

Review on the Application of Porous Minerals in the Removal of Volatile Organic Compounds: as Adsorbent or Catalyst Carrier

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## Abstract

Due to their damage to environment and human health, the removal of volatile organic compounds (VOCs) is of great significance. A large number of processes have been developed for VOCs removal such as adsorption, photocatalysis, catalytic combustion and so on. Among which, porous materials play an important role as adsorbent or catalyst carrier. Natural porous minerals, e. g. montmorillonite and diatomite, have commonly different pore structures and considerable specific surface areas. Compared with other porous materials, the cost of porous minerals with abundant reserves is lower. According to the literatures, many porous minerals have been used directly or indirectly for the removal of VOCs and showed perfect performance. On the one hand, porous minerals are used as adsorbent of VOCs. On the other hand, porous minerals play a role of carrier of noble or non-noble metal catalyst. In this review, we would systematically arrange the research productions in recent years, analyze the role of porous minerals in the removal of VOCs, and then provide reference for future research.

**Keywords:** Porous minerals; Volatile organic compounds; Adsorption; Catalyst; Carrier.

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## 1. Introduction

Volatile Organic Compounds (VOCs) have serious damage to environment and human health [1-2]. To remove VOCs from atmospheric environment, a series of processes have been developed in recent years. On the one hand, some processes aim to separate VOCs from gas bulk, for example, adsorption, absorption and membrane separation [3-4]. On the other hand, numerous methods have been used for the conversion of VOCs, such as photocatalysis, catalytic combustion and plasma technology [5-9]. For the processes of catalysis and adsorption, the carrier of catalyst or sorbent plays an important role on the removal efficiency of VOCs. Hence, the selection of carrier or sorbent is one of the links that could not be ignored. Generally, porous materials which possess large specific surface area, abundant pores and good stability are benefit to the catalysis and adsorption process of VOCs. Besides, considering economic factors, the cost of porous materials should be as low as possible. Therefore, the natural porous minerals become one of the excellent options of carrier of catalyst and sorbent for VOCs removal.

Natural porous materials have commonly well-developed pore structures and considerable specific surface areas, which allow them become excellent candidates for different requirement [10-11]. Common natural materials conclude montmorillonite, diatomite, bentonite, kaolin, palygorskite and so on, with different pore structures and properties. Therefore, natural porous materials have been used widely as catalyst carrier and adsorbent for many fields such as environment and chemistry [12-15]. Herein, we would systematically arrange the research productions in recent years, analyze the role of different porous minerals in the removal of VOCs.

## 2. The application of natural porous materials in the removal of VOCs

### 2.1. Montmorillonite

Consisting of hydrous aluminosilicate, montmorillonite is a layered clay mineral with two silicon oxygen tetrahedron sheets sandwiching an aluminum oxygen octahedron sheet. The  $\text{Al}^{3+}$  could be replaced by other cations such as  $\text{Mg}^{2+}$ , which allow water molecular and other cations existing in the interlayer space. As a result, montmorillonite possesses an excellent adsorption capacity for water and other compounds. What's more, the high stability and unique structure of montmorillonite make it an excellent candidate as catalyst carrier.

Morrissey *et al.* [16] investigated the adsorption/desorption performance of VOCs (acetone, benzene and toluene) on three clay minerals (kaolinite, illite and montmorillonite). The sorption experiment was conducted by passing  $\text{N}_2$  flow with a certain concentration of VOCs through oven-dried clay minerals at room temperature. Among the three absorbent, montmorillonite possessed the largest specific surface area ( $800 \text{ m}^2/\text{g}$ ) and showed the highest adsorption capacity for three VOCs:  $0.110 \text{ g/g}$  for acetone,  $0.150 \text{ g/g}$  for benzene and  $0.100 \text{ g/g}$  for toluene, respectively.

To study the adsorption mechanism, Shih *et al.* [17] characterized the adsorption capacity montmorillonite for a series of VOCs at different levels of relative humidity. It was found that the equilibrium adsorption capacity of 22 VOCs on montmorillonite decreased sharply with the increase of relative humidity. Besides, the linear solvation energy relationship (LSER) was used to analyse the adsorption behavior. The result showed that the dispersion interaction dominates the interaction of montmorillonite and VOCs molecular at a low relative humidity, whereas, the dispersion interaction is replaced by hydrogen-bond interaction as the relative humidity increasing. Later, the HDTMA (hexadecyltrimethyl ammonium) modified organomontmorillonite was synthesized by cation exchange reaction [18-19]. The adsorption capacity of organomontmorillonite for VOCs decreased due to the smaller specific surface area. The LSER analysis showed that the dominate interaction is dispersion interactions for organomontmorillonite at all tested relative humidity.

Georgiy Morozov and coworkers [20] investigated the sorption behavior of three VOCs, n-hexane, benzene and methanol, on a K-10 montmorillonite at different humidity using a static adsorption experiment. They found that the adsorption capacity of n-hexane and benzene decreased with the sharp increase of residual water content of montmorillonite. By contrast, the adsorption capacity of methanol increased obviously as the humidity increasing, due to the dissolution of hydrophilic methanol on the adsorbed water films as well as the hydration of cations and the surface of montmorillonite. Besides, because of the same adsorption sites, the adsorption of three VOCs was competitive. The binary adsorption experiment showed that the adsorption of benzene was priority to n-hexane, and methanol was priority to benzene.

