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Abatement of gaseous volatile organic compounds: A material perspective

Teresa Gelles, Anirudh Krishnamurthy, Busuyi Adebayo, Ali Rownaghi, Fateme Rezaei*

Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO, 65409-1230, United States

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ABSTRACT

Volatile organic compounds (VOCs) are a class of organic liquid compounds with low vapor pressures, which enables them to vaporize at ambient conditions. VOCs are largely toxic, carcinogenic, and mutagenic, and have profound adverse effects on human health and the ecological environment. Many VOCs cause ruinous health effects even at very low concentrations (ppm) and therefore control of these organic compounds is essential for ensuring good air quality. Rising levels of VOCs in the outdoor environment, particularly in urban areas, has sparked considerable research into the abatement of VOCs. This has evolved into a myriad of pollution control technologies, including thermal catalytic oxidation, photocatalytic oxidation, non-thermal plasma, adsorption, and hybrid adsorption-oxidation processes. In order for catalytic and adsorption-based process to emerge as a promising method for VOC abatement, development of efficient materials is a crucial step. This review discusses recent developments made in the fields of catalysis and separation, with an emphasis on catalytic materials, including noble-metal catalysts, transition metal-oxide catalysts, perovskites, titania and ceria based catalysts, and dual-functioning adsorbent/catalysts. Various capture materials, such as activated carbons, zeolites, and metal organic frameworks (MOFs), are also discussed for the purpose of providing insight into the efficacy of adsorbent inclusion in hybridized separation-destruction processes.

1. Introduction

Volatile organic compounds (VOCs) are organic compounds which vaporize easily under ambient indoor conditions. They are defined as “any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions” by the U.S. EPA. There are, however, some compounds that may be described by this classification, but may not fulfill other criteria to be classified as a VOC under the code of regulations (Code of Federal Regulations, 40: Chapter 1, Subchapter C, Part 51, Subpart F, 51,100). These compounds are organic in nature, as the name suggests, and only contain carbon, nitrogen, sulfur, oxygen and chlorine. Since the days of rapid industrialization, emission levels of VOCs have been steadily increasing to a point of concern. According to the National Emission Inventory (NEI), archival data suggests that the largest emission of VOCs from anthropogenic sources is released from the industry due to the use of solvents and high-volume emission levels, closely followed by automotive exhaust (Fig. 1). High emission industries include paper factories, petroleum refineries and textile manufacturers [1].

Exposure to VOCs has three broad effects, namely, biological, environmental, and human health. Outdoor VOC pollution has significant environmental impacts, namely soil quality, groundwater contamination, smog formation, and ozone imbalance, while VOCs in the indoor environment are highly toxic and have larger biological effects, such as cancer-causing and respiratory health effects. In the indoor environment, VOCs are emitted from paints, wood finish, and improperly ventilated cooking.

The molecular structure of the type of VOC encountered is of great importance when determining the most suitable abatement method. VOCs can be broken down into three distinct classes, (i) carbonyl, (ii) aromatic, and (iii) halogenated. Carbonyl compounds is the largest classification type and includes aldehydes and ketones [2–4]. Aromatic compounds include some of the most commonly encountered VOCs. They frequently contaminate soil and water through vapor sorption or liquid discharge and therefore must be considered when assessing outdoor air quality [5–7]. Halogenated compounds are of particular importance due to their strong toxicities and abundance in a variety of products. They have been known to contaminate air and groundwater systems making them of particular interest for abatement [8,9]. Some of the most commonly emitted VOCs are BTX (Benzene, Toluene, and Xylene) compounds, acetone, and formaldehyde [10,11]. Table 1 below provides an overview of many commonly encountered VOCs, their classifications, and structure.

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* Corresponding author.
E-mail address: rezaeif@mst.edu (F. Rezaei).

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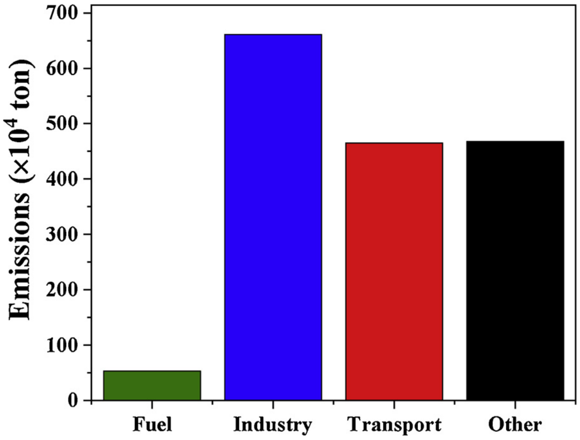
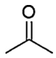
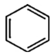
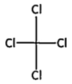
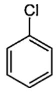
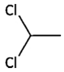
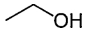
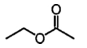
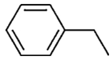
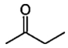
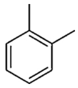
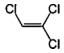
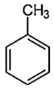


Fig. 1. VOC emissions in the United States by tier [1].

Table 1
The name, classification, and structure of many commonly encountered VOCs.

Name	VOC Type	Structure
Acetone	Carbonyl	
Benzene	Aromatic	
Carbon tetrachloride	Halogenated	
Chlorobenzene	Halogenated	
Dichloroethane (DCE)	Halogenated	
Dichloromethane (DCM)	Halogenated	
Ethanol	Carbonyl	
Ethyl Acetate (EA)	Carbonyl	
Ethylbenzene (EB)	Aromatic	
Hexane	Carbonyl	
Methanol	Carbonyl	
Methyl ethyl ketone (MEK)	Carbonyl	
o-Xylene	Aromatic	
Trichloroethylene (TCE)	Halogenated	
Toluene	Aromatic	

Considering these prominent issues to human civilization, many investigations have been performed on various abatement technologies, including capture, destruction, or hybridized capture and destruction methods. Capture methods are largely material based, and focus primarily on adsorption whereas destruction methods, such as thermal catalytic oxidation, photocatalytic oxidation, non-thermal plasma technology, are heavily influenced by catalytic properties. Catalysts are essential in ensuring that these destruction methods operate efficiently. They lower the activation energy required for thermal and photocatalytic oxidation, providing both cost-effective and safer reaction conditions. Frequently used catalysts include noble-metal [12,13] and mixed metal oxides [14–17], and perovskites [18,19]. Noble-metal based catalysts have been widely reported to have the highest activity in removing VOCs at low temperatures [20]. Research has shown that doping with noble metals such as Pd, Pt, Ni, Au, and Rb can significantly enhance the VOCs abatement ability of materials [21–24]. They are, however, expensive to use which limits their feasibility in a number of processes. In contrast, mixed-metal oxide catalysts (MMOs) are cheaper to make and prevent degradation of the active materials. MMOs work synergistically, where one metal oxide acts as the active material and the other acts as the support. Compared with single metal oxides such as SiO_2 [25] and TiO_2, the use of MMOs, such as NiO_2/SiO_2 [26], MnO_2/SiO_2, TiO_2/SiO_2 [27,28], and ZrO_2/SiO_2 exhibit better performance as catalysts for the oxidation of VOCs. Perovskites are calcium-titanium oxide minerals composed mainly of calcium titanate ($CaTiO_3$). Many different cations can be embedded in perovskites, thereby increasing their thermal stability and activity. [19,29,30]

Adsorptive capture materials have also been investigated for VOC capture due to high surface areas and pore volumes which allow for the capture of VOCs in dilute gaseous streams. Activated carbons, zeolites, and mesoporous silicas are robust and well-established adsorbents that have been shown to be particularly effective in the abatement of many kinds of VOCs. Activated carbon is a processed carbon of small, low-volume pores and high surface areas [31,32] suitable for adsorption of VOCs [31–35]. Zeolites are microporous, aluminosilicate minerals with well-defined pore structures and adjustable acidities that make them highly attractive adsorbents or catalysts for molecules of certain sizes and shapes [36]. Zeolites have been widely used as adsorbents for VOCs capture and degradation. More recently, metal organic frameworks (MOFs) have arisen as viable materials for VOC capture. They consist of metal ions coordinated to organic ligands and form one-, two-, or three-dimensional structures. Their high adsorption capacities and exceptional surface areas make them particularly promising for VOC capture [37–41]. Although specific reviews have been published in the past with regards to VOC pollution problems and abatement materials [42–47], this review seeks to perform a succinct study on the recent material developments made in the areas of catalysis and separation, with an emphasis on catalytic materials, including noble-metal catalysts, transition metal-oxide catalysts, perovskites, titania and ceria catalysts, and dual-functioning adsorbent/catalysts.

2. Catalysts used in the abatement of VOCs

VOC abatement is commonly carried out using capture, destruction, or hybridized capture and destruction methods. These are classified under prevention methods and involve the abatement of a VOC at the exhaust of the process. The most common destruction methods used in industry include thermal catalytic oxidation, photocatalytic oxidation, and non-thermal plasma technologies. However, these methods suffer from numerous disadvantages, including high energy penalties associated with elevated temperatures. To overcome this, the use of catalysts as a means of activation energy reduction are frequently employed. Through the use of catalysts, these processes can achieve total oxidation of different types of VOCs between 150–250 °C [1]. Frequently used catalysts include noble metal based [12,13], metal [14,15] and mixed metal oxide based [16,17], fibers [48], and zeolites [49,50]. These catalysts types are further discussed in detail in this section.

2.1. Noble metal-based catalysts

The most commonly used catalysts for the complete combustion of VOCs are noble metal-based catalysts. These are usually used in place of supported noble metals, due to their high cost. Noble metal-based catalysts tend to show higher conversion rates at lower temperatures as compared to other catalyst types. Commonly used noble metals are palladium (Pd), platinum (Pt), and Rubidium (Ru) [51]. They are supported on materials with a high oxygen mobility, such as metal

Table 2
Summary of noble metal-based catalysts used in the total oxidation of some common VOCs.

