Research of Advanced Materials for Volatile Organic Compounds Treatment

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Abstract. Volatile organic compounds (VOCs) are one of the important pollutants, which are easy to cause serious harm to the environment and human body. In this paper, solid adsorbents based on carbon-based adsorbents and porous molecular sieves, organic adsorbents and chemical materials based on chemical catalysts and photocatalysts are introduced. The effects of pore structure, specific surface area and acid base functional groups on the saturated adsorption capacity of carbon based adsorbents and porous molecular sieves were discussed. The differences between volatile organic solvents and new microemulsion systems and ionic liquids in terms of volatility, solubility and selectivity were compared. The latest progress of conventional thermal catalysts (noble metals, transition metals) and Photocatalysts (Metal/Nonmetal Doping, Nanomaterial Composite, Dye Sensitization) in VOCs treatment was discussed. The application prospects of new materials around biosurfactants and ionic liquids in the treatment of volatile organic compounds were pointed out.

Keywords. VOCs, environmental remediation, materials.

1. Introduction

Volatile organic compounds (VOCs) usually have boiling point below 250°C under quasi-atmospheric pressure. They can be discharged into the air in the form of gaseous molecules, including aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, aldehydes, ketones, alcohols and ethers. VOCs is one of the by-products of the rapid development of China's industry. In 2015 alone, the total annual emissions reached 31.17 million tons, far exceeding NO\textsubscript{X} and PM2.5. It mainly enters the atmosphere, soil and water through fuel combustion, traffic discharge, landfill, chemical sewage discharge, etc. It is an important precursor of O3 and SOA, and will seriously endanger human health. Therefore, in recent years, the VOCs control work has been paid more and more attention. In 2017, China promulgated the "13th Five-Year Plan of Volatile Organic Compound Pollution Prevention and Control Work Program" (State Office issued No. 3, 2017). By 2020, the total VOCs emissions in key areas and key industries will be reduced by more than 10%, indicating that China has already reduced the total VOCs emissions. VOCs should be included in the key prevention and control areas. In view of
this, it is of great significance to study VOCs processing technology. In recent years, the treatment materials of VOCs include physical materials, chemical materials and biological materials. In this paper, combined with the latest development in recent ten years, the related physical and chemical materials are reviewed, and the development trend is prospected.

2. Solid Adsorbent Material

2.1. Carbon-based Adsorbents

Porous carbon is the most widely used commercial adsorbent because of its low cost and high adsorptive capacity. At present, porous carbon has been applied to the undifferentiated adsorption and capture of most VOCs, such as alkanes, aromatics, ketones and aldehydes. The results show that porous carbon is mainly based on activated carbon and its modification technology. By changing the physical structure of activated carbon, the adsorption performance of VOCs can be improved. Qiu [1] expanded the pore volume of activated carbon from 0.1 cm$^3$/g to 0.3 cm$^3$/g by CO$\text{2}$/microwave modification, which reduced the heat of adsorption by 50%, and formed a hierarchical pore structure, which was more conducive to VOCs adsorption and desorption. Chen [2] modified activated carbon with iodine ion, found that iodine ion can effectively prevent the pore collapse of activated carbon, which is of great help to the stability and regeneration of activated carbon. At the same time, some new materials have attracted the attention of researchers. Tsai [3] evaluated the adsorption performance of pitch-based activated carbon fibers on VOCs. The results showed that the specific surface area (1518 m$^2$/g) of activated carbon fiber was 1.03-1.88 times that of activated carbon, the adsorption equilibrium time was 3-4 times shorter than that of activated carbon, and the saturated adsorption capacity (600 mg/g) was 2 times that of activated carbon. Yang[4] found that the adsorption capacity of activated carbon fibers was significantly higher than that of activated carbon when VOCs concentration was less than 50 mg/m$^3$, which was attributed to the fact that the short and straight ultrapore on the surface of activated carbon fibers was more conducive to the enrichment of low concentration VOCs(Figure 1). However, the content of oxygen groups on the surface of activated carbon fibers is only 735-865 μmol/g, which is less than that of AC (1570-4289 μmol/g), and the polar VOCs cannot be effectively adsorbed. The cost of biochar is only 1/6 of that of activated carbon, and its toxicity is small, but its adsorption capacity is less than that of activated carbon, so most of it is used to remove VOCs in daily life. In addition, there are some nano-scale porous carbon, such as carbon nanotubes and graphene, which have larger surface area and much higher adsorption capacity than activated carbon. However, the potential ecological toxicity of carbon nanotubes and graphene is still in the research stage.