The adsorption performance of calcium-based montmorillonite ( $\text{Ca}^{2+}$ -Mt) and sodium-based montmorillonite ( $\text{Na}^+$ -Mt) for benzene was investigated by Deng *et al.* [21]. The  $\text{Na}^+$ -Mt was prepared by ion exchange reaction of  $\text{Ca}^{2+}$ -Mt. It was found that the  $\text{Ca}^{2+}$ -Mt treated at  $120^\circ\text{C}$  showed the highest benzene adsorption capacity ( $141.2 \text{ mg/g}$ ). The authors attributed the phenomenon to the large interlayer space which could accommodate benzene molecular. After calcination at  $600^\circ\text{C}$ , the adsorption capacity of both  $\text{Ca}^{2+}$ -Mt and  $\text{Na}^+$ -Mt decreased to nearly  $70 \text{ mg/g}$  due to the collapse of interlayer space. Besides, DRIFT results proved that the adsorption of benzene on montmorillonite was physical adsorption.

To make full use of montmorillonite and further improve the adsorption performance for VOCs, Liu and co-workers [22] synthesized an Al-pillared Montmorillonite@Carbon composite named Al-Mt@C through hydrothermal carbonization reaction. The characterization results showed that the composite possessed a relatively large specific area and good thermal stability. According to the dynamic adsorption experiment, the composite Al-Mt@C with an Al-pillared Montmorillonite to carbon precursor glucose mass ratio of 3/5 showed the best toluene adsorption performance ( $39.9 \text{ mg/g}$ ). Furthermore, the absorbent could be regenerated well for at least 4 times by treated at  $150^\circ\text{C}$  for 0.5 h.

Variety of catalysts have been used for VOC removal, and the carrier plays an important role among the factors which impact the catalytic performance. Some work has used montmorillonite as catalyst carrier.

Noble metals show excellent catalytic performance for VOCs oxidation. Zuo *et al.* [23-24] used Al-pillared calcium montmorillonite and rare earths/Al-pillared calcium montmorillonite as carrier of palladium catalysts for catalytic combustion of benzene. The composite catalyst was prepared by an impregnation method. It was found that the introduction of Al increased the specific surface area, porosity as well as basal spacing. As a result, the catalytic performance for deep oxidation of benzene was improved obviously. For catalyst of Ce/Al-pillared montmorillonite with palladium, the optimum temperature for catalytic oxidation was 280°C-290°C. Later, the team [25] investigated the catalytic performance of Pd-containing catalyst supported on Al/Al-Ce pillared Na-montmorillonite for the deep oxidation three VOCs, acetone, benzene and ethylbenzene. The pillared treatment could improve the specific surface area and pore volume of catalyst, and then the dispersion of Pd on catalyst was enhanced. As a result, the catalytic oxidation performance was improved with the enhancement of adsorption capacity of catalyst for VOCs which attribute to the above changes. In the presence of Pd/AlCe pillared Na-montmorillonite, the acetone and benzene could be oxidized completely at about 240°C, and ethylbenzene at about 180°C.

Except of noble metal, montmorillonite could be used as carrier of oxide of transition metals. Mishra's team [26] synthesized a series of Fe and Mn mixed oxide pillared Na-exchanged-montmorillonite for the catalytic decomposition of acetone and trichloroethylene. The specific surface area of catalyst increased as the metal oxide was introduction. For acetone, the catalyst with a manganese to iron molar ratio of 16/4 showed the best catalytic performance, and the acetone decomposed to CO<sub>2</sub> completely at 200°C under a concentration of 500-550 ppm. The long term experiment showed that the catalyst could be used for at least 20 h with a slight decrease of decomposition rate. On the other hand, nearly 100% trichloroethylene decomposed in the existence of the catalyst with a manganese to iron molar ratio of 8/12 at about 340°C under a concentration of 300-350 ppm. However, the catalytic performance decreased obviously in the next hours, accompanied by the decrease of specific surface area which may resulted from the formation of HCl. Li and coworkers [27] prepared Fe and Al pillared Na-montmorillonite for the deep catalytic oxidation of toluene and chlorobenzene. It was found that the pillared treatment could improve the surface area and pore volume of catalyst obviously. The catalytic activity decreased in the order: Fe pillared Na-montmorillonite > Al pillared Na-montmorillonite > initial Na-montmorillonite. The catalytic performance of Fe pillared Na-montmorillonite improved with the increase of the content of Fe in the catalyst. Under the optimal condition, the temperature of complete oxidation of toluene was 350-400°C, and chlorobenzene could be oxidized completely at about 500°C. Besides, according to the life test, the Fe pillared Na-montmorillonite could run at 400°C for at least 96 h without obvious decrease of catalytic activity.

Motak *et al.* [28] studied the influence of NO on the catalytic oxidation of ethanol. Two kind of montmorillonites were used as carrier of Ag and Cu. They found that the acid treatment was beneficial to the catalytic reaction. The source of montmorillonites played a decisive role on the catalytic performance. The catalytic activity of the montmorillonite from *Milowice* with Cu and Ag reached above 90% at 400°C, and NO showed no obvious effect on its catalytic activity. Xue and coworkers [29] synthesized an yttrium-zirconium-pillared montmorillonite supported Ce catalyst for the catalytic oxidation of acetone, toluene and ethyl acetate. It was found that the new catalyst of 8.0% Ce showed a satisfactory performance for the deep oxidation of VOCs. The acetone, toluene and ethyl acetate could be oxidized completely at about 220, 300 and 220°C, respectively, which was attributed to the better dispersion of Ce on the support.

