation of VOCs. *Catal. Today* **2023**, *423*, 114292. [[CrossRef](#)]
138. Liu, W.; Zhu, H.; Jiang, S.; Zhang, X.; Song, Z. Preparation of Au@ Cu-MnO₂ and its application in the catalytic oxidation of VOCs. *Mater. Lett.* **2023**, *340*, 134109. [[CrossRef](#)]
139. He, C.; Ao, C.; Ruan, S.; Xu, K.; Zhang, L. Catalytic combustion of propane over Zr-modified Co₃O₄ catalysts: An experimental and theoretical study. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *641*, 128617. [[CrossRef](#)]
140. Wang, Z.; Xiao, W.; Zhang, F.; Zhang, S.; Jin, W. Experimental study and kinetic model analysis on photothermal catalysis of formaldehyde by manganese and cerium based catalytic materials. *J. Air Waste Manag. Assoc.* **2023**, *73*, 345–361. [[CrossRef](#)]

141. Yang, Q.Q. Research Progress of Supported Catalysts Based on Porous Materials for Catalytic Oxidation of VOCs, China. *Chem. Eng. Des. Commun.* **2023**, *49*, 70–77.
142. Chen, X.; Yu, E.; Cai, S.; Jia, H.; Chen, J.; Liang, P. In situ pyrolysis of Ce-MOF to prepare CeO₂ catalyst with obviously improved catalytic performance for toluene combustion. *Chem. Eng.* **2018**, *344*, 469–479. [[CrossRef](#)]
143. Du, Z.; Yuan, Y.; Zhou, C.; Li, W.; Wang, H.; Wu, H.; Zhang, Z.; Yang, H. Gaseous toluene heterogeneous oxidative degradation by iron-based hypercrosslinked polymeric resin LXQ-10. *Fuel* **2023**, *344*, 128080. [[CrossRef](#)]
144. Ma, X.; Wang, W.; Zhang, X.; Li, H.; Sun, J.; Liu, X.; Sun, C. MOF-derived FeOx with highly dispersed active sites as an efficient catalyst for enhancing catalytic oxidation of VOCs. *J. Environ. Chem. Eng.* **2024**, *12*, 111966. [[CrossRef](#)]

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