Catalyst	VOC	Concentration	Reaction temperature (K)	Removal efficiency	Ref
Ru/TiO_2	Chlorobenzene	500 ppm_v	560	90	[59]
Rh/TiO_2	Chlorobenzene	500 ppm_v	613	90	[59]
$Ru\text{-}Ce/TiO_2$	Chlorobenzene	500 ppm_v	563	90	[60]
1.5 wt.% Pd/HY	Methanol	4 v/v %	393	90	[61]
Au/FeO_x	Formaldehyde	80 ppm_v	293	75	[62]
$Pt/\gamma\text{-}Al_2O_3$	Formaldehyde	230 ppm_v	293	92	[63]
Rh/TiO_2	Formaldehyde	100 ppm_v	348	100	[64]
$Au\text{-}Ce\text{-}TiO_2$	Toluene	1000 ppm_v	< 673	100	[65]
$Au\text{-}Fe\text{-}TiO_2$	Toluene	1000 ppm_v	< 673	100	[65]
1 wt. %Au–Pd/3DOM Co_3O_4	Toluene	1000 ppm_v	453	100	[66]
0.1 wt.% Pt/0.2 wt.% Pd/MCM-41	Toluene	500 ppm_v	453	100	[67]
Pd-Au Fe_2O_3/CeO_2	Benzene	42 g cm^{-3}	473	100	[68]
Pd-Ni/SBA-15	Benzene	1000 ppm	630	100	[69]

oxides [52], aluminosilicates, or perovskites [53]. Multiple studies have been made on the total oxidation of VOCs using catalytic thermal oxidation. During the selection of the dopant noble metal, multiple parameters are considered, such as dispersion and loading [54]. Table 2 provides an overview of noble metal catalysts that have been used in the total oxidation of common VOCs. In a study done by O'Malley et al. [55], it was found that apart from the aforementioned parameters, the reaction rate of a VOC in an oxidation reaction depends on the strength of the weakest C–H bond in Pt based catalysts. The effect of synthesis procedure and support material also plays a large role in the performance of these catalysts [56]. In low temperature catalysis, adsorption and activated surface oxygen species [57] were also found to be an important factor. Naturally, the effect of the support plays an important role. For example, in a study done by Chen et al. [58], it was found that Pt mounted on AlOOH showed the best catalytic activity for the oxidative removal of formaldehyde in room temperature when compared to other support metal oxides investigated.

Due to their high surface area, low cost, easy synthesis procedure, and accessible surface oxygen species, transition metal/mixed metal oxides are frequently used as supports for noble metals. They also have high thermal resistivity and have a strong resistance towards deactivation [70]. In circumstances with a higher sulfur content in the gas feed, mixed metal oxides have been shown to outperform noble metals [71], thereby increasing its utility in the catalysis of different kinds of VOCs, such as S-VOCs. Ru based catalysts are frequently used in the destruction of C-VOCs [72]. For example, in a study by Liu et al. [59] on the oxidation of chlorobenzene over different noble metals supported by TiO_2, the Ru based catalyst showed complete destruction of the VOC at the lowest temperature (300 °C). Furthermore, on analysis of polychlorinated by products, it was found that Ru/TiO_2 had the lowest concentration, revealing the significance of Ru for the specific control of halogenated VOCs. Similarly, Ye et al. [60], investigated Ru based catalysts supported on TiO_2 and a mixture of Ce and TiO_2 along with a host of other metal oxides for the total oxidation of chlorobenzene. It was revealed that TiO_2 had better catalytic activity at lower temperatures when compared to all other metal oxides tested, such as ZrO_2, $\gamma\text{-}Al_2O_3$ and SiO_2 (Fig. 2).

It has also been inferred that the phase of the titania present influences reaction rates. Dang et al. [73] presented an Ru based catalyst supported by high surface area mixed metal oxides, such as titania-silica or zirconia-silica, for the oxidative removal of VOCs and halogenated VOCs at low temperatures, achieving 100% destruction at 300–350 °C. By keeping loading percentages low and durability high, this is a cost effective noble metal-based catalyst for the destruction of VOCs. Gold based catalysts are also frequently used for the catalysis of VOCs. Gold nanoparticles (NPs) doped onto metal oxides have enhanced VOC catalysis.

Illustrated by Fig. 3, Sinha et al. [74] compared the efficiencies of $\gamma\text{-}MnO_2$ and Au/ $\gamma\text{-}MnO_2$ for the removal of acetaldehyde and toluene. It is suggested that an oxygen spillover effect caused by Au into the vacancies in the metal oxide causes a synergistic effect that promotes VOC attraction. Three-dimensionally ordered macropore (3DOM) structures have also been frequently used in tandem with noble metals and have several advantages such as interconnected pore systems and high surface areas, providing large contact areas. [75] These are a combination of transition metal and metal oxides. Jian et al. [75] investigated the potential of gold NPs on 3DOM structures mounted on perovskites. It was found that 1.67 wt. % Mn_3O_4-2Au/3DOM LSCO ($La_{0.6}Sr_{0.4}CoO_3$) had the lowest T_{90} at 230 °C when compared to other weight ratios. Absorbed oxygen species and strong interactions between NPs was found to be the reason for its enhanced catalytic performance. Bimetallic materials have also been used in this scenario. Xie et al. [76] studied the destructive potential of Au–Pd/3DOM Mn_2O_3 for methane

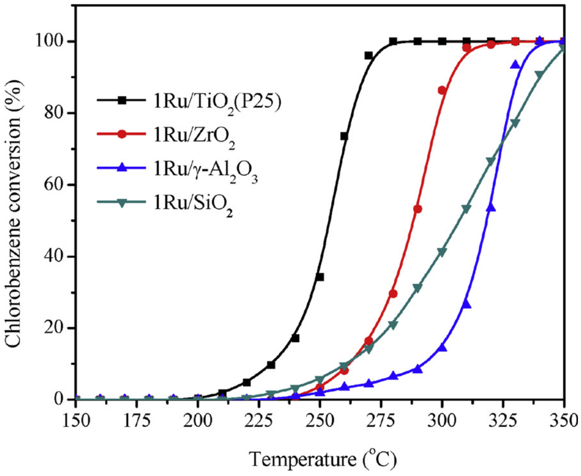


Fig. 2. Catalytic activity of Ruthenium supported by various metal oxides [60], where P25 refers to a mix of rutile and anatase phases of titania.

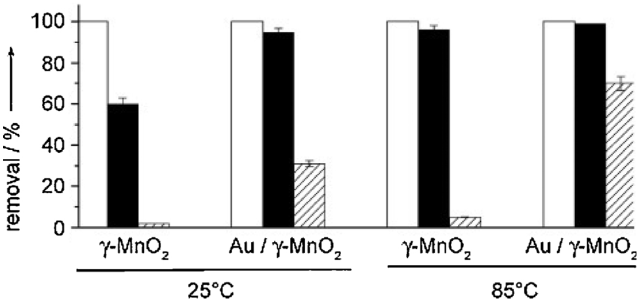


Fig. 3. Removal efficiencies of $\gamma\text{-}MnO_2$ and Au/ $\gamma\text{-}MnO_2$ for acetaldehyde (empty), toluene (solid) and hexane (pattern) [74].

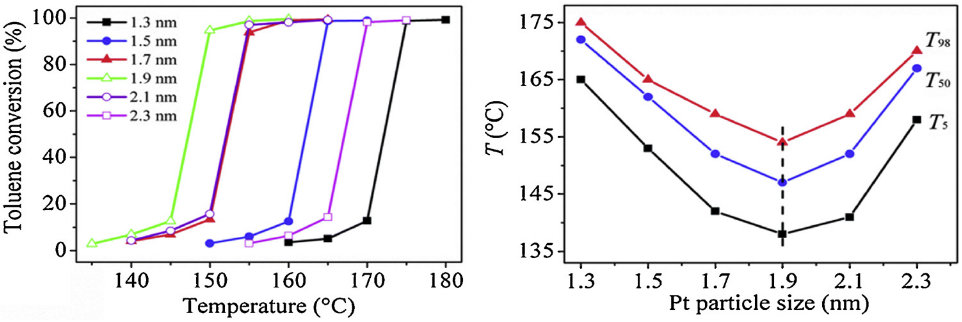


Fig. 4. Conversion of toluene and light off temperatures compared to particle size [79].

and o-xylene. The bimetallic Au-Pd-0.22 wt. % Fe/3DOM Mn_2O_3 showed a 90% destruction at 213 °C, much lower than other metals tested (Cr, Mn and Co) suggesting the potential of doping a transition metal, in this case Fe, onto a NP based catalyst to provide an increase in surface oxygen species due to greater interaction. Incorporation with polymer templating has also been explored. For example, Liu et al. [77] studied the oxidation performance of mesoporous Co_3O_4 impregnated by Au nanocatalysts with a polymer based template for the destruction of BTX compounds and CO. The BTX compounds were fed at a concentration of 1000 ppm_v. The strong association between Au NPs and the ceria resulted in an enhanced catalytic activity at temperatures $>$ 250 °C. Pt based catalysts are one of the most efficient of this material class for VOC oxidation and are characterized by lower light off temperatures when compared to other noble metals. [54] Particle size and dispersion is said to strongly influence the catalytic performance of Pt based catalysts [78]. Chen et al. [79] compared the effect of Pt particle size supported on ZSM-5 with the conversion of toluene (Fig. 4). A steady increase in performance was observed from the increase from 1.3 nm to 1.9 nm particle size and then started to decrease. Results revealed an optimum particle size that yielded the lowest light off temperatures, which was due to a balance between Pt dispersion and proportion.