Non thermal plasma has been applied for VOCs removal due to its high efficiency. Gholipour *et al.* [30] used alkali activated montmorillonite as carrier of NiMn for hybrid plasma-catalytic oxidation of VOCs. Under the condition of 20 kV, 9.8 kHz, the presence of catalyst with a Mn content of 6 wt% improved the conversion rate of benzene from 73% to 92% with an initial

concentration of 1000 ppm. For the mixture of three VOCs, the conversion rates of toluene and xylene were higher than that of benzene under the same condition. The current applicable studies of montmorillonite on VOCs removal are summarized in Table 1.

Table 1. The current applicable studies of montmorillonite on VOCs removal

The role of montmorillonite	Source	Finished product	VOCs	Highest removal performance	Reference
adsorbent	Apache County, Ward's Scientific	untreated	acetone, benzene and toluene	0.110 g/g for acetone, 0.150 g/g for benzene and 0.100 g/g for toluene, respectively	[16]
adsorbent	Clay Minerals Society Source Clays Repository (MO, USA)	untreated	22 common VOCs	-	[17]
adsorbent	The same as above	Organomontmorillonite, modified by HDTMA	The same as above	-	[18, 19]
adsorbent	K-10 montmorillonite from Aldrich		n-hexane, benzene and methanol	380 $\mu$ L/g for methanol; 179 $\mu$ L/g for benzene; 185 $\mu$ L/g for n-hexane at $P/P_0 = 0.4$	[20]
adsorbent	Inner Mongolia province of China	calcium-based montmorillonite ( $Ca^{2+}$ -Mt) and sodium-based montmorillonite ( $Na^+$ -Mt)	benzene	141.2 mg/g for $Ca^{2+}$ -Mt	[21]
adsorbent	Inner Mongolia, China	Al-pillared Montmorillonite@Carbon	toluene	39.9 mg/g	[22]
catalyst	Neimenggu, China	Ce/Al-pillared montmorillonite supported palladium	benzene	the optimum temperature for catalytic oxidation: 280°C-290°C	[23, 24]
catalyst	Mainburg area, Germany	Fe and Mn mixed oxide pillared Na-exchanged-montmorillonite	Acetone and trichloroethylene	For acetone, decomposed completely at 200°C; for trichloroethylene, at about 340°C	[26]
catalyst	-	Al/Al-Ce pillared Na-montmorillonite supported Pd	acetone, benzene and ethylbenzene	For acetone and benzene, be oxidized completely at about 240°C; for ethylbenzene, at about 180°C	[25]
catalyst	Kunimine Industries Co. Ltd.	Fe and Al pillared Na-montmorillonite	toluene and chlorobenzene	For toluene, be oxidized completely at 350-400°C; for chlorobenzene, at about 500°C.	[27]
catalyst	Milowice	modified montmorillonite supported Ag or Cu	ethanol	above 90% at 400°C	[28]
catalyst	Mongolia (China)	yttrium-zirconium-pillared montmorillonite supported Ce	acetone, toluene and ethyl acetate	For acetone, be oxidized completely at 220°C; for toluene, at 300°C; for ethyl acetate, at 220°C	[29]
hybrid plasma-catalyst		alkali activated montmorillonite supported NiMn	Toluene, xylene and benzene	For benzene, the conversion rate could reach 92% with an initial concentration of 1000 ppm	[30]

## 2.2. Bentonite

Bentonite is a kind of layered silicate clay mineral with montmorillonite as its main component. Hence, the property of bentonite is similar to montmorillonite. A number of works have used bentonite as adsorbent for VOCs removal. Zhu *et al.* [31] used LSER to analyze the adsorption mechanism of VOCs on organobentonite which modified with CTMAB (cetyltrimethylammonium bromide). The predominant interaction between VOCs and organobentonite was recognized as dispersion interaction. And then, the teams [32] used virgin and spent CTMAB-bentonite and CPC (cetyl pyridinium chloride)-bentonite used for wastewater purification to synthesize porous clay heterostructures (PCHs). It was found that the PCHs possessed

a relatively large surface area compared with the organobentonites. The PCHs showed a high adsorption capacity for benzene and  $\text{CCl}_4$ . Later, the adsorption performance of six common VOCs (acetone, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene) on PCHs was studied [33]. The PCHs was synthesized by modification of bentonite using CTMAB and DDA (dodecylamine). The result showed that the PCHs was more applicable to the adsorption of aliphatic hydrocarbon compound compared with aromatic compounds due to quantum chemistry theory. Besides, the team [34] synthesized silylated pillared bentonite using hydroxyaluminum polycation and alkylchlorosilanes gradually. The VOCs adsorption capacity of synthesized material was identified by several VOCs adsorption experiment. The VOCs adsorption capacity of silylated pillared bentonite showed no obvious improvement.

