Review

# Exploring depletion of volatile organic compounds (VOCs) in the air using Faujasite zeolite catalysts from fundamental to advanced

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# Abstract

The emission of volatile organic compounds (VOCs) has resulted in various environmental hazards. Thus, developing technology that efficiently removes VOCs is necessary to mitigate the negative effects. Among several VOC elimination methods, zeolite catalyst usage in heterogeneous catalysis is a more popular and successful technique. Faujasite zeolite is a commonly used zeolite type in catalysis and VOC remediation as not only its high porosity with ion exchangeability but also can easily be synthesized in the laboratory using aluminosilicate precursors. This article aims to review VOC remediation studies mainly with FAU zeolite from fundamental to advanced. It has been observed in many publications that the zeolite synthesis parameters and their alterations directly affect the rate of VOC degradation. In this article, the catalytic oxidation method for removing VOCs in individual and mixtures from gas streams is briefly discussed with an emphasis on Faujasite zeolites and their characteristics. More than 140 papers were studied to build up this article. Although zeolites with larger pore sizes are more effective for removing VOCs, there are limited studies on the use of zeolite catalysts for cleaning up mixtures of VOCs. To enhance catalytic systems for industrial and environmental applications, advanced oxidation is being explored. More research is needed to modify zeolite's structure for a variety of VOCs to penetrate its inner surfaces and rapidly oxidize.

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# **Graphical Abstract**



 $\textbf{Keywords} \ \ Catalyst \cdot Faujasite \ zeolite \cdot Mixtures \ of \ VOC \cdot Oxidation \cdot VOC$ 

# Abbreviations

AC	Activated carbon
AOPs	Advanced oxidation processes
BTEX	Benzene, Toluene, ethylbenzene and xylene
CFA	Coal fly ash
CWPO	Catalytic wet peroxide oxidation
DAY	Dealuminated Y zeolite
EPA	Environmental protection agency
FAU	Faujasite Zeolite
GCMC	Grand canonical Monte Carlo
HDTMA	Hexadecyl trimethyl ammonium
HP	Hierarchical porous
IAST	Ideal adsorbed solution theory
IE	lon exchange
IM	Incipient moist impregnation
IUPAC	International Union of Pure and Applied Chemistry
MEK	Methylethylketone
MIBK	Methyl-isobutyl ketone
MOF	Metal–organic framework
NTP	Non-thermal plasma
OSDAs	Organic structure directing agents
PC	Plasma catalysis
PCO	Photocatalytic oxidation
PDMS	Poly dimethyl siloxane
PM	Particulate matter
RE	Rare earth
SBU	Secondary building unit
SOA	Secondary organic aerosol
TPR	Temperature-programmed reductions
TPSR	Temperature-programmed surface reaction



USY Ultra-stable zeolite Y

VOC Volatile organic compounds

## 1 Introduction

The issue of air pollution attracts a lot of attention, and many researchers are working to find new solutions to address it. Among gases contributing the air pollution such as CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub>; Volatile Organic Compounds (VOC) are also hazardous component that greatly affects human health and the environment. Under UV light, VOCs undergo photochemical oxidation, resulting in harmful air pollutants like secondary organic aerosol (SOA), ozone precursors and particulate matter (PM) posing a risk to public health[1]. Catalytic oxidation of VOCs using zeolite-based materials is highly effective due to their high efficiency in pollutant removal and selectivity for specific VOCs, and chemical and thermal stability [2]. As Zeolite requires lower energy and produces fewer harmful by-products, this technique is more cost-effective and eco-friendly than other methods such as membrane separation [3], condensation [4], thermal oxidation [5], plasma catalysis [6, 7] photocatalytic oxidation [8–10] etc. Table 1 summarizes the limitations of these techniques. Recent studies emphasize the superior performance of zeolite-supported catalysts, highlighting their potential for various applications in air purification and environmental protection.