The room temperature catalytic oxidation of formaldehyde is another common application for Pt based catalysts. Most commonly, Pt supported by TiO_2 is used for this process, where, Pt functions as the active phase, while the mixed metal oxide support provides oxygen vacancies [80]. A study by Nie et al. [81] revealed the importance of support geometry for the RT catalysis of HCHO. Pt supported by metal oxide based hollow sphere composite materials with a hierarchical meso-macropore system showed much better catalytic activity and CO_2 production when compared to conventional powder based catalyst. Additionally, Pt and TiO_2 composite catalysts have arisen as attractive modes of formaldehyde capture and destruction at ambient conditions (Fig. 5) [82]. Pt-based catalysts, however, have a tendency to get deactivated in the presence of chlorinated hydrocarbons which is usually overcome by higher loading percentages [83]. In an investigation by Huang et al. [84], the effect of reduction treatment was studied and it was revealed that with the right treatment, complete conversion of HCHO at low concentrations (10 ppm) was achieved even at 0.1 wt. % Pt loadings due to the presence of rich chemisorbed oxygen species.

Alkali earth metals, on addition to Pt based catalysts, have enhanced catalytic performances for the oxidation of HCHO by altering the reaction pathway by the activation of the hydroxyl group [85]. Deactivation of the catalysts can due to a number of causes, such as sulfur or halogen poisoning and its interactions and thermal degradation [83]. This can cause a problem when dealing with these materials on an industrial scale, and therefore, the utility of noble metal based catalysts is limited.

2.2. *Transition metal oxide-based catalysts*

Due to noble metals being so expensive to use, transition metal oxide-based catalysts have been studied frequently to achieve similar conversion rates. They are commonly transition metal elements, usually from groups III-B through II−B with respect to the periodic table [54]. However, unlike noble metals, light off temperatures for these types of catalysts are generally higher. The following properties of the material have been identified to be very important in catalysis over transition metal oxides [86]:

(i) Lattice oxygen;
(ii) Metal-oxygen bond;
(iii) Host structure;
(iv) Redox properties;
(v) Multifunctionality of active sites;
(vi) Site isolation; and
(vii) Cooperation of the phases within the material

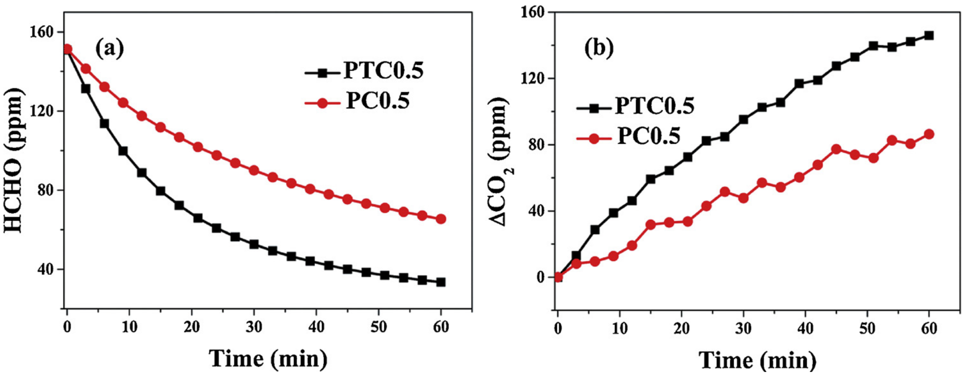


Fig. 5. Changes in formaldehyde concentration for a Pt/TiO_2 (PTC0.5) composite and Pt (PC0.5) catalyst at room temperature (a) HCHO conversion (b) Product formation (CO_2) [82] – Published by the Royal Chemistry Society.

Cerium oxide, CeO_2, that has been prepared by precipitation or combustion method has been shown to be very active for VOC and CO oxidation, due to its oxygen storage capacity [87,88]. Quite often, using different transition metal oxides enhances activity rates. In a study done by Balzer et al. [88], which investigated ceria based materials for the catalytic oxidation of different VOCs, γ-Al_2O_3-CeO_2 revealed to have comparatively lower light off temperatures in all cases when compared to the pure ceria catalyst. Addition of metals such as Zr also increases surface acidity of the catalysts [89]. While Cr and V based catalysts have been shown to have a good oxidation performance, they pose a challenge due to their increased solid toxicity [90,91]. Mn based materials are less toxic can overcome this issue. They are also more cost effective. Mn based catalysts are frequently used for VOC oxidation [92]. Multiple factors contribute to the effectiveness of manganese oxide catalysts, such as increased oxygen mobility through the crystal lattice [93]. It is also interesting to note that structural influences of the manganese oxide also contribute to activity rates, for example, the polyvalent character and freely accessible surface oxygen species of γ-MnO_2 makes it a good candidate for oxidative reactions [94]. Lahousse et al. [95] investigated the effects of crystallographic characters for the total oxidation of VOCs, ethyl acetate (EA) in particular. The effect of different phases of manganese oxide on the conversion of EA is illustrated by Fig. 6.

As we can observe, the effectiveness of the manganese dioxide in EA conversion was highest in its nsutite phase (γ-MnO_2) and gradually reduces from ramsdellite to pyrolusite (β-MnO_2) respectively which was loosely attributed to the MnO_x octahedral arrangement, coordination number of the oxygen anion species and the presence of atomic vacancies. The type of manganese oxide can also alter the reaction pathway [96]. To enhance the activity of manganese oxides, other transition metals may be added, such as Zr or Ce, to enhance the surface acidity of the material and it can potentially be used in a variety of situations, like the abatement of chlorinated compounds such as trichloroethylene (TCE) or oxygenated VOCs such as butanol due to redox coupling [97,98]. Both Ceria and MnO_x have also been shown to be very effective when dealing with C-VOCs [99]. While Mn and Ce based oxides are frequently used, the use of other transition metal oxides can have its own special advantages. For example, iron oxide has a high sintering temperature, and can therefore avoid deactivation relatively better in high temperature situations [100]. Similarly, distortion of the crystal lattice by another metal may potentially enhance O_2 mobility, while doping with rare earth metals can potentially improve oxygen vacancies [101].

2.3. Perovskites

Perovskite catalysts are a class of composite material frequently encountered in catalysis. These materials were first introduced in the 1970s, as a means to serve as an alternative for precious metal based catalytic converters in automobiles [102]. They can be represented by the empirical formula ABO_3, where A is a cation which is usually an alkaline, alkaline earth or lanthanide metal, while B refers to a cation of transition metal configuration. They have low surface characteristics when compared to metal oxide or MOF based catalysts. The mechanism of VOCs on these materials is represented by Fig. 7.

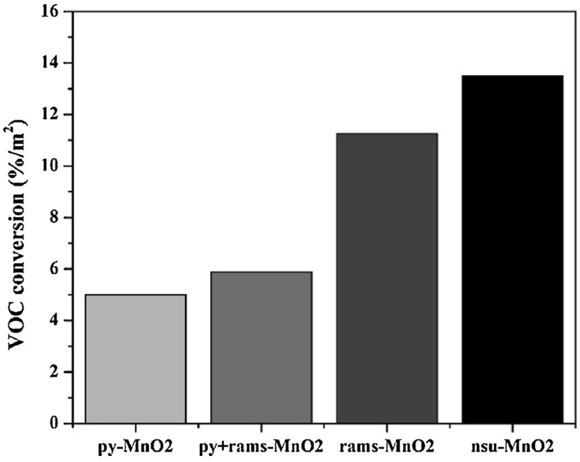


Fig. 6. Effect of different phases of MnO_2 on the total oxidation of EA [95].

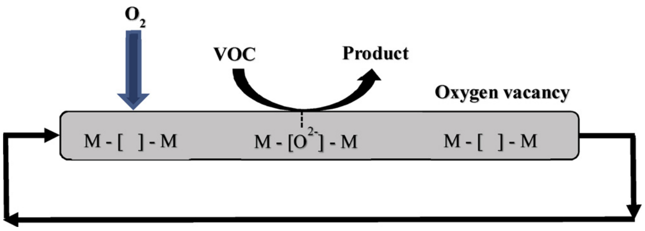


Fig. 7. Mechanism of VOC oxidation over perovskite catalysts.

Utilizing the unique property of polyvalency of the d block elements in the structure, multiple possible charge distributions are encountered throughout the structure of the material [103]. This results in tunable redox properties, which can be greatly advantageous in heterogeneous catalysis. They are also used frequently as supports for noble metals. Not many studies have been performed in the investigation of these materials for VOC oxidation. Manganese based perovskites have been shown to be efficient in VOC oxidation. Deng et al. [104] investigated the potential of hydrothermally prepared manganese oxide based perovskite catalysts of the structure $La_{0.5}Sr_{0.5}MnO_{3}$-δ. A dependence on the synthesis procedure was revealed, which could suggest the importance in preparation methods for the materials. Surface enrichment of Mn and surface oxygen vacancies were found to be the important factors in determining VOC oxidation efficiency. However, Mn based catalysts are sensitive to sulfur poisoning, and hence are limited by their application in the abatement of SVOCs. This is attributed to the screening effect, caused by the combination of the A or B cation with the sulfur anion, which leads to rapid deactivation [30]. In a recent study done by Izadkhah et al. [105], Co based perovskites performed better when doped with other transition metals, namely, Mn and Fe in this case, for the total oxidation of toluene.