Zaitan *et al.* [35] investigated the adsorption-desorption performance of o-xylene on bentonite. The adsorption capacity of o-xylene on bentonite was about 1 mmol/g, lower compared with commercial  $\text{Al}_2\text{O}_3$  at 27°C. A relatively high regeneration performance was observed through  $\text{N}_2$  stripping. Then, the team [36] contrasted the adsorption performance of bentonite and several commercial adsorbents such as  $\text{SO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . The adsorption experiment of di-methyl benzene (dMB) was conducted in a fixed bed reactor, and the economic factor was also taken into account. The adsorption capacity of dMB on bentonite was identified as about 1 mmol/g, which was lower than  $\text{SiO}_2$  (1 mmol/g) and  $\text{Al}_2\text{O}_3$  (1 mmol/g), higher than  $\text{TiO}_2$  (0.89 mmol/g). A lower temperature was proved to be advantageous to the adsorption process and the exhausted bentonite could be regenerated using  $\text{N}_2$  stripping. Considering the low cost of bentonite, the team thought it a potential adsorbent for VOCs removal.

Three modified clays were prepared and used for benzene and toluene adsorption [37]. The VOCs adsorption capacity of organo-bentonite modified by CPC showed a superior adsorption performance compared with Al-pillared bentonite and inorganic-organic bentonite, which was attribute to the preeminent organophilic property of organo-bentonite. Amari *et al.* [38] modified bentonite using  $\text{H}_2\text{SO}_4$  and applied for the adsorption of toluene at 25-60°C. The synthesized adsorbent could remove toluene completely for hour. It was found that a low temperature is beneficial to the adsorption due to exothermic reaction. Besides, the linear driving force (LDF) model was proved to fit the experiment data excellently. Dammak and coworkers [39] synthesized organo-bentonite using didodecyltrimethylammoniumbromide (DDMA) and hexadecyltrimethylammoniumbromide (HDTMA), respectively. The synthesized organocalys was used for adsorption of O-xylene at 20, 30 and 40°C. It was found that the adsorption reaction preferred lower temperature. The adsorption capacity of O-xylene on HDTMA-bentonite could reach above 0.6 g/g. On the other hand, the bentonite was used as raw material for the synthesis of NaX zeolite. However, the adsorption capacity of synthesized zeolite is far lower than that of organo-bentonite.

Except adsorbent, bentonite is a potential catalyst carrier for the catalytic oxidation of VOCs. The pillared Al-bentonite containing Fe and Ce was prepared for catalytic oxidation of 2-propanol in gas phase [40]. The characterization proved the formation of oxide nanoparticles. The catalytic experiment showed that the 2-propanol was oxidized to  $\text{CO}_2$  with intermediary products of propene and acetone. The 2-propanol decomposed completely at 150°C catalyzed by Al-pillared bentonite with Ce or Ce and Fe. Oliveira's team [41] used Al-pillared bentonite supported by Cr/Pd for the catalytic oxidation of aromatic VOCs. They found that the introduction of Cr improved the catalytic performance of catalyst. However, the Cr-containing catalyst showed a low stability and inactivated quickly due to the formation of volatile  $\text{CrO}_2\text{Cl}_2$ , collapse of structure and carbonization. For Pd-containing catalyst, the catalytic performance is high and stable at 600°C, but the formation of a poisonous by-product, hexachlorobenzene, was observed in the oxidation process of chlorobenzene.

Cu was also used as promoter of bentonite-based catalyst for catalytic oxidation of ethanol [42]. Motak investigated the catalytic performance of several modified or no modified bentonite, e.g. acidic modification, Al-pillaring and Ag/Cu impregnation. The results showed that the introduction of CuO improved the catalytic performance and selectivity of  $\text{CO}_2$  significantly compare with other modification methods.

Colman-Lerner et al. used Pt/Mn to modify bentonite for the catalytic oxidation of ethanol and toluene [43]. The modification catalyst was prepared by the process of immersion and calcination. The introduction of Pt/Mn showed no obvious effect on the surface area of bentonite. For the oxidation of ethanol, the catalytic activity of Pt/Mn modified bentonite (Pt/Mn/B) was similar to that modified by Pt (Pt/B) alone. Ethanol was oxidized to CO<sub>2</sub> completely at nearly 300°C, and a small amount of acetaldehyde was formed at relatively low temperature. For toluene, the Pt/Mn/B showed the highest catalytic activity, and 90% of toluene could be oxidized to CO<sub>2</sub> at 324°C. Besides, the catalytic performance of catalyst for the oxidation of mixed VOCs was also investigated. It was found that the presence of ethanol promoted the oxidation of toluene, which was ascribed to a local heating effect, however, the presence of toluene made the formation of acetaldehyde shift to higher temperature.

According to Motak's work [28], Al-pillared bentonite supported Cu showed a relatively high catalytic performance for the oxidation of ethanol. About 91% of ethanol could be removed at 400°C. The effect of NO on the catalytic activity of bentonite-based catalyst was uncertain due to different modification method. Sanchis et al. [44] prepared PCH from bentonite and used as support of FeOx for the catalytic oxidation of toluene. It was found that the catalytic activity depended on the dispersing performance of FeOx on bentonite. 90% of toluene could be oxidized at 188°C in the presence of PCH catalyst with a Fe content of 15.6 wt%.

In addition of catalytic oxidation, photocatalytic oxidation is also an excellent process for the removal of VOCs. Sharmin and Ray [45] investigated the performance of ultraviolet light-emitting diode photocatalysis (UVLED) for the removal of toluene and xylene. Sodium bentonite and silica was used as carrier to prepare clay/TiO<sub>2</sub>. For clay/TiO<sub>2</sub> catalyst, the highest removal efficiency of toluene and xylene using UVLED could reach 22.5% and 23.0%, respectively.