Zeolite is a mineral that occurs naturally, whereas it can also be synthesized using aluminosilicate precursors. Many researchers focus on zeolite for VOC remediation due to its properties such as a high surface area, large porosity, stability, selective adsorption ability of organic compounds and availability. These properties are directly involved in enhancing the effective remediation of VOC as discussed above. Among various zeolite topologies, FAU is of utmost importance because it has acid sites that can activate reactant molecules. Also, it's able to selectively adsorb organic molecules due to hydrophobicity and super-cage structure. To develop zeolite catalysts for VOC abatement, numerous synthesis techniques have been established. In this review Faujasite zeolite is taken into account because it has required properties in VOC removal as well as there are convenient synthesis procedures compared to other zeolite types. Faujasite zeolite which has been metal-impregnated or ion-exchanged is utilized to catalytically remove VOC mostly through oxidation. Numerous experiments based on zeolites have proven the importance of research into the most effective VOC reduction technique.

The objective of this review is to provide comprehensive background information for new researchers in the field to build advanced research on previously published work. Almost all published review articles on VOC remediation with Zeolite focus on advanced theoretical concepts, but they lack fundamental knowledge. Therefore, the main goal of the current study is to provide an overall idea of this topic from basic to advanced. Additionally, the study aims to address the research gap in the remediation of various mixtures of volatile organic compounds (VOC) using modified zeolite. The first section of this paper includes an overview of VOC and recently developed methods for VOC removal. Next, zeolite and porous materials for VOC abatement were briefed. Then, a small introduction to faujasite zeolites is provided with its structural properties. The sub-section of this section focuses on the common synthesis and modification of FAU zeolite. The majority of this review paper is covered in the final section which provides an overview of the literature on the catalytic oxidation of volatile organic compounds (VOCs) using faujasite-type zeolites. The sixth part covers the most significant subtopics about the oxidation and catalysis of VOC individuals and mixtures. The review concluded with a discussion few more VOC catalytic processes using FAU-zeolite catalysts.

# 2 Methodology

The articles for this work were found by using keywords on common search platforms and databases such as Google Scholar, PubMed, and Mendeley. Some articles were also discovered through reference lists and manual searches. The selected articles were mostly published between 2000 and 2022. The keywords used during the search included "volatile organic compounds/VOC remediation/removal/abatement", "zeolites/porous materials for VOC removal", "FAU/Faujasite/Zeolite-Y/Zeolite-Y/Zeolite-X", "Faujasite zeolite Synthesis/modification", "catalysis/catalyst/heterogeneous catalytic oxidation/catalytic oxidation for VOC removal", "advanced catalytic processes", and "VOC removal in mixtures/mixture of VOC remediation". Initially, the titles and abstracts of all identified articles were screened to select the most relevant ones. More than 130 research and review articles were studied to identify the research gap for the relevant topic of this article. Finally, a critical evaluation was carried out based on fundamental theories to address the research gaps in previous studies.



Table 1 Some VOC F	Removing Technologies and The	ir Limitations	
VOC Removal Techn	ologies	Details	Limitations
Recovery method	Membrane Separation	<ul> <li>Organophilic membranes</li> <li>Polydimethylsiloxane (PDMS)and silicon rubber are the most used</li> </ul>	• Expensive Membrane : • Membrane fouling
	Condensation	<ul> <li>Separate volatile components of a vapor mixture from the other vapors</li> </ul>	<ul> <li>Limited to evaporative solvents</li> <li>Disposal of used coolants</li> <li>Water condensation in humid environments</li> </ul>
	Absorption	Selective transfer of one or more components to a suitable solvent     The final recovery efficiency of the process is constrained by	Used solvent disposal from an absorber     In the presence of water vapor, VOCs and water molec     commare for absorption