Qin et al. [106] studied the conversion of EA over silver doped $LaBO_3$, where B was Co, Mn, Ni and Fe. Similar to other studies, Co based catalysts were shown to have an enhanced efficiency in EA conversion. The active sites in xylene oxidation on cobalt based oxides [107] were identified to be Co^{2+} species concentration, which were the main species for surface oxygen activation. The synergistic effect of the silver particles on the surface was discovered to be a significant factor along with its high redox activity rates in the performance of Ag/$LaBO_3$ when compared to the variations of the bare perovskite. This is illustrated in Fig. 8. With the objective of enhancing catalytic performance of these materials, Pan et al. [108] prepared a double perovskite catalyst, which is a perovskite with two different and synergistic transition metal cations. These materials were tested for multiple different VOCs, such as toluene, isopropyl alcohol and ethylene at fairly dilute concentrations (300 ppm). Results indicated a lower light off temperature for the bimetallic catalyst when compared to the single metal perovskite. From Fig. 7, it is inferred that the doping with two different metals would cause a much higher concentration of lattice oxygen and vacancies, thereby increasing catalytic performance. The effect of humidity is another aspect to consider in this situation, as it tends to effect the electrical properties of the perovskite [109]. When devising a VOC sensor, for example, high humidity situations [110] have been shown to effect response times, which could suggest an effect on catalytic affinity of these compounds. Liu et al. [111] prepared an active samarium manganese oxide based perovskite catalyst for the abatement of different VOCs with varied morphologies. The net like morphology along

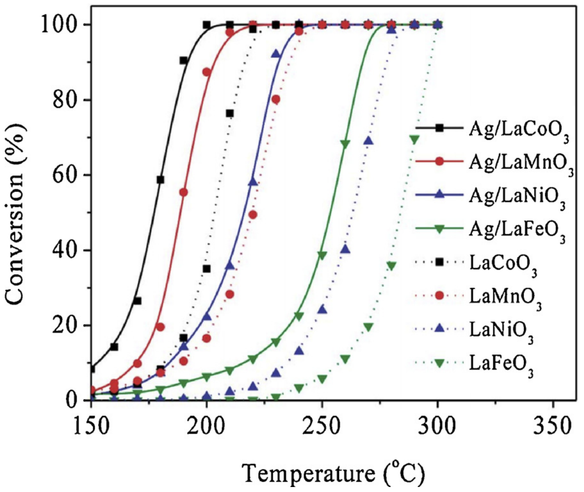


Fig. 8. Conversion of EA over various perovskites and their Ag doped counterparts [106] - Published by the Royal Society of Chemistry.

with increased chemical properties such as surface Mn^{4+}/Mn^{3+} species and lattice oxygen concentration resulted in a low temperature complete conversion of toluene, benzene and o-xylene to CO_2 at 240, 270 and 300 °C, significantly lower than many other metal oxide-based catalysts and even some noble metal ones. It has also been revealed that the incorporation of Ce in a manganese oxide based perovskite structure yields a much better activity towards VOCs due to an increased Mn^{4+} concentration and consequently, better redox properties [112]. He et al. [113] incorporated Ce and Ni with manganese based perovskites for the total oxidative catalysis of TCE and it was revealed that the addition of these metals enhanced the redox properties of Mn^{4+}/Mn^{3+} within the structure, yielding a lower light off temperature. Complete conversion was achieved, indicating the potential of these materials for C-VOCs.

2.4. Zeolite catalysts

Transition metals, metal oxides and noble metals incorporated onto zeolite structures through ion exchange have also shown to have a good potential for VOC oxidation [114–116]. Zeolites are materials with high surface to volume ratio, along with a 3D tetrahedral structure (TO_4) bonded by oxygen atoms and are commonly known as ‘molecular sieves’. They are a combination of Si and Al based oxides, with the general formula $M_x/n[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$, where M refers to the ion exchanged cation or proton. Catalytic activity is usually dependent on the atom used to replace the M position. The faujasite (FAU) structure has been found to be particularly effective for VOC oxidation [117].

There exist two primary types of zeolites, acidic and basic. The behavior of acidic zeolites is a little more complex and coking is found to be a larger problem [116,118]. Common zeolites are generally microporous, and are difficult to handle when considering continuous flow operations. Furthermore, they lead to increased coke formation within the pore system [50]. Crystal size and active site spatial distribution was found to be one of the most important factors in determining zeolite catalytic activity. These issues can be tackled in zeolitic materials with comparative ease using organic structure directing agents (OSDAs) [119]. Apart from shape and size selectivity and stable physiochemical properties, the ion exchange capacity of zeolite materials make them excellent oxidative catalysts as well [120]. Basicity of the zeolite has been found to be related to the catalytic activity of VOCs [121]. Mochida et al. [122] performed one of the first VOC oxidation studies on transition metal exchanged zeolites, using Na-Y. Supported noble metals (Pd, Pt) showed the lowest activation energy, followed by Cu, which suggested the potential of these materials for this operation. Commonly, Pd and Pt are the noble metals used in this particular scenario. The type of framework selected also has a large effect on catalytic performance of VOCs. For example, The effect of the framework used was investigated in a study done by Tidahy et al. [121], using the commonly used frameworks (illustrated by Fig. 9). Interestingly, catalytic activity was shown to be the reverse when comparing both FAU and beta polymorph A (BEA) type zeolites, which was explained due to the dispersion of Pd particles, among other factors.

Tidahy et al. [114] assessed the catalytic performance of Pd supported by an FAU zeolite framework for the total oxidation of toluene and compared it to commonly used transition mixed metal oxides. Basic zeolites performed much better than acidic zeolites, with significantly lower light off temperatures for Pd doped materials when compared to mixed metal oxides used. Jabłónska et al. [61] studied Pd particles deposited on acidic zeolite (HY) and FAU-Na zeolite (NaY) for the low temperature decomposition of methanol. The HY doped with Pd (1.5 wt. %) showed much better performance, with T_{90} of 120 °C. when compared to the basic zeolite. Blanch-Raga et al. [123] prepared Cu and Co modified β-zeolites for the conversion of TCE. The best performance was obtained by Cu exchanged zeolite, with a T_{90} of 360 °C, which was attributed to a better combination of redox properties.

The challenges faced by the use of these materials for the catalytic thermal oxidation of VOCs are the high toxicity of some halogen and sulfurous compounds, coking and the presence of water vapor. There are different kinds of coke, but dealing with VOCs frequently results in either carbonaceous or sulfurous coke. This is commonly indicated by a dark colored deposition on the catalyst. There exists two pathways in which coking can occur, namely, internal and external. This is another reason why adsorbent materials such as activated carbons are not commonly used, as regeneration temperatures are commonly too high for material recovery. When dealing with CVOCs, HCl poisoning is of

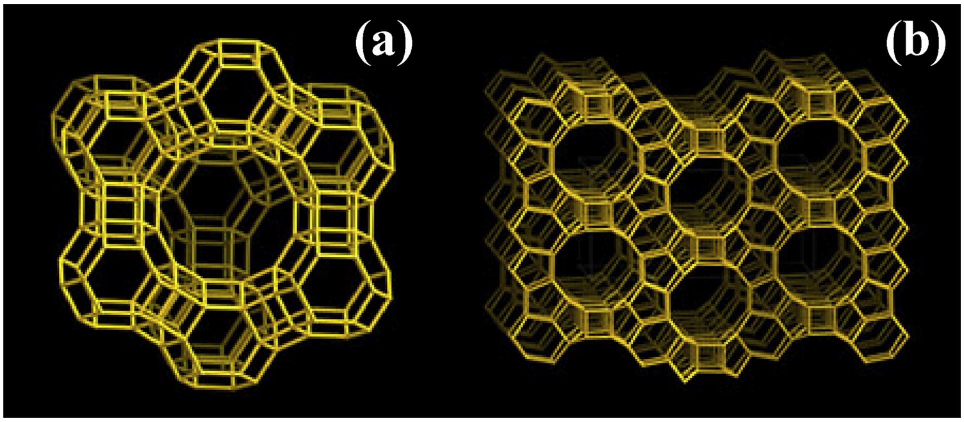


Fig. 9. Zeolite frameworks commonly used in VOC oxidation, (a) FAU (b) BEA framework (Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures).

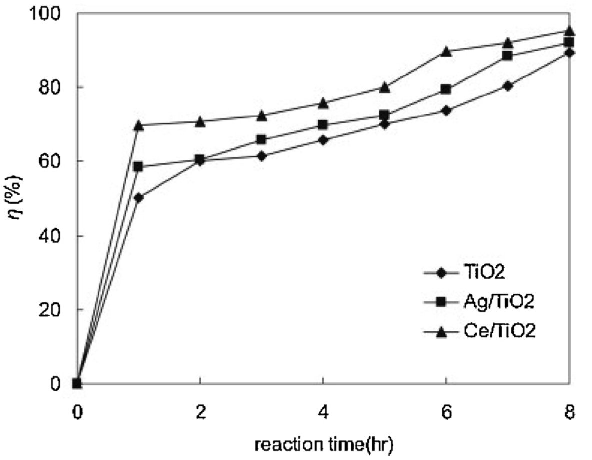


Fig. 10. Effect of dopants on HCHO degradation over TiO_2 based photocatalysts [134].

particular concern due to its corrosive nature. Ce and Mn based catalysts have been shown to be resistant to such poisoning.