Bentonite was used as carrier of TiO<sub>2</sub> to prepare structured hybrid material (BTi) as adsorbent-photocatalyst of formaldehyde (HCHO) [46]. The photocatalytic experiment was conducted under UV. The result showed that a calcination temperature of 300°C was beneficial to the photocatalytic reaction compared with higher temperature due to the difference of porosity, crystal size and surface area. The HCHO could be removed nearly completely at 200°C in the presence of photocatalyst. The catalytic performance of hybrid material which introduced clay was higher than commercial TiO<sub>2</sub>.

Mishra et al. [47] prepared TiO<sub>2</sub>/bentonite nano-composites using microwave treatment at 180°C for 10 min. The characterization results indicated the formation of TiO<sub>2</sub> nanoparticles on the surface of bentonite. The synthesized material possessed a higher surface area and more uniform pore distribution. For the removal of chlorobenzene, the bentonite-based nano-composite showed high UV photocatalytic activity as well as adsorption capacity. Nearly 50% of chlorobenzene could be adsorbed without UV light, and the residual was photocatalytic oxidized to CO<sub>2</sub> and H<sub>2</sub>O finally within 20 min under the UV light. Besides, the nano-composite was proved to possess excellent regeneration performance. Then, the team [48] loaded Ag on the synthesized nano-composite through wet impregnation method. They found that the introduction of Ag enhanced the photocatalytic activity for oxidation of chlorobenzene obviously. The nano-composite with an Ag content of 1.5 wt% showed the highest photocatalytic activity under both UV light with a catalytic efficiency of nearly 100% within 10 min and visible light with a catalytic efficiency of 92% within 60 min. Similarly, the Ag-nano-composite showed excellent regeneration performance for at least 5 times. The current applicable studies of bentonite on VOCs removal are summarized in Table 2.

Table 2 The current applicable studies of bentonite on VOCs removal

The role of bentonite	Source	Finished product	VOCs	Highest removal performance	Reference
adsorbent	Zhejiang Province, China	bentonite modified with CTMAB	22 VOCs	-	[31]
adsorbent	Inner Mongolia, China	PCHs from spent CTMAB/CPC-bentonite	benzene and CCl <sub>4</sub>	For benzene, above 0.7 g/g; for CCl <sub>4</sub> , above 0.8 g/g at high relative partial pressure	[32]

The role of bentonite	Source	Finished product	VOCs	Highest removal performance	Reference
adsorbent	Inner Mongolia, China	PCHs from CTMAB/DDA-bentonite	acetone, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene	About 2-5 mmol/g at 25°C	[33]
adsorbent	Inner Mongolia, China	silylated pillared bentonite	22 VOCs	-	[34]
adsorbent	North of Morocco (Nador area)	-	o-xylene	About 1 mmol/g	[35]
adsorbent	Nador province in Morocco	-	di-methyl benzene	About 1 mmol/g	[36]
adsorbent	Perfobent, Mexico City	organo-bentonite, Al-pillared bentonite and inorganic-organic bentonite	Toluene and benzene	For toluene, about 0.4 g/g; for benzene, about 0.45 g/g	[37]
adsorbent	-	bentonite modified by H <sub>2</sub> SO <sub>4</sub>	toluene	remove toluene completely for nearly 130 min	[38]
adsorbent	Jebel Sbih deposits located in the south of Tunisia from the area of Skhira	DDMA/HDTMA-bentonite	O-xylene	About 0.6 g/g	[39]
catalyst	Valle del Cauca, Colombia	Al-bentonite supported Fe and Ce	2-propanol	decomposed completely at 150°C	[40]
catalyst	San Juan, Argentina	Al-pillared bentonite supported Cr/Pd	chlorobenzene and xylene	decomposed almost at 600°C	[41]
catalyst	Riedel-de Haën	Bentonite modified by Cu	ethanol	decomposed almost at 400°C	[42]
catalyst	North Patagonia, Argentina	bentonite modified by Pt/Mn	ethanol and toluene	For ethanol, be oxidized to CO <sub>2</sub> completely at nearly 300°C; for toluene, 90% be oxidized at 324°C.	[43]
catalyst	-	Al-pillared bentonite supported Cu	ethanol	About 91% of ethanol be removed at 400°C.	[28]
catalyst	"Sierra de Níjar" in Spain	Bentonite-based PCH supported FeOx	toluene	90% of toluene could be oxidized at 188°C	[44]
photocatalyst	Sigma Aldrich	Clay supported TiO <sub>2</sub>	toluene and xylene	the highest removal efficiency of toluene and xylene using UVLED could reach 22.5% and 23.0%, respectively	[45]
photocatalyst	Tolsa	structured hybrid material	formaldehyde	The formaldehyde could be removed nearly completely at 200°C	[46]
Adsorbent and photocatalyst	Sigma-Aldrich, USA	TiO <sub>2</sub> /bentonite nano-composites	chlorobenzene	Nearly 50% of chlorobenzene could be adsorbed without UV light, and the residual was oxidized within 20 min under the UV light.	[47]
photocatalyst	Sigma-Aldrich, USA	nano-composites loaded Ag	chlorobenzene	For UV light, catalytic efficiency reached 100% within 10 min; for visible light, 92% within 60 min	[48]

## 2.3. The other minerals

### 2.3.1 Minerals as adsorbent

In 1998, Ruiz *et al.* [49] investigated the adsorption behavior of seven VOCs and water on three minerals (quartz sand, limestone and muscovite). It was found that the muscovite possessed the highest adsorption capacity ranging from 10<sup>-6</sup> to 10<sup>-3</sup> mol/g. The three adsorbents were all favor polar compounds compared with aliphatic and aromatic compounds.

