

Review (Special Issue on Environmental Catalysis and Materials)

Adsorptive and catalytic properties in the removal of volatile organic compounds over zeolite-based materials



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ABSTRACT

Volatile organic compounds (VOCs) are a major component in air pollutants and pose great risks to both human health and environmental protection. Currently, VOC abatement in industrial applications is through the use of activated carbons as adsorbents and oxide-supported metals as catalysts. Notably, activated carbons easily adsorb water, which strongly hinders the adsorption of VOCs; conventional oxides typically possess relatively low surface areas and random pores, which effectively influence the catalytic conversion of VOCs. Zeolites, in contrast with activated carbons and oxides, can be designed to have very uniform and controllable micropores, in addition to tailored wettability properties, which can favor the selective adsorption of VOCs. In particular, zeolites with selective adsorptive properties when combined with catalytically active metals result in zeolite-supported metals exhibiting significantly improved performance in the catalytic combustion of VOCs compared with conventional oxide-supported catalysts. In this review, recent developments on VOC abatement by adsorptive and catalytic techniques over zeolite-based materials have been briefly summarized.

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1. Introduction

Volatile organic compounds (VOCs) usually refer to organic compounds having boiling points within the range of 50–260 °C [1–5], principally attributed to combustion engine and industrial emissions as well as domestic products. VOCs generally have high-risk biological toxicity properties, which pose significant threat to the human health. Additionally, VOCs are precursors to ozone and photochemical smog, which is a global issue for environmental protection. Therefore, VOC abatement has received ever increasing attention. Hitherto, there are numerous reported processes dealing with established VOC

abatement, such as adsorption [6], thermal incineration [7], photocatalytic [8], plasma catalytic oxidation [9], and catalytic combustion [10]. Among these techniques, VOC abatement by adsorption is widely employed at present because of simple operational procedures and economic viability in industrial applications, while catalytic combustion has been considered as one of the most effective methods because of its economically feasibility and high efficiency. Furthermore, the catalytic combustion process generates CO₂ as the only combustion product. Thus, there is a current need to develop highly efficient tailored adsorbents and catalysts.

Zeolites are regarded as one of the most industrially rele-

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vant adsorbents and catalysts because of their large surface areas, high adsorption capacity, high thermal and hydrothermal stability and the ability to tailor properties such as wettability and auxiliary mesopore generation in the crystals. Additionally, the presence of well-defined micropores exhibiting excellent shape-selectivity also contributes to their success. Such physicochemical properties allow zeolites to selectively adsorb VOCs. Furthermore, a series of zeolite-supported metals as highly efficient catalysts have been well developed for the catalytic combustion of VOCs by combination of selective adsorption onto zeolites with catalytically active metal centers. This review presents recent developments regarding the adsorption and catalytic properties in VOC abatement over zeolite-based materials.

2. Adsorption of VOCs over zeolites

Adsorption is one common and simple technique for the condensation and recovery of VOCs. Currently, activated carbons are the most useful adsorbents for VOC uptake [11–14], however, employing activated carbons still has practicality issues, such as flammability [15], difficulties in regeneration [16], and humidity control [17]. Compared with activated carbons, zeolites exhibit unique features, such as non-flammability, excellent regeneration by calcination, and controllable surface hydrophobicity hydrophilicity. Therefore, zeolites have shown to be useful alternative adsorbents for selective adsorption of VOCs [18].

Chintawar et al. [19] investigated ambient adsorption of gaseous trichloroethylene (TCE) over chromium exchanged ZSM-5 zeolites with various SiO_2/Al_2O_3 ratios under a humid air atmosphere. The study found that when increasing the SiO_2/Al_2O_3 ratio from 30 to 120 the TCE saturation capacity of the zeolite increased from 6.0 to 10.1 wt%, attributed to an increase in zeolite surface hydrophobicity. Trichloroethylene adsorption is favored over water molecules as the surface hydrophobicity increases. Bhatia et al. [20] studied the adsorption behaviors of butyl acetate in air over silver-loaded Y (Si/Al = 40) and ZSM-5 (Si/Al = 140) zeolites. As shown in Fig. 1, the presence of water vapor in the feed strongly suppresses butyl acetate adsorption of AgY; however, the adsorption capacity of

AgZSM-5 is only marginally affected because of the higher hydrophobicity of the zeolite. Huang et al. [21] investigated the changes in hydrophobicity and toluene adsorption-desorption properties of a commercial ZSM-5 zeolite as a function of Si/Al ratio and reported that an increase in zeolite Si/Al ratio obviously improved the zeolite hydrophobicity, resulting in the favorable adsorption of toluene.

To understand the adsorption of VOCs and water on zeolites, molecular simulation has been employed [22–24]. For example, Güvenç et al. [24] used Monte Carlo simulations to study the relationship between the Si/Al ratio of MFI-type zeolites and their adsorptive performance in the removal of hydrophilic methyl tert-butyl ether (MTBE) and hydrophobic trichloroethylene (TCE) mixed with water. Adsorption simulations on the MFI-type zeolites with three different Si/Al ratios (∞ , 191, and 95) were performed, showing that increasing zeolite hydrophilicity may significantly reduce MTBE removal from water; while increasing TCE concentration in the TCE-water mixtures leads to water exclusion in high silica zeolites, which may minimize the performance loss of these materials in TCE removal because of the presence of any hydrophilic defects in their structures (Fig. 2) [24].

As size exclusion is a desirable property in zeolite molecular sieves, tuning the zeolite pore size to effectively target the size of the VOCs is also an important factor for the adsorption of VOCs over zeolites. Bulky VOCs, whose size exceeds the zeolite pore dimensions hinders effective adsorption. Nicolas et al. [25] investigated toluene adsorption as a function of zeolite channel size and pore structure using three commercial hydrophobic zeolites: mordenite (MOR), ZSM-5, and faujasite (FAU) zeolite. They evidenced that toluene could be readily absorbed by FAU zeolite, however, decreased adsorption capacities were observed when using MOR and ZSM-5, suggesting the importance of the zeolite structures. Similar results have also been reported by Cosseron et al. [26]. Here they synthesized four pure silica zeolites: chabazite (CHA-structure type), SSZ-23 (STT-structure type), silicalite-1 (MFI-structure type), and beta (*BEA-structure type) for sorption of n-hexane, p-xylene, and acetone. As the pure silica CHA-type zeolite possesses smaller 8-member rings there was an obvious decrease in the adsorption capacity as a function of increasing molar volume of the



Fig. 1. Butyl acetate uptake by zeolite AgY with Si/Al ratio of 40 and AgZSM-5 with Si/Al ratio of 140. (a) GHSV = 5000 h⁻¹, C_{voc} = 4500 ppm; (b) GHSV = 5000 h⁻¹, C_{voc} = 1000 ppm. Reproduced from Ref. [20].

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