2.5. Titania and ceria catalysts

Titania based catalysts have been screened to have superior efficiencies for PCO due to their physiochemical stability under high energy radiation, photochemical properties and relative non-toxicity [124,125]. Similar to other processes, anatase phase of titania is more active than the rutile phase [126] due to better charge pair generation, higher molecular oxygen affinity, higher surface hydroxyl group concentration and lower charge recombination rate. Surface characteristics such as morphology of the material has been identified to be an important factor in determining reaction rates. For example, in a study done by Tellez et al. [127], TiO_2 of anatase modification (UV100) and photocatalyst (P25) phases of titania employed as films were examined for the conversion of MEK. The former had a much better conversion when compared to the latter. Furthermore, one of the controlling factors was revealed to be surface density when keeping the surface chemistry consistent, with higher values corresponding to higher conversion. The inference was that the higher light transmission through the UV100, superior production of $OH^{\bullet}$ radicals and extended residence times from the high degree of microporosity resulted in a better performance.

Structural dimensionality of the titania is another important factor to consider. One-dimensional (1D) structures, such as rods, fibers or nanotubes (NTs), have shorter pathways during charge carrier diffusion and good light scattering properties. Two-dimensional (2D) structures, such as sheets, have better contact surfaces and adhesion rates, while three-dimensional (3D) structures such as monoliths benefit greatly from an interconnected porous framework, which results in higher charge carrier mobility.

With the advent of this technology, investigation into different materials has been initiated. The properties of titania can be modified by [128] (i) increasing charge separation to reduce charge recombination effects, (ii) increasing wavelength response range, (iii) modifying selectivity by exploring adsorption mechanisms. This can be achieved by doping with noble metals or other transition metals. By the immobilization of these materials onto specific supports, quantum efficiency of the photocatalyst can be enhanced. This imparts several useful properties on the catalyst, such as greater exposure to irradiation, good surface characteristics and high pollutant selectivity [129]. Doping with rare-earth metals such as Pd, Pt and Ag increases light absorption potential and decreases electron and hole recombination [130], which could potentially shift the required energy from a high energy spectrum like UV to low energy spectrum like the visible light spectrum. In a study done by Mogal et al. [131], various factors influencing photocatalytic properties were examined for silver doped TiO_2 catalysts. It was found that optimum doping amounts of silver effectively enhanced multiple properties of titania, such as, control of particle growth and agglomeration, surface qualities and photochemical properties. Grabowska et al. [132] incorporated noble metal nanostructures into TiO_2 microsphere composites for the total oxidation of phenol and toluene using the photodeposition method. While highly efficient decontamination was observed in the UV spectrum, significant decomposition was detected even in the visible spectrum at optimum loading percentages due to a high absorbance potential. Size selectivity and dispersion of the noble metal particles were found to be controlling factors in degradation efficiency. The doping of noble metals can also potentially influence phase behavior of the titania, maintaining the anatase phase and preventing the transition to the less active rutile phase [133].

Ceria based catalysts have frequently been used in the destruction of hydrocarbons and VOCs, and have shown to be active catalysts for that purpose [135]. Gaseous formaldehyde (HCHO) was destroyed over various modified TiO_2 films in a study done by Liang et al. [134] When comparing reaction efficiencies, it was revealed that doping with Ce and Ag increased the photocatalytic performance of base TiO_2, with the former showing superior reaction rates (Fig. 10). Ceria based catalysts showed a superior performance when compared to all other samples tested. A Ce-modified TiO_2 photocatalyst exhibited enhanced stability and efficiency for formaldehyde degradation (83%) at room temperature (Fig. 11). [136]

Synergistic effects between thermocatalytic and photocatalytic operations were investigated over ceria based titania catalysts in a comprehensive study performed by Zeng at al. [137]. The synergistic effect gave rise to enhanced benzene conversion, and is attributed to the promotion of CeO_2 reducibility due to the photocatalysis on the TiO_2 surface. Cerium doping gives rise to other interesting results. For example, Fiorenza et al. [138] studied the decomposition of 2-propanol over Au/TiO_2 and Au/TiO_2-CeO_2. Results indicated that while Au/TiO_2 showed superior conversion rates, cerium doping increased the CO_2 selectivity.

Mineral supported TiO_2 has been explored for PCO in the past [139]. Diatomite is a porous non-metal mineral with a mixture of various metal oxides. In a study done by Wang et al. [140], diatomite with immobilized TiO_2 particles was synthesized via a modified sol-gel method. It was inferred that the calcination temperature had an effect in surface hydroxyl group content, thereby effecting photocatalytic activity. In yet another study, Zhang et al. [141] prepared TiO_2/diatomite composite materials for the abatement of gaseous HCHO using the hydrolysis deposition of titanyl sulfate. While surface characteristics decreased after the composite preparation, activity rates greatly

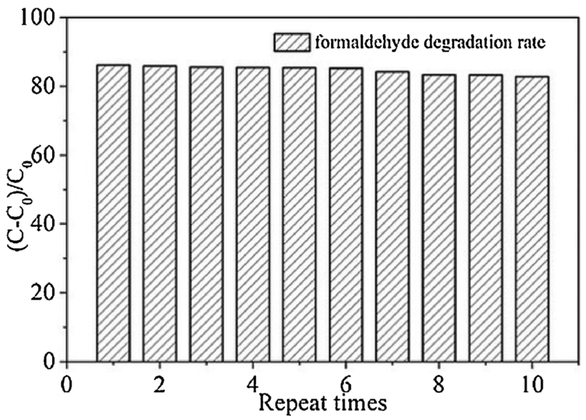


Fig. 11. Stability testing of HCHO degradation over a Ce modified TiO_2 based photocatalysts [136].

increased when compared to bare titania along with a greater reusability. Li et al. [142] prepared a novel fluorine doped TiO_2/diatomite composite material via facile sol-gel method. This shows the potential of these materials, as enhanced activity was detected with visible spectrum light. Clays are tetrahedral sheet like silicate materials with good surface qualities such as high surface area and porosity. Due to this, they have multiple interesting properties that could be utilized in catalysis of VOCs [143], albeit frequently in the liquid phase. Some common examples of expanding clays are vermiculite and smectite, while non-expanding clays are Kaolinite and Mica. Mishra et al. [144] studied the effects of different kinds of clay supports on the degradation efficiency of different VOCs. Clay texture was an important factor to consider, along its optical properties. Following this, Mishra et al. [145] doped a TiO_2/bentonite composite with noble metals and compared their efficiency for the degradation of chlorobenzene and benzaldehyde under UV light. Ag doped materials showed the best efficiency, when compared to bare and other doped samples, suggesting the enhancement of degradation of contaminants due to the doping process. Mounting of Titania on zeolitic frameworks has also been explored, with increased efficiencies resulting from much better surface qualities and unique properties, such as acid leaching properties that stabilize metal dispersion rates [146].

3. Capture materials used in VOC abatement

Hybridized capture and destruction methods have been of particular interest in recent years. Conventional catalytic reactors require high VOC concentrations in gaseous inlet streams in order to achieve optimum conversion rates, and oftentimes, VOCs exist in relatively minute concentrations that can render low destruction conversions and high energy penalties for these catalytic methods. Therefore, the incorporation of an adsorptive capture method working in tandem with a reaction destruction method allows for both the effective capture and destruction of VOCs from dilute gaseous streams at ambient conditions. Adsorptive materials, including activated carbons (Section 3.1), zeolites (Section 3.2), silicas (Section 3.3), and metal organic frameworks (MOFs) (Section 3.4) have all been investigated as potential VOC abatement adsorbents that have the capacity to be retrofitted into hybridized systems. These materials have all successfully been retrofitted into structured materials and have been tested for long-term stability and durability in industry-simulated environments. Additionally, several adsorbents have arisen as promising adsorbents for VOC abatement, namely hypercrosslinked polymer networks (HCP) (Section 3.5) and composite materials (Section 3.6). These materials are outlined in this section in order to provide a robust overview of the different solid adsorbents that have been investigated for VOC abatement.

3.1. Activated carbon

VOC abatement by means of activated carbon (AC) is currently the most widely-used commercial adsorbent due to its high adsorptive capacity, high versatility, cost efficiency, and high chemical stability. AC is a microcrystalline non-graphitic form of carbon with a high surface area and porosity that makes it ideal for gas separation processes. AC is a versatile material and has been utilized for VOC abatement in various powdered and structured forms, including beads, granules, fibers, NTs, and monoliths [42,147–149]. AC has been used in the capture and recovery of most types of hydrophobic VOCs, including acetone, cyclohexane, EA, hexane, methane, xylene, and toluene [150,151]. This versatility in VOC capture is due primarily to its surface area (commercial AC Brunauer–Emmett–Teller (BET) surface areas reported between 900 - 1300 m^2/g) and pore volumes (commercial AC reported values between 0.40 – 0.70 cm^3/g) [152]. However, adsorption capacities can vary between commercial ACs depending upon these characteristics. Das et al. [153] compared the effect of surface area on the adsorption of toluene and found that breakthrough times were four times longer in commercial AC with a surface area of 1700 m^2/g compared that with a surface area of 1000 m^2/g. Another study compared the adsorption capacities of acetone, hexane, and TCE, and found increased capacities at larger surface areas [154]. With respect to the influence of pore volume, it has been shown that its small micropores dominate VOC adsorption. One study found that benzene adsorption capacity is enhanced at pore sizing smaller than 0.70 nm [155]. However, narrower pores can also cause diffusional resistances, resulting in slower adsorption kinetics [156]. This causes economic inefficiencies in large industrial processes when longer desorption times are required. However, fixed beds of AC have been successfully regenerated at atmospheric pressure and room temperature, increasing its economic feasibility [157].