	Condensation	<ul> <li>Separate volatile components of a vapor mixture from the other vapors</li> </ul>	<ul> <li>Limited to evaporative solvents</li> <li>Disposal of used coolants</li> <li>Water condensation in humid environments</li> </ul>	[4]
	Absorption	<ul> <li>Selective transfer of one or more components to a suitable solvent</li> <li>The final recovery efficiency of the process is constrained by both the absorbing capacity and the subsequent regeneration of VOCs from the supplied solvent [21]</li> <li>Auxiliary devices are also needed for the absorption system [21]</li> </ul>	• Used solvent disposal from an absorber • In the presence of water vapor, VOCs and water molecules compete for absorption	[25]
	Adsorption	<ul> <li>Physical and/or chemical adsorption</li> <li>Employing an appropriate adsorbent (such as zeolite, MOF, activated carbon, polymeric adsorbents, etc.)</li> </ul>	<ul> <li>Financially feasible only when fewer VOCs are present in a flue gas stream</li> <li>High cost</li> <li>Requirement for regular adsorbent renewal</li> </ul>	[21]
Destruction methods	Thermal Incineration	<ul> <li>Oxidized generally at (over 1000 °C)</li> <li>Necessitates extra fuel and temperature-resistant materials</li> </ul>	<ul> <li>Inefficient thermal combustion can produce unwanted byproducts including dioxins and carbon monoxide</li> </ul>	[ <mark>2</mark> ]
	Plasma Catalysis	<ul> <li>Plasma is propelled by electrical energy</li> <li>Degraded during plasma operation via electron impact reactions</li> </ul>	<ul> <li>Production of stable undesirable byproducts</li> </ul>	[26]
	Biological degradation	<ul> <li>In a solid-phase reactor, VOC is eliminated during biofiltration, where contaminated gas is entered from the bottom and passed through active layers of filters called biofilms</li> <li>VOC mass transfer takes place through diffusion and convection, with target VOC passing to the biofilm degrading into CO<sub>2</sub>, water, and microbial biomass from active enzymes or aerobic bacteria</li> </ul>	<ul> <li>Less removal if a high concentration of VOC</li> <li>Operation/maintenance is expensive</li> </ul>	[4]
	Photocatalytic oxidation (PCO)	• UV light and nano-semiconductor catalysts are used in air purification • Ti( $OC_3H_7$ ),4 is the precursor to most photocatalysts, while • nonmetal-doped TiO <sub>2</sub> photocatalysts are efficient under visible light	• The relatively low oxidation rate • Formation of toxic by-products • Catalyst deactivation	[10]
	Catalytic Oxidation <sup>a</sup>	<ul> <li>Minimal energy needs and a smaller carbon impact</li> </ul>		

O Discover

[3, 24] Refs.

# 3 Volatile organic compounds

## 3.1 An overview of VOC

Volatile organic compounds (VOCs) are substances that are vaporizable or gaseous and can enter the atmosphere. They have defining characteristics, including high vapor pressure, a low boiling point, and strong reactivity [11, 12] VOCs, which can be released via transportation, industrial activities, and the usage of organic solvents, for example; methane, benzene, xylene, propane, and butane [12]. They also include any carbon molecule that participates in atmospheric photochemical reactions, barring those listed by the EPA as having low photochemical reactivity, such as carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate [13]. Up to now, more than 300 VOCs have been reported according to their molecular structure, polarity, and boiling point [14]. Fig. 1 shows the VOC groups based on their classification criteria which are extracted from some literature [15, 16]

Sometimes, VOCs are also divided into indoor VOC and outdoor VOC by the environment where they will be emitted [11]. Due to the negative impacts of VOCs on the environment, the US Environmental Protection Agency (US-EPA) has imposed regulations on the regulation of organic vapor pollutants in the air. The maximum concentration of hydrocarbons for three hours is 0.24 ppm, and it shouldn't be exceeded for at least a year [17]. When utilizing items and materials that contain indoor VOCs, such as cleaning supplies, paint, furnishings, office equipment, pesticides, perfume, and cigarette smoke; a significant number are released into the environment [18]. According to the US EPA, indoor VOC levels are typically 5 to 10 times higher than outdoor VOC levels [19].

The impact of indoor VOCs on health is significant, leading to immediate and long-term conditions such as cancer, tumors, irritability, migraines, memory loss, and vision impairment [11]. A publication by the US EPA provides an in-depth overview of the challenges of indoor air pollution for health professionals, emphasizing acute conditions and offering diagnostic guidance [20]. Also, outdoor VOC can result in ground-level ozone, photochemical smog, and climate change, they can be detrimental to human health and the environment. Therefore, it's crucial to lower their concentration indoors as well as outdoors to preserve the environment and public health [11].

## 3.2 Recently developed methods for VOC removal

VOCs are numerous and varied as described above and with adverse effects on both human health and the environment emphasizing the critical need for effective removal technologies. Therefore, various efficient technologies have been investigated to control their emissions and reduce their concentrations in the air to achieve air quality regulation. There seem to be two types of methods reported: recovery methods and destruction methods [17]. Table 1 summarizes some of these technologies with their limitations. Some recovery methods are membrane separation [3], condensation [4], absorption and adsorption (commonly using Activated carbon and Zeolite) [21]. These methods are based on the physical nature of VOC. VOC can be recovered using recovery methods, as the name implies, but not through destruction methods. In approaches focused on destruction, VOCs are changed by chemical processes like oxidation into

**Fig. 1** Different Classifications of VOC based on various criteria [15, 16]





non-hazardous compounds like carbon dioxide and water. Thermal incineration or thermal oxidation [5], plasma catalysis [6, 7], biofiltration [4, 22] photocatalytic oxidation [8–10], and catalytic incineration or catalytic oxidation methods are under destruction methods [23].