![Figure 1. Diffusion of VOCs on Activated Carbon and Activated Carbon Fibers](image)

2.2. Porous molecular sieves

Porous molecular sieves have high thermal stability, chemical stability and regular pore size. They are mostly used for selective capture and separation of valuable VOCs in industry. Zeolite molecular sieves are the most representative materials in porous molecular sieves. Natural zeolites are easy to adsorb unsaturated hydrocarbons and VOCs containing polar groups (-OH, -COOH, -NH$_2$, -SO$_3$H, etc). But at the same time, water molecules easily occupy the acidic sites of zeolites, which hinders the adsorption of VOCs. Current studies show that many synthetic zeolites with high silica-alumina ratio can be used.
Improving the hydrophobicity of zeolite is favored by people. Narin[5] studied the penetration curves of olefins and alkanes on 13X zeolite. The results showed that olefins with large dipole moment were easier to diffuse into molecular sieves when their diameters were similar. At the same time, it was found that low concentration could inhibit the transverse interaction of adsorption molecules and improve the overall adsorption strength. A molecular sieve MIL-101 with better physical properties was synthesized by Ferey [6]. Its pore channels are more orderly and its pore volume is larger. The volume of a single cage is 702nm$^3$, and its specific surface area is between 5500-6200m$^2$/g. Yang [7] studied the adsorption properties of MIL-101 for several types of VOCs. It was found that the saturated adsorption capacity of MIL-101 for benzene was 1291+77mg/g, which was 2-3 times that of zeolite. The filling mechanism of VOCs in MIL-101 pore indicated that most molecules entered MIL-101 pore with minimum diameter plane, while o-xylene and m-xylene entered MIL-101 pore according to the principle of methyl preference. Fill in the hole. The results show that MIL-101 is the preferred choice for VOCs with low steric hindrance, which can be used for the separation of isomers. However, compared with zeolite, MIL-101 has higher cost and lower thermal stability, and is prone to skeleton collapse in the synthesis process, which affects the separation effect (Figure 2).

![Figure 2. Scheme of ethylbenzene, p-xylene, o-xylene and m-xylene entering into MIL-101 pores](image)

**3. Organic Absorbents**

At present, light mineral oils such as light diesel oil and lubricating oil are mostly used as VOCs absorbents in China. In the early stage, toluene was adsorbed by diesel oil No. 0 sold on the market. However, the light components in diesel oil escaped with the entrainment of air, resulting in secondary pollution. After a lot of adsorption of mineral oil by surfactant/water microemulsion system, the volatility of the system decreased significantly, while toluene absorption increased. This indicated that the water compound solvent could be used to treat medium concentration of VOCs, but the disadvantage was that the dosage was large and it could not be recycled. ILs is a new kind of green solvents, only composed of anions and cations, which is liquid at room temperature. As a green functional material for VOCs absorption, ILs has some unique advantages, such as good solubility, very low saturated vapor pressure, low vapor loss and solution recovery loss, and is an excellent "liquid molecular sieve". Different ILs can achieve efficient absorption of specific VOCs. Lechter and Deenadayalu [8] used ionic liquids 1-methyl-3-octyl-imidazole chloride to absorb benzene for the first time. It was found that the imidazole ring formed a pi-conjugated system with the benzene ring, which had a good absorption effect on aromatic organic compounds. In recent years, some researchers in China have used water-soluble DDMIM DCA to absorb toluene with an initial absorption rate of 98%, a saturated adsorption concentration of 53390.0mg/m$^3$, and the reabsorption efficiency of the absorbent remains basically unchanged. Ma [9] used [Emim][BF$_4$] to absorb VOCs from mixed phase. The adsorption capacity of benzene was 9 times higher than that of cyclohexane. With the increase of alkane chain (nonane > octane heptane > hexane), the selectivity coefficient of the system increased, which made ILs easier to extract benzene from mixed phase. Zhou [10] evaluated the absorption performance of [Bmim][PF$_6$] for VOCs. It was found that [Bmim][PF$_6$] had higher selectivity than [Emim][BF$_4$], and showed a great advantage in the adsorption of low concentration benzene (< 15 mol%). This phenomenon was mainly due to the hydrophobicity of [PF$_6$], but [PF$_6$] was easy to form HF, resulting in the stability of [Bmim][PF$_6$] was lower than [Emim] [BF$_4$]. Current studies have shown that some ionic liquids can also absorb olefins, alcohols and acids from olefins/alkanes, alcohols/alkanes (esters/water), acid/alkanes systems, indicating that ionic liquids are highly selective for VOCs, and can be used in high temperature and high concentration VOCs extraction process.
4. Chemical Catalytic Materials

4.1. Catalytic Oxidation Materials
Noble metals are the most commonly used metal catalysts, but because of their high price and easy contact with Cl and S, they are often replaced by supported noble metal catalysts. Rui [11] explored the conversion efficiency of Pt catalysts supported by AAO with different properties. In order to change the specific surface area, average pore size, pore volume and particle size, AAO was hydrothermally treated at different degrees (HWT). The optimum conversion rate of trace toluene (300μg g\(^{-1}\)) catalyzed by Pt/AAO was 95% when HWT was equal to 18 h. Joung[12] catalytic combustion of toluene (134mg/m\(^3\)) with Pt supported on CNT at 109\(^\circ\)C can even achieve 100% conversion. With the continuous development of nanotechnology, carriers are not limited to carbon nanotubes, but more good carriers are emerging: zeolite molecular sieves (HZSM-5, ZSM-5), nanorods (CeO\(_2\)-r), MOFs (ZIF-8, MIL-101) and so on. Nano-scale noble metal supported catalysts increase the selectivity of noble metal catalysts, and their properties are superior to those of noble metal monomers in many aspects.