There are, however, several drawbacks to ACs. AC is naturally a non-polar adsorbent which limits its usefulness towards hydrophilic VOCs. AC also suffers from thermal instabilities and a low spontaneous ignition set-point, eliminating its usability for high temperature applications. Moreover, ACs micropores hinder the transport of VOC molecules with large kinetic diameters. Lastly, AC is characterized by disordered pore sizing. This increases the likelihood of diffusional resistances as VOC molecules enter and leave AC crystals [42]. Progress has been made in recent years to address these drawbacks and enhance the adsorptive capacities of AC. Alternative synthesis methods have been investigated to increase the specific surface area of AC, with successes up to 3000 m^2/g. Studies have also focused on surface functionalization for the capture of hydrophobic VOCs. A recent study by Baur et al. [158] functionalized AC fibers with amine for formaldehyde removal at low concentrations. Chemical modification of ACs via acids and bases has also been investigated in order to increase the adsorption capacities of single and binary VOC mixtures, as well as increase aromatic/alcoholic VOC selectivity at low concentrations [159,160]. Additionally, alternative materials have been investigated for formulation. Traditionally, AC is synthesized from carbon-rich materials such as wood, coal, or petroleum pitch through the processes of carbonization and activation. Agricultural waste such as rice straw, cotton stalks, coconut shell, and rubber-seed shell have been investigated as ecologically sustainable alternatives [161]. Rice straw has emerged as a viable material, producing AC with a BET surface area of 997 m^2/g and pore volume 0.9 cm^3/g [162].

3.2. Zeolite-based adsorbents

Zeolites are another established sorbent for the removal/recovery of VOCs. Zeolites are crystalline aluminosilicates that exhibit high thermal and chemical stabilities, and are characterized by well-defined pore structures and unique surface chemistries that make them well-suited for a large number of gas separation applications. Though not as widely used commercially as ACs, molecular sieve 13X (MS13X) zeolite, and dealuminated Y-zeolite (DAY) have been extensively studied for the removal of alcohols, aromatics, and aldehydes from exhaust streams. Zeolites have the ability to abate both hydrophobic and hydrophilic VOCs, depending on the zeolite type chosen for capture, and, similar to ACs, the largest adsorption capacities are found amongst zeolites with large surface areas and pore volumes [163]. MS13X is a hydrophilic adsorber, and has been utilized for the recovery of aromatic and aldehyde compounds at low concentrations [164]. At 25 °C, adsorption of toluene and MEK was found to have uptakes of 3.7 and 10.8 mmol/g, respectively [165]. MS13X has also been studied for volatile alcohol abatement. In order to highlight the importance of both VOC concentration and gas stream flow rates on adsorption, dynamic adsorption studies of ethanol, methanol, and iso-propanol have been performed, exhibiting uptakes between 2.95–3.18 mmol/g at concentrations ranging 2800 – 7300 ppm [166]. However, the impact of water moisture on gas adsorption for MS13X is a critical factor which must be addressed, especially for the purposes of indoor air control. In humid environments, water vapor has been shown to occupy actives sites, decreasing the uptake of both hydrophobic and hydrophilic VOCs [167]. Studies have further revealed that the for adsorption of toluene, water vapor will replace preadsorbed toluene in a phenomena known as "roll over" [164]. MS13X also requires high regeneration temperatures (> 400 °C) in order to ensure complete water removal. These are important considerations for indoor air capture, as ambient air generally contains high concentrations of water [163].

DAY-zeolite has been studied for the abatement of VOCs. DAY is a hydrophobic zeolite, and has been investigated for the removal of acetone, toluene, and xylene. DAY-zeolites have BET surface areas recorded between 500 - 900 m^2/g and pore volumes between 0.28 – 0.40 cm^3/g [168,169]. In dry conditions at 25 °C, it exhibits adsorption capacities for toluene and MEK of 11.6 mmol/g and 10.5 mmol/g, respectively [165]. Comparing the results of toluene and MEK for MS13X and DAY, it's clear that hydrophobic zeolites achieve much higher adsorption capacities for non-polar VOCs. In situations where it is desirable to capture a variety of VOCs, DAY-zeolites will serve as a more robust adsorbent [168]. While DAY-zeolite is considered hydrophobic due to its high Si/Al ratio, it still exhibits water uptake when exposed to ambient air conditions (characterized by water concentrations > 5000 ppm). In a recent publication by Nigar et al. [170] competitive adsorption was displayed in binary mixtures containing water and *n*-hexane. Upon saturation with water, DAY shows a 12.6 wt. % water uptake. Though not as extreme as the MS13X water uptake (30 wt. % [171]), it can still affect adsorption properties and result in diminished adsorptive capacities. In a recent study by Kang et al. [172], FAU and MFI zeolites were compared for the adsorptive removal of DCM vapor. They found ZSM-5 exhibits both superior adsorptive working capacities and desorption kinetics (Fig. 12) over NaX and NaY zeolite and was not affected by water vapor due to both a low Al content and evenly dispersed active sites.

3.3. Amine-modified mesoporous silica

The utilization of ordered mesoporous silica eliminates the limitations placed on zeolites and ACs for the capture of large VOC molecules. Mesoporous silicas are characterized by large pore volumes, high surface areas, a narrow distribution of pore sizing, and open pore structures which makes them ideal for gas separation processes [173,174]. In particular, Santa Barbara Amorphous-15 (SBA-15) and mobile composition of matter No. 48 (MCM-48) are two types of silica which have been studied for the abatement of VOCs due to a unique pore system. Known as a "bimodal pore system," complementary micropores in the silica walls connect to the mesopores, giving the silica both microporous and mesoporous characteristics. This makes the materials ideal for both the capture and diffusion of a wide variety of VOCs [175,176]. SBA-15 consists of two-dimensional hexagonal arrays of uniform cylindrical mesopores and MCM-48 consists of three-dimensional bicontinueous cubic arrangements of mesopores. However, silica possess silanols (Si – OH) on its wall surface. These silanols decrease both the hydrophobicity of the material and its adsorption capacities for non-polar VOCs in the presence of water [177,178]. In order to overcome this, the surface chemistry of silica can be tailored through the organic functionalization of amines [179]. Bare silica has been studied for its capture capacities towards commonly encountered VOCs, including toluene and hexane. Amine-functionalized silica, however, has been focused on the capture and recovery of formaldehyde.

Pre-functionalized bare SBA-15 has been investigated for the adsorption of hexane and toluene. SBA-15 with a BET surface area of 685 m^2/g and a total pore volume of 0.75 cm^3/g, yielded adsorption uptakes of 7.58 mmol/g and 6.40 mmol/g of hexane and toluene, respectively [180]. The higher capacity for hexane illustrates the influence of the silanol surface groups [181,182]. MCM-48 has been studied for a much wider range of commonly encountered VOCs. Unlike most of the adsorbents discussed up to this point, MCM-48 has defined hydrophilic properties which make it suitable for the capture of polar VOCs [183]. MCM-48 is characterized by larger BET surface areas and pore volumes than SBA-15 (1100 m^2/g and 1.08 cm^2/g, respectively), and has been studied particularly for the abatement of VOCs at low partial pressures [184]. Due to the influence of the silanol groups, significant uptakes of methanol, and acetone are observed for MCM-48 at low partial pressures [183–186]. The adsorption capacities of various VOCs at 30 °C are shown in Table 3.

Amine-impregnated silica (aminosilica) is a relatively new technology that has been investigated for its promising effects on formaldehyde abatement for the purpose of indoor capture [158,187–189]. The amine is impregnated onto the surface and into the channels of the silica where it reacts covalently with formaldehyde. Generally, SBA-15 serves as the silica support for amine functionalization [189]. Amines can be loaded onto the silica at different weight amounts in order to optimize maximum adsorption capacity and selectivity for a particular VOC [190–192]. At low amine loadings, optimal adsorption capacities may not be reached, while high loadings may block pore entrances and result in decreased surface area and adsorption. Therefore, finding the optimal amine to silica ratio is the current research focus. Many different types of polymeric amines have been tested, including linear poly(ethyleneamine) (PEI), poly(allylamine) (PAA), branched poly(ethyleneamine) (PEIBR), and tetraethylenepentamine (TEPA) [187,189]. Investigations at low vapor concentrations of formaldehyde (100–200 ppm) have revealed promising results. Bare SBA-15 has no affinity for formaldehyde, however, when loaded with 48 wt. % PEIBR, it yields a capacity of 4.3 mmol/g. Similarly, SBA-15 loaded with 35 wt. % PEILI yields a 3.1 mmol/g capacity [189]. While these results are promising, more detailed analyses must be performed on these materials in order to determine regenerative capacities and chemical and thermal stabilities. Many

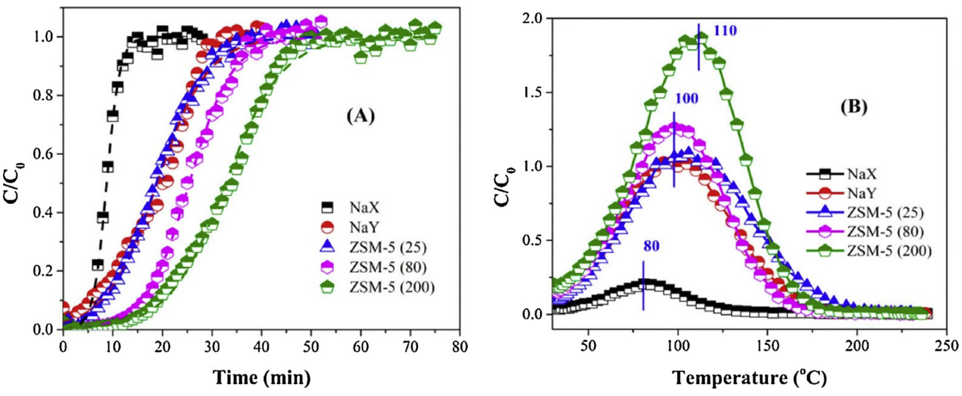


Fig. 12. (A) Breakthrough and (B) desorption curves of DCM for FAU and MFI zeolites. Reprinted with permission from *J.* Chem. Eng. Data 2018, 63, 6, 2211-2218. Copyright 2018 American Chemical Society.