In Morrissey's work [16], the adsorption performance of three VOCs on kaolinite and illite was studied. For kaolinite, the adsorption capacities of acetone, benzene and toluene were 0.003, 0.009 and 0.009 g/g, respectively. For illite, larger adsorption capacities were observed (0.030, 0.050, 0.050 g/g, respectively). Four common VOCs, 1, 1, 1-trichloroethane, trichloroethylene, methanol and propanone, were adsorbed by Al/Zr pillared smectite (microporous material) and laponite (mesoporous material) [50]. An unexpected result showed that VOCs could be adsorbed on mesoporous material well to some extent. Cheng and Reinhard [51] investigated the desorption behavior of trichloroethylene on silica sand, kaolinite and smectite, and found that the micropore volume and hydrophobicity plays an important role on the adsorption of VOCs.

A series of Moroccan clay minerals were chosen as adsorbent for the removal of VOCs [52]. The clays were consisted of many minerals such as montmorillonite and kaolinite. For *o*-xylene, the highest adsorption capacity of three powdered clays was identified as 416  $\mu\text{mol/g}$  at 27°C. Then, the team prepared honeycomb-shape monoliths from two Moroccan clay minerals for the adsorption of *o*-xylene [53]. The adsorption capacity of the prepared materials could reach above 140  $\mu\text{mol/g}$ . Nunes *et al.* [54] synthesized PCHs by modifying a natural Portuguese clay using bis(triethoxysilyl)benzene (BTEB) and tetraethyl orthosilicate (TEOS). The synthesized PCHs were identified as outstanding porous materials with large surface area as well as micropore and mesopore volume. According to the adsorption experiment of methanol, methyl ethyl ketone, toluene and trichloroethylene, the PCHs should be hydrophobic adsorbents and possessed relatively high adsorption capacities for hydrophobic VOCs.

Raw and modified Tunisia clay was used as adsorbent for the removal of VOCs [55]. The clay was modified by didodecyldimethyl ammonium bromide. It was found that the adsorption capacity of modified clay for cyclohexane, toluene and chlorobenzene could reach 2.5, 2 and 3.0 mg/g, respectively. Then, the clay was used as raw material for the preparation of Na saturated clay and organoclay modified by HDTMA [56]. The adsorption results of *o*-xylene showed that the highest adsorption capacities of Na saturated clay and organoclay were 0.476 and 8.765 mg/g, respectively, at 20°C. Furthermore, the hexadecyltrimethylammonium bromide (HDTMABr) modified clay was used for the adsorption of five VOCs, *o*-xylene, *m*-xylene, *p*-xylene, benzene, and toluene [57]. The result showed that the modified clay showed a far higher adsorption capacity compared with raw clay. Among five VOCs, the adsorption capacity of xylene was the highest, which could reach about 10 mg/g. Affouri *et al.* [58] modified Tunisia limestone material by sodium salt and calcination. They found that the modification treatment could enhanced the porosity and surface area of raw materials significantly. The highest adsorption capacity of chlorobenzene could reach 120 mg/g at 25°C.

The adsorption capacity of diatomite for dMB was identified as 420  $\mu\text{mol/g}$  in Zaitan's work [36], which was lower than that of bentonite. Besides, the team investigated the adsorption performance of Morocco natural clay for VOCs [59]. The adsorption capacities of toluene, methanol and benzaldehyde was identified as 0.89, 8 and 3.1 mmol/g, respectively at 27°C.

A series of plaster constituents and zeolites including metakaolin, clinoptilolite and natrolite were used as adsorbents for the removal of four VOCs, chlorobenzene,  $\alpha$ -pinene, 2-ethoxyethylacetate and pentanal [60]. It was found that the natural materials possessed a certain adsorption capacity for VOCs. Porous diatomite was modified by phenyltriethoxysilane (PTES) and applied for the adsorption of benzene [61]. It was found that the adsorption capacity of diatomite was enhanced obviously after modification and could reach 28.1 mg/g.

Zhu and coworkers [62] used HCl with different concentrations to treat palygorskite. The acid treatment was proved to enhance the surface area and porosity of palygorskite. The adsorption experiment showed that acid-activated palygorskite possessed excellent adsorption performance for toluene. The palygorskite treated using 5 mol/L HCl was found the strongest adsorbent for toluene with a highest adsorption capacity of 90.4 mg/g as well as the largest surface area and micropore volume.

Kaolinite was modified by polyethylenimine (PEI) and used for the adsorption of aldehydes, carboxylic acids, and organodisulfides [63]. The results showed that the VOCs removal rate of modified kaolinite could reach above 99%. Furthermore, the pilot scale adsorption experiment

of a series of volatile fatty acids on the prepared adsorbent was conducted, and the removal rates ranged at 60-99%.