Supported noble metals can catalyze VOCs at lower temperatures. In order to improve the selectivity, the supported transition metals with low cost, easy access, strong tolerance and long life can be used to improve the surface area and reduce the catalytic temperature. Yun [13] used KIT-6 and SBA-16 as templates to prepare three-dimensional ordered mesoporous Co\(_3\)O\(_4\) catalysts (Co-KIT6 and Co-SBA16) with a surface area of 118-121m\(^2\)/g, much higher than calcined bulk Co (10m\(^2\)/g) and Co3O4 (98m\(^2\)/g). The highest catalytic conversion of 1000mg/L toluene (90%) was achieved at 180\(^\circ\)C and 188\(^\circ\)C respectively. Feng [14] immersed CeO\(_2\) and Sr-CeO\(_2\) in Co(\(\text{CH}_3\text{COO}\))\(_4\)\(\text{H}_2\text{O}\) solution, respectively. The highest conversion of toluene (100%) was achieved at 380\(^\circ\)C and 330\(^\circ\)C for Co/CeO\(_2\) and Co/Sr-CeO\(_2\) catalysts respectively. The addition of Sr reduced the crystalline size of CeO\(_2\). For Co/Sr-CeO\(_2\), the increased oxygen vacancies and the stronger interaction between CoO\(_X\) and CeO\(_2\) were observed. It can weaken the Co-O bond, enhance the oxygen mobility and improve the catalytic efficiency.

4.2. Photosensitive Catalytic Materials
Photosensitive catalysts react with VOCs by electron-hole pairs generated by photon absorption in the forbidden band. TiO\(_2\) has been extensively studied because of its non-toxicity, low price and chemical stability. However, the wide band gap (≈ 3.2eV) of TiO\(_2\) limits its effective catalysis under visible light. Current studies show that metal/non-metal doping, nano-material compounding and dye sensitization can reduce the band gap of the catalyst (Figure 3). Lv[15] synthesized GO/TiO\(_2\)/Bi\(_2\)WO\(_6\) nanocomposites by one-step solvothermal method. Structural characterization showed that GO and TiO\(_2\)/Bi\(_2\)WO\(_6\) combined to form multiple heterojunctions, which reduced the band gap to 2.88eV, and the degradation rate of ethylene was 5.8 times that of pure TiO\(_2\). Hoang[16] doped 1.08at% nitrogen atoms into the lattice of TiO\(_2\) at 500\(^\circ\)C. The results show that N-TiO\(_2\) can reduce photoelectric recombination, reduce the bandgap to 2.4eV, and have a strong absorption effect for 520nm visible light. In recent years, some low bandgap non-TiO\(_2\)-based photocatalysts (Bi\(_2\)O\(_3\), CdS, WO\(_3\), etc.) have also been studied in VOCs treatment. Cheng [17] et al. selectively synthesized α-Bi\(_2\)O\(_3\), β-Bi\(_2\)O\(_3\) and δ-Bi\(_2\)O\(_3\) with a band gap of 2.80, 2.48 and 3.01 eV by solution method. They decomposed 4-chlorophenol under visible light irradiation, and β-Bi\(_2\)O\(_3\) showed similar photocatalytic performance to N-TiO\(_2\). However, due to the photocorrosion of Bi\(_2\)O\(_3\), modification was needed to improve its corrosion resistance. Zhu [18] prepared nested Bi\(_2\)WO\(_6\) with a band gap of 2.75 eV by hydrothermal method. When catalytic degradation of gaseous toluene, the optimum photodegradation efficiency reached 100% within 20 minutes, and it could be reused at least 8 times without change of catalytic activity.
5. Conclusion
Nowadays, the treatment technology of VOCs is a hot research topic. Surfactants, ionic liquids, MOFs and other new materials have obvious advantages as green and efficient treatment materials. High performance solid adsorbents and environmentally friendly liquid adsorbents were studied. New catalysts and specific microorganisms were found to reduce energy consumption. For example, the optimal absorption efficiency of VOCs by anionic/nonionic surfactants and imidazole ionic liquids is over 90%. Compared with traditional high boiling point organic solvents, they have the characteristics of low waste and recyclability. The combination of nanoporous materials (zeolites, nanorods, MOFs) and catalytic materials increases the conversion efficiency of VOCs to 95%~100%. It can reduce the catalytic conditions and improve the economy. Among them, the diversity and porous structure of MOFs are much higher than that of carbon materials in physical adsorption of VOCs, and they can be used for different shapes and junctions. The selective separation of VOCs and MOFs supported photocatalysts or other metal catalysts also showed good results.

There are several aspects worth discussing in the research process. For example, focusing on the induction of microbial communities by surfactants and the degradation of surfactants by microorganisms, the mechanism of surfactants and VOCs is deeply studied. The coupling technology of new surfactants and microorganisms may be the focus of attention in the field; some green materials. Ionic liquids (such as ionic liquids) are still in the stage of theoretical research, so the choice of reasonable preparation methods and economic control conditions is also of far-reaching significance to the practicability of materials. At the same time, the combination of chemical materials and biological materials will effectively promote technological upgrading.

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