Table 3
Equilibrium Data of VOCs over MCM-48 at 30 °C [184].

VOC	Pressure (kPa)	Amount Adsorbed (mmol/g)
Benzene	1.103	1.853
Toluene	1.110	7.243
Hexane	0.991	0.497
Cyclohexane	1.311	0.468
Methanol	1.012	2.355
Acetone	1.280	2.434

amines decompose at moderate temperature ranges (90 °C–120 °C), which may eliminate the use of temperature swing adsorption for regeneration. Amines are also prone to leeching, which would affect the shelf-life and durability of aminosilicas [193,194]. Therefore, further research is required for these promising sorbents.

3.4. Metal-Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) represent a departure from the traditional solid-state adsorbents outlined above (AC, zeolites, silicas) into more advanced materials. MOFs are three-dimensional hybrid materials that consist of metal ions coordinated to organic ligands through strong covalent bonds. MOFs exhibit large surface areas and open crystalline structures, and, unlike traditional adsorbents, MOF surface chemical functionalities can be tailored to meet a wide variety of different gas separation demands, including the gas separation of low concentration VOCs [195]. Over the past several years, two promising MOFs have emerged for this purpose: Material Institut Laviosier (MIL-101) and Hong Kong University of Science and Technology (HKUST). Both MIL-101 and KHUST exhibit exceptional thermal and chemical stabilities and have been successfully modified into structured adsorbents. This increases their versatility for incorporation into a wide range of industrial, commercial, and even domestic applications. MIL-101 is a Cr/Fe-based MOF linked with terephthalate groups. MIL-101 has both large surface areas (BET surface areas greater than 3000 m^2/g) and cell pore volumes (total pore volumes of 1.75 cm^3/g and greater), making it favorable for VOC adsorption. It also has a higher synthesis yield compared to other comparable MOFs and excellent desorption kinetics. Saturation-regeneration cycles have shown that MIL-101 has a VOC desorption efficiency of over 97% [196]. Upon comparison to SBA-15 and other silicates, MIL-101 displays higher capacities towards commonly encountered VOCs at low pressures [197,198]. MIL-101 has only recently been tested for the removal of aromatic and halogenated VOCs, including xylenes, benzene, EA, and DCE, referenced in Table 4 [196,197,199,200], and has shown superior adsorptive capacities for these VOCs at low concentrations.

MIL-101 exhibits preferential selectivity towards polar sorbents. This is the result of favorable interactions between polar molecules and the MIL-101 framework [202]. Most of the adsorbents outlined thus far have preferential capacities for non-polar VOCs, making MIL-101 an attractive option for the capture of hydrophilic VOCs. Regardless of its preference for polar sorbents, at similar temperature and pressure conditions, the adsorption of benzene (a non-polar molecule) on MIL-101 were still much higher than those for silicas SBA-15 and Silica-1 as well as zeolite ZSM-5 [196]. Recent studies have investigated the adsorption capacities of VOC capture in packed beds of MIL-101 in humid environments. What has been found is that water vapor competitively adsorbs to MIL-101 actives sites, decreasing active sites available to VOC capture [196]. Therefore, the effect of water vapor must be properly accounted for the purposes of VOC abatement for both wet flue gas streams and indoor air conditions. Overall, MIL-101 is a superior adsorbent for the capture of both polar and non-polar VOCs.

Table 4
Equilibrium adsorption of Various VOCs over MIL-101.

VOC	S_{BET} (m^2/g)	Temperature (K)	Pressure (kPa)	Amount Adsorbed (mmol/g)	Ref.
Acetone	3,980	298	55.0	22.3	[198]
Benzene	3,054	298	0.55	15.0	[201]
Benzene	3,360	308	0.08	5.5	[196]
EA	3,360	308	0.08	3.3	[196]
DCE	3,360	308	0.08	9.7	[196]
p-xylene	3,054	298	0.06	9.5	[199]
Toluene	3,980	298	55.0	14.0	[198]

Another promising MOF that has exhibited exceptional adsorption capacities towards VOCs is HKUST-1 (also called Cu-BTC). HKUST-1 is a Cu-based MOF and well known for a uniform micropore sizing and good hydrothermal stability. Its cages are slightly smaller than those of MIL-101, which gives it a stronger adsorption affinity towards VOCs with smaller kinetic diameters [203–205]. HKUST-1 was first investigated for the capture and storage of acetylene, where it exhibited an uptake of 8.97 mmol/g at 25 °C and 1 atm (Fig. 13a), and exhibited a superior heats of adsorption compared to the other MOFs investigated (Fig. 13**b**) [206]. From this, the study of HKUST-1 has expanded to include studies of benzene and water vapor. At 25 °C and at relative pressures up to 0.16, HKUST-1 exhibits a benzene uptake of almost 10 mmol/g [207]. This study has HKUST-1 as a promising candidate for benzene capture at low concentrations. However, similar to MIL-101, in binary trials of benzene and water vapor, competitive adsorption has been observed, resulting in reduced benzene adsorption [207]. Overall, MIL-101 and HKUST-1 are promising adsorbents for VOC capture. However, they must be further examined in order to determine their economic feasibility. MOFs are currently very costly to make and require detailed and complicated synthesis methods which, if synthesized incorrectly, result in diminished porosity and render them impractical to use in large industrial scales.

3.5. Hypercosslinked polymer networks (HCP)

Hypercrosslinked polymer networks (HCP) are a class of porous organic polymers (POPs). They are microporous adsorbents that are comprised of an entirely rigid porous polymer framework [208,209]. HCPs are produced by further crosslinking polymers in a particular solvent and represent a class of materials that exhibit high surface areas (between 600 – 2200 m^2/g), large pore volumes, and are easier to synthesize than MOFs. Historically, HCPs have been studied for the purposes of water treatment, however, research within the last 10 years has turned its focus on the removal of VOCs from gas streams [210]. HCP adsorbents with a poly (styrenedivinylbenzene) matrix (HY-1) and polymeric resin (NDA-201) are two promising HCP adsorbents for the abatement of benzene, MEK, and chlorinated VOCs [211,212]. In a study by Long et al. [211], HY-1 was investigated against AC for its adsorption capacities to benzene and MEK. As shown in Table 5, at 30 °C and 9 kPa, HY-1 shows superior capacities to AC for both VOCs. Additionally, when exposed to increased temperatures, reduced adsorption capacities were more pronounced in HY-1 than AC. This emphasizes the that, along with superior adsorption capacities, HY-1 is more efficient to regenerate in a temperature swing process compared to AC [211].

NDA-201 is another type of HCP that has been studied for the abatement of chlorinated VOCs. NDA-201 is a hydrophilic adsorbent, which makes it ideal for capturing polar chlorinated VOCs. In a second study by Long et al, the adsorption capacities of TCE, tetracloromethane (TCM), and DCE are investigated at 30 °C and low partial pressures, shown in Table 5. Three favorable adsorption isotherms were exhibited for these VOCs [212]. Further research is required for HY-1 and NDA-201 in order to ascertain both thermal and chemical stabilities and large-scale deployment feasibility.

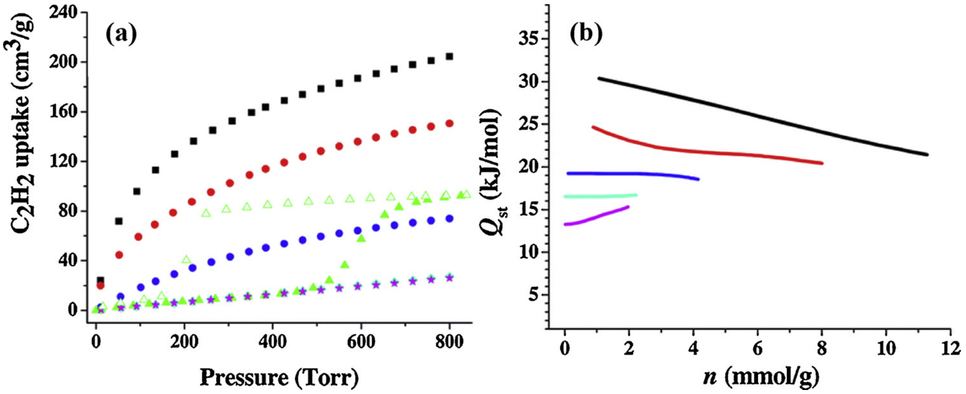


Fig. 13. (a) Acetylene adsorption isotherms of microporous MOFs at 22 °C and (b) heat of adsorption of acetylene for several MOF types (black represents HKUST-1 in both figures). Reprinted with permission from [206]. Copyright 2009 American Chemical Society.

Table 5
Equilibrium adsorption of various VOCs over HCPs and AC at 30 °C.