However, VOC removal methods are complex and diverse, and the selection of a proper method to remediate all kinds of VOC is still a challenge. This is because the remediation technique is influenced by concentration, toxicity, presence or absence in a mixture, and market value. The above methods are applicable with further developments and optimizations such as VOC removal in a mixture, humidity resolving issues, catalyst replacement, material toxicity control, and so on. Then catalytic oxidation is an efficient, eco-friendly, and financially feasible method for mineralizing VOCs into CO<sub>2</sub>, water, and other less hazardous molecules, and is subject to further study in section five.

## 4 Zeolite and porous materials in voc abatement as adsorbents and catalyst supports

Scientists are fascinated by porous materials because of their ability to interact with specific substances and efficiently separate them due to superior features such as large specific surface area, unique pore structure, low density, tunable pore properties, etc. They also have distinct physical, thermal, mechanical, and electrical properties. The shape, arrangement and size of pores, as well as porosity (the ratio of total pore volume to the apparent volume of material), are characteristics of porous materials [27].

Since every porous material has a solid framework with high chemical and mechanical stability under application conditions, they are used in many applications such as catalyst supports, adsorption, separation or purification, drug delivery, gas separation/storage, heat insulation, electrical applications, etc. [27]. Porous materials such as Zeolite, alumina, Metal–organic framework (MOF) and Activated carbon (AC) have been extensively used in many previous studies and real-time applications to remove VOCs through membrane processes, adsorption, and catalysis [28, 29]. Considerations for selecting a suitable porous material should include high activity, selectivity, ease of handling, ease of separation from pollutants, ability to be regenerated or reused for cost-effectiveness and environmental friendliness with safe disposal [30].

For mass transfer diffusion to occur inside the porous medium, a proper porous material must have an appropriate pore structure and a substantial contact area. Porous surfaces with a high density of functional groups capable of forming stable hydrogen bonds with volatile organic compound (VOC) molecules. This process serves to facilitate adsorption and capacity determination while also promoting the degradation of pollutants [31]. IUPAC recommends classifying porous materials into three groups based on their pore size: microporous (pore diameter < 2 nm), mesoporous (2 nm < pore diameter < 50 nm), and macroporous (pore diameter > 50 nm) [30]. Zeolites and activated carbons fall under the category of microporous materials.

In terms of VOC abatement, zeolites offer several advantages compared to other porous materials. Zeolites demonstrate high chemical and thermal stability, allowing them to operate effectively under harsh conditions without degradation. Their superior ion exchange capacity enables efficient adsorption and retention of VOCs. Furthermore, the ability to enhance adsorption capacity through metal loading further enhances their effectiveness. Zeolites also require less frequent regeneration than activated carbon, reducing operational costs and downtime. Additionally, their high selectivity for specific VOCs provides a tailored approach to abatement, which is often superior to the more generalized adsorption characteristics of alumina and activated carbon [32].

## 4.1 In VOC adsorption

Many novel porous materials have been developed for gas adsorption and those are carbon-based (eg: Activated carbon), oxygen-based (eg: zeolite), organic polymers, etc. [27]. Adsorption is one of the most promising VOC treatments which is in the under-recovery category. This method is attractive since it has a flexible operation and has low energy consumption hence low cost. In current research studies, surface area, thermal stability, hydrophobicity, and adsorption capacity are being experimented with along with modifications to adjust specific surface area, pore structure, charge density and chemical functional groups to enhance adsorption performance [33]. According to US-EPA, it's noted that zeolite, organic polymers and activated carbon are the most popular adsorbates used for VOC treatment [27].