Deng *et al.* [21] investigated the adsorption performance of kaolinite and halloysite for benzene. They found that heat treatment of clays at 120°C was beneficial to the adsorption reaction. The highest adsorption capacity of kaolinite and halloysite was identified as 56.7 and 68.1 mg/g, respectively. Zhang *et al.* [64] adsorbed VOCs used diatomite, stellerite and vitric tuff. They found that acid treatment could improve the surface area and total pore volume of minerals effectively. The acid treated stellerite showed the highest capacity ranging from 51.3-81.1 mg/g for different VOCs including butyl propionate, 2-heptanone, 1,2,4-trimethylbenzene and 2-butoxyethanol. Besides, higher temperature and relative humidity were not conducive to the adsorption reaction. The current applicable studies of minerals on VOCs removal as adsorbent are summarized in Table 3.

Table 3. The current applicable studies of minerals on VOCs removal as adsorbent

Mineral	Source	Finished product	VOCs	Highest removal performance	Reference
quartz sand, limestone and muscovite	-	-	n-hexane, n-heptane, n-octane, toluene, xylene, ethylbenzene and methyl ethylketone	$10^{-6}$ to $10^{-3}$ mol/g	[49]
kaolinite and illite	Ward's Scientific	-	acetone, benzene and toluene	For kaolinite, 0.003, 0.009 and 0.009 g/g, respectively. For illite, 0.030, 0.050, 0.050 g/g, respectively	[16]
clay	Morocco	Al/Zr pillared smectite and lap-onite	<i>o</i> -xylene	416 $\mu$ mol/g	[52, 53]
clay	Portuguese	BTEB/TEOS based PCHs	methanol, methyl ethyl ketone, toluene and trichloroethylene	-	[54]
clay	Tunisia	Clay modified by didodecyldimethyl ammonium bromide	cyclohexane, toluene and chlorobenzene	2.5, 2 and 3.0 mg/g, respectively	[55]
clay	Tunisia	organoclay modified by HDTMA	<i>o</i> -xylene	8.765 mg/g	[56]
clay	Tunisia	HDTMABr modified clay	<i>o</i> -xylene, <i>m</i> -xylene, <i>p</i> -xylene, benzene, and toluene	For xylene, 10 mg/g	[57]
limestone	Tunisia	limestone material modified by sodium salt and calcination	chlorobenzene	120 mg/g	[58]
diatomite	Nador province in Morocco	-	dMB	420 $\mu$ mol/g	[36]
clay	Marocco	-	toluene, methanol and benzaldehyde	0.89, 8 and 3.1 mmol/g, respectively	[59]
diatomite	Changbai deposit in Jilin province, China	diatomite modified by PTES	benzene	28.1 mg/g	[61]
palygorskite	Mingguang city, Guanshan, Anhui Province, China	Palygorskite with acid treatment	toluene	90.4 mg/g	[62]
Kaolinite	-	Kaolinite modified by PEI	aldehydes, carboxylic acids, and organodisulfides	the VOCs removal rate could reach above 99%	[63]
kaolinite and halloysite	Guangdong province of China; the Shanxi province of China, respectively	clays with heat treatment	benzene	56.7 and 68.1 mg/g, respectively	[21]

Mineral	Source	Finished product	VOCs	Highest removal performance	Reference
diatomite, stellerite and vitric tuff	Jilin Beifeng Diatomite Company, China; Guangxi Guilin Aiteli New Material Company, China; Hunan Weiji Bioengineering Company, China, respectively	acid treated clays	butyl propionate, 2-heptanone, 1,2,4-trimethylbenzene and 2-butoxyethanol	51.3-81.1 mg/g	[64]

### 2.3.2 Minerals as catalyst carrier

Except of bentonite, Motak *et al.* [42] studied the catalytic performance of modified vermiculite for the oxidation of ethanol. The Cu/Ag modified vermiculite showed the highest catalytic performance. It was found that 90% of ethanol was oxidized to CO<sub>2</sub> at about 350°C. Al-pillared smectite and delaminated smectite were chosen as the carriers of transition metal for the catalytic oxidation of ethanol [65]. According to experiment result, the delaminated smectite supported Co and Cu exhibited the highest catalytic activity, and 90% of ethanol could be oxidized to CO<sub>2</sub> at 297°C in the presence of above catalyst.

Natural zeolite, clinoptilolite was used as raw material for the synthesis of Cu/c clinoptilolite-CeO<sub>2</sub> nanocatalyst [66]. The characterization results showed that the ultrasonic treatment could enhance the dispersity and uniform of catalyst. The catalyst with a Cu content of 15% was identified as the best catalyst for the oxidation of toluene. The removal efficiency of toluene could reach 98% at 350°C in the presence of ultrasonic treated Cu(15%)/clinoptilolite-CeO<sub>2</sub> nanocatalyst.

Carrillo and Carriazo [67] supported Cu/Co on halloysite for the catalytic oxidation of toluene. They found that the halloysite modified by Cu and Co was an excellent catalyst. The toluene was oxidized to CO<sub>2</sub> with a conversion rate of 50% at about 260°C and 90% at 300°C in the presence of halloysite-based catalyst. Motak *et al.* [28] found that vermiculite supported Ag or Cu showed a high catalytic oxidation performance of ethanol. The removal rate of ethanol reached above 90% at 400°C, and NO showed a negative effect on the catalytic activity. Gatica's team [68] applied Spain clay as raw materials for the preparation of honeycomb monoliths supported manganese for the catalytic oxidation of acetone and propane. In the presence of catalyst, 92% of propane could be oxidized to CO<sub>2</sub> and H<sub>2</sub>O at 450°C, and acetone be oxidized completely at 350°C.