Adsorbent	VOC	S_{BET} (m^2/g)	Pressure (kPa)	Amount Adsorbed (mmol/g)	Ref.
HY-1	Benzene	1,244.2	9	6.40	[211]
	MEK	1,244.2	9	6.24	[211]
AC	Benzene	1,015.2	9	4.48	[211]
	MEK	1,015.2	9	4.16	[211]
NDA-201	TCE	855.6	8	6.85	[212]
	TCM	855.6	22	8.38	[212]
	DCE	855.6	9	8.16	[212]

3.6. Composite materials

In recent years, composite materials have risen as an attractive adsorbent alternative to VOC capture. Composite materials combine two different solid-state adsorbents for the purposes of enhancing adsorptive capacities. Composite adsorbents are synthesized by either pretreatment or post-treatment methods, and effective composite materials will maintain the physical, thermal, and chemical characteristics of both adsorbents but will have VOC adsorption capacities and selectivities greater than the those of the parent components, and should also have surface areas and pore volumes greater than the individual components. To date, a wide variety of composite materials have been researched for the purposes of VOC capture for both hydrophobic and hydrophilic VOCs. One of the most researched composite types are carbon derivatives. Carbon-silica composites (CSC) have been researched as good candidates for VOC adsorption due to high surface areas and pore volumes. With these composite materials types, carbon becomes embedded into the mesopores of the silica reducing the pore size and shortening the path of diffusion, both of which have been attributed to VOC adsorption. The pore sizing can be controlled by the amount of AC loaded. This allows for the direct tuning of pore size, and subsequently for the tuning of specific VOCs. In a study by Janus et al. [213], MEK adsorption was tested for CSCs and was found to be higher than that of the parent silica material. In another study by Dou et al. [214], the adsorption of benzene was tested over CSC. At 25 °C, the adsorption capacity of the CSC was greater than that of the AC alone (5.06 mmol/g to 4.37 mmol/g, respectively). CSCs also have been thoroughly characterized and along with superior adsorption capacities, they also have higher ignition temperatures than AC, making them a more appropriate adsorbent to use in industrial processes [215]. MOF-carbon composites are a novel branch of adsorbents that have been researched for the abatement of hexane and acetone. In a recent study, MIL-101 and graphene (CrO@MIL-101) composites were successfully synthesized and tested for acetone removal. GrO@MIL-101 was found to have both a BET surface area and pore volume greater than the bare MIL-101 (2928 m^2/g and 1.43 cm^3/g to 2651 m^2/g and 1.29 cm^3/g, respectively) and exhibited an acetone uptake of over 44% more than the bare MIL-101 at 15 °C [216,217]. In another study, CrO@MIL-101 was synthesized with different amounts of graphite (between 2–15 wt. %) and tested for hexane adsorption. The GrO@MIL-101 with a 5 wt.% loading had a superior BET surface area and pore volume (3502.2 m^2/g and 1.75 cm^3/g) and had a hexane uptake twice that of the bare MIL-101 at 25 °C [216]. Lastly, in a novel study by Saini and Pires, MOF-199 was loaded into zeolite ZSM-5 for the adsorption of the common indoor VOCs: benzene, hexane, and cyclohexane. The composite yielded a higher BET surface area than the ZSM-5 parent (957 m^2/g to 363 m^2/g, respectively) and enhanced the adsorption capacity of the ZSM-5 by 150%, 283%, and 468% for hexane, benzene, and cyclohexane, respectively. This is the first study where a MOF-zeolite composite was developed and investigated for VOC capture. Moreover, MOF-199 is a Cu-based MOF that is both inexpensive and easy to synthesize, making this composite material an attractive adsorbent for commercial applications [218].

4. Materials designed for hybrid processes

In recent years, many materials have been investigated for the specific purpose of utilization in hybridized capture and destruction processes. These include the study of dual or bi-functional materials and hybrid adsorbent/catalysts. Dual or bi-functional materials, which are a class of materials that share efficient removal rates in the different operations considered in the system. Bifunctional materials is also a term used for materials can that be used in the same process for different pollutants [219,220]. For example, Karthik et al. [221] studied the simultaneous catalytic abatement of VOCs and NOx compounds over Cu-Al-MCM-41, a proposed bifunctional catalyst. It was inferred that the Cu^{2+} ions in the presence of the Al sheets showed an increased NO_x selectivity and provided moderate removal rates of acetone. This material was also superior to the commonly used Cu-ZSM-5, which while showed better performance earlier on, suffered from heavy coke formation. In yet another investigation, Jin et al. [222] studied the potential of Pd/Cr_2O_3-ZrO_2 for the oxidation of DCM, a CVOC, EA and toluene respectively. It was found that the Cr containing materials showed improved conversion rates for DCM and EA when compared to the other materials tested, while the presence of Pd greatly improved toluene conversion. This shows us the importance of selecting the composition of the catalyst when considering a process.

Multiple studies have been performed on the performance of adsorptive reactor technology for the abatement of VOCs in the past. Zeolite based materials have been the focus of this concept due to their superior surface characteristics, acidic properties and high activity rates due to ordered structures [223,224]. For example, in an early investigation by Greene et al. [225], this technology was used to assess the conversion of halogenated VOCs. Cr ion exchanged ZSM-5 zeolites were used for this study, and close to 60–90 % energy savings were observed. In another study performed by Atwood et al. [226], the potential of Cr-ZSM-5 was investigated for the adsorptive reaction of TCE at 350 °C. A very high conversion of 99% was achieved which a much greater energy efficiency, when compared to a conventional packed column. Sinha et al. [227] investigated Cr based mesoporous materials using a neutral templated synthesis route for dual functionality in the elimination of toluene. High conversion rates along with strong selectivity towards the VOC indicated the potential of these materials for the use in a hybrid system. Cr based materials have also shown to have a good adsorptive performance for commonly encountered VOCs [14].

The influence of material structure is also important. For example, Wang et al. [37] demonstrated the use of Ru/hierarchical HZSM-5 zeolite as efficient bi-functional (hybrid) adsorbent/catalyst for bulky aromatic VOCs elimination under the presence of other parameters such as relative humidity. Their results proved that Ru/hierarchical HZSM-5 zeolite shows increased external surface and mesoporous volume, shortened diffusion length and enhanced low-temperature reducibility compared with Ru/conventional HZSM-5 zeolite. In addition to improved conversion rates, the former was able to establish cyclic carbon conservation without any production of secondary pollutants like NO_x. Research study by Zaitan et al. [228] employed hydrophobic synthetic zeolite, ZSM-5, as an adsorbent/catalyst bi-functional to abate toluene. Adsorbed toluene was thereafter oxidized, releasing mainly CO_2 and H_2O, indicating a total oxidation process. After four successive cycles of adsorption/oxidation, the adsorption efficiency was not affected (92% – 99%), which reveals the reusability and lifetime of this catalyst.

5. Conclusion and outlook

VOCs represent some of the most common and worrisome pollutants due to both their toxicity and their precursor role in chemical smogs. While the use of VOCs in common household implements, such as paint, is decreasing, outdoor emissions are rising to a point of concern, particularly in many urban areas. A number of abatement technologies have been investigated over the years in order to develop an overarching process that can successfully remove a variety of VOCs from gaseous streams. Capture, destruction, and hybridized capture-destruction methods have arisen as promising methods. When selecting an appropriate system, the material chosen as to serve as the adsorbent or catalyst is essential in the overarching efficacy of the system.

Noble-metal based catalysts are the most commonly used catalysts for the complete destruction of VOCs, showing high conversion rates at low temperatures. However, these catalyst types are expensive, making them largely inefficient for large-scale deployment. Transition metal oxide catalysts are a more cost-effective alternative to noble-metal catalysts and can achieve similar conversion rates. However, they exhibit higher light-off temperatures which drives up energy-demands and reduces large-scale feasibility. The surface areas, pore volumes, and hydrophobic properties of many adsorbents allow for affinities towards a myriad of VOCs. AC, DAY-zeolite, and amine-modified mesoporous silicas are well-established adsorbent materials and have demonstrated enhanced VOC capture capacities and water stability characteristics. More recently, MOFs, including MIL-101 and zeolite/MOF composite materials, have arisen as attractive adsorbents.

In recent years, many investigations have been performed to find dual-functioning materials and hybridized adsorbent/catalysts that can both be retrofitted into capture and destruction systems and used to abate a myriad of different VOC types. Many promising materials have arisen, including Cr ion exchanged ZSM-5 and Cu/hierarchical ZSM-5, both of which operate effectively as dual-functioning hybridized materials. Influenced by these recent advances, future work will focus on similar adsorbent/metal ion composite materials that utilize the adsorbent as the support bed where noble or transitional metal ions can be doped on the surface in order to enhance catalytic properties and lower material costs. The use of zeolites, ACs, and mesoporous silicas as supports are durable and inexpensive adsorbents that can be customized to fit a variety of VOC abatement needs. Future work will also focus on the use of MOFs, particularly MIL-101(Cr), as support beds for catalyst doping due to exceptional surface areas and the high potential for surface characteristic tenability, which allows for effective functionalization with a number of sulfates and metal ions in order to increase catalytic activity. Additionally, future work will also focus on the development of bifunctional materials that can accommodate the in-tandem capture and destruction of VOCs and SO_x/NO_x from automotive and industrial exhaust streams. Materials such as Cu-Al-MCM-41 have already proven to be effective in the abatement of acetone and NO_x compounds. These composite materials are highly advantageous for the abatement of rising VOC emissions in cities, and have the potential to be expanded upon in order to mitigate a number of different VOC types in conjunction with many other hazardous pollutants.

We have summarized recent progresses made in the development of adsorbents and catalysts for the capture and destruction of VOCs. The past several years have witnessed a breakthrough in the development of advanced materials for such applications, and in light of recent material advancements, we have proposed future directions based on the incorporation of adsorption and reaction in order to improve the overall feasibility and cost-efficacy of these materials. In conclusion, the abatement of VOCs is a complex matter that involves the consideration of many different parameters that can vary significantly depending on the particular VOC or VOC class it is desired to abate. Although great progress has been made on the abatement of these volatile compounds, the effective incorporation of these materials into industrial processes requires further investigations.

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