A series of work about the application of mineral for the photocatalytic oxidation of VOCs has been published. Kibanova *et al.* [69-70] used hectorite and kaolinite as carrier of TiO<sub>2</sub> for the photocatalytic oxidation of toluene. The load of TiO<sub>2</sub> was conducted by a sol-gel method. The characterization indicated that the TiO<sub>2</sub> has dispersed on the surface of minerals. The structure of hectorite changed significantly after the load of TiO<sub>2</sub>, and for kaolinite, the phenomenon was no observed. The introduction of both minerals enhanced the photocatalytic activity of TiO<sub>2</sub>. The photocatalytic experiment was conducted under two UV lamp with different wavelength. It was found that the toluene removal efficiency could reach nearly 60% under a UVC lamp ( $\lambda_{\max} = 254 \text{ nm}$ ) due to the formation of short-lived radical species such as O<sub>3</sub>. A moderate relative humidity was found to be beneficial to the removal of toluene.

Papoulis's team [71] investigated the photocatalytic activity of palygorskite supported TiO<sub>2</sub> for the oxidation of toluene. The addition of palygorskite to TiO<sub>2</sub> enhanced the catalytic activity under either irradiation or solar-light irradiation compared with commercial TiO<sub>2</sub>. The catalyst with a palygorskite content of 30% showed the highest reaction rate of about  $6 \times 10^{-8} \text{ mol s}^{-1} \text{ g}^{-1}$  under UV irradiation. Besides, the oxidation product of toluene was identified as CO<sub>2</sub> and benzaldehyde. It was found that the for UV irradiation, the content of CO<sub>2</sub> reached the highest

when the content of palygorskite was 80%. However, for solar-light irradiation, the optimal palygorskite content was 70%.

For the photocatalytic oxidation of HCHO, Portela *et al.* [46] used sepiolite, mordenite and kaolinite as carriers of TiO<sub>2</sub> to prepare structured hybrid material. They found that the dispersion of TiO<sub>2</sub> on clays, especially for mordenite and kaolinite, enhanced the UV photocatalytic activity significantly. According to Mishra *et al.*'s work [47], TiO<sub>2</sub>/clay nano-composites was prepared from bentonite, Kunipia-F clay and kaolin using microwave treatment. They found that for the removal of chlorobenzene, the bentonite-based nano-composite showed the highest UV photocatalytic activity compared with Kunipia-F clay and kaolin based catalysts.

A combined process for the removal of VOCs from organic waste treatment plant has been developed by Dobslaw's team [72]. The VOCs-containing gas was treated by non-thermal plasma firstly and adsorbed by halloysite-containing mineral adsorber. The removal rate of VOCs could reach 43.2-62.9%. The current applicable studies of minerals on VOCs removal as catalyst carrier are summarized in Table 4.

Table 4. The current applicable studies of minerals on VOCs removal as catalyst carrier

Mineral	Source	Finished product	VOCs	Highest removal performance	Reference
vermiculite	Sigma-Aldrich GmbH	Cu/Ag modified vermiculite	ethanol	90% of ethanol was oxidized to CO <sub>2</sub> at about 350°C.	[42]
smectite	Tolima, Colombia	delaminated smectite supported Co and Cu	ethanol	90% of ethanol was oxidized to CO <sub>2</sub> at 297°C	[65]
clinoptilolite	Mianeh mine	Cu/clinoptilolite-CeO <sub>2</sub> nanocatalyst	toluene	The removal efficiency of toluene could reach 98% at 350°C	[66]
halloysite	Mondonedo	halloysite modified by Cu and Co	toluene	The toluene was oxidized to CO <sub>2</sub> with a conversion rate of 50% at about 260°C and 90% at 300°C	[67]
vermiculite	Sigma-Aldrich GmbH	vermiculite supported Ag or Cu	ethanol	The removal rate of ethanol reached above 90% at 400°C	[28]
clay	Spain	honeycomb monoliths supported manganese	acetone and propane	92% of propane could be oxidized to CO <sub>2</sub> and H <sub>2</sub> O at 450°C, and acetone be oxidized completely at 350°C.	[68]
kaolinite and hectorite	Washington County, Georgia; San Bernardino County, California, respectively	Hectorite/kaolinite loaded TiO <sub>2</sub>	toluene	the toluene removal efficiency could reach nearly 60% under a UVC lamp ( $\lambda_{\max} = 254 \text{ nm}$ )	[69, 70]
palygorskite	Ventzia continental basin, Western Macedonia, Greece	palygorskite supported TiO <sub>2</sub>	toluene	the highest reaction rate of about $6 \times 10^{-8} \text{ mol s}^{-1} \text{ g}^{-1}$ under UV irradiation	[71]
Kunipia-F clay and kaolin	Kunimine Industries Co. Ltd. Japan; Himedia, India	TiO <sub>2</sub> /clay nano-composites	chlorobenzene	-	[47]

### 3. Conclusion

The removal of VOCs is of great significance for environment and human health. A large number of literatures have been published for VOCs removal. Porous materials possess unique properties such as low cost, easy access and high stability. In this review, the current applications of porous natural mineral were arranged systematically. It is clearly that the porous natural minerals play an important role for the adsorption or catalytic oxidation of VOCs. Hence, the application of minerals as adsorbent or catalyst carrier is a promising process for the removal of VOCs. Especially, considering the low cost and wide distribution, the application of porous natural minerals instead of synthetic materials should be paid more attention.

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