Activated carbon (AC) is not costly but zeolite has the advantages of being thermally stable, non-flammable, hydrophobic and reusability [17]. Carbon materials as AC need to be carefully handled due to their flammability. This requires controlling the desorption temperature strictly, usually keeping it below 100 °C to ensure safe desorption procedures. However, this cautious approach often leads to insufficient desorption of volatile organic compounds (VOCs) during the thermal regeneration process, limiting the wider practical use of carbon materials for VOC desorption [32]. Also, Zhu [27] summarized adsorption performance of AC on VOC is influenced by adsorption conditions and it's suitable to use VOC at moderate temperatures, low medium concentrations and in an N<sub>2</sub> atmosphere. Moreover, the pore-blocking and high transmission resistance of AC and the requirement of humidity control when using AC are restricting its broad application coverage in that article [27]. The organic polymer has complex synthesis processes and therefore in the real application, large-scale coverage is difficult. It can be seen that zeolites are therefore favored for the treatment of waste gases even in the presence of water, and the capability to regenerate the adsorbate by heating for reuse is an additional benefit[34].

The VOC adsorption depends on the textural properties and surface chemistry of the porous structure. A prime concern should be given to the pore size of porous material since a large variety of kinetic molecular diameters in VOC are to be adsorbed to the pore of the material. Zeolite has a broader range of pore sizes. The pore structure and surface physicochemical characteristics of zeolites have a direct impact on their ability to adsorb substances. One typical method of adsorbing non-polar alkanes via the Van der Waals force is micropore filling, in which the amount of surface area and micropores in the adsorbent determines its adsorption capacity[35]. The specific interaction between zeolites and target VOC varies depending on the surface composition of the zeolites and the nature of the VOC, involving  $\pi$ -complexation and hydrogen bonds, among some other factors [35].

Therefore, in the physical adsorption of VOC to the zeolite, it's a positive point to have a high pore volume and large surface area. Generally, zeolites have a high surface area, which is 400 m<sup>2</sup>/g [36]. Surface functional groups such as Silanol groups (Si–OH), Aluminol groups (Al–OH) and framework defects (presence of non-bridging oxygen atoms such as Si–O-) of zeolites assist in the chemical adsorption of VOC. Other than these, the molecular size and weight of VOC and polarity boiling point also affect efficient adsorption to the porous material [27]. The hydrophobicity of zeolite has an affinity to most aromatic VOC compounds since they are non-polar. Dealumination of zeolite makes it hydrophobic and its chemical replacement is done to aluminium with silicon without changing the crystal structure [37, 38].

Fernandes and Pires's study on the adsorption of a series of volatile organic compounds of various sizes and polarities, such as ethanol, acetone, trichloroethane, cyclohexane, benzene, toluene, methylethylketone, n-hexane, and acetone, in Zeolite-L at near ambient temperature and low pressures; revealed that this zeolite can adsorb VOC between 8 and 12.5% in weight [39]. The author also mentioned in his article that the adsorption values obtained for Zeolite L are less than for Faujasite zeolites. Here the absorption percentages are low and it may be because the used Zeolite-L type does not have enough acid sites [40].

Yin et al. [41] have studied high-temperature hydrothermal treatment for the production of hydrophobic zeolites. The adsorption amount of toluene has been increased from 11.26 to 128.85 mg/g after this treatment and water adsorption has also been reduced. The simplicity of this alteration was said to depend on the type of cation. For instance, it has been noted that sodium ions stabilize the framework structure of NaY zeolite, which influences the rate of the dealumination process [41]. Figure 2 shows the same experimental design for the phenol compound as its kinetic diameter is also less than the Zeolite Y pore size. Researchers Diaz and co-workers [42] used inverse chromatography to determine the adsorption parameters of several VOCs (aromatic hydrocarbons, alkanes, cyclic hydrocarbons, and chlorinated compounds) on various adsorbates (zeolites 13X and 5A, alumina, and activated carbon). They also discovered that by increasing the acidity of the adsorption for alkanes and benzene increases due to physicochemical interactions. This appears to be advantageous in FAU zeolites as the surface is acidic in nature (see Sect. 5.2.3.). Furthermore, cyclic and chlorinated compounds adsorb more strongly on zeolite 13X than on zeolite 5A and alumina [42]. This observation is clear since zeolite X is a Faujasite zeolite with a higher Si/Al ratio than zeolite A types. Zeolite 5A means the replacement of sodium by calcium [43]. This finding is reappearing in a study by Li et al. as they showed that the Si/Al ratio and pore size were the most important factors affecting the adsorption of p-xylene. The Y zeolites outperformed commercial zeolites, which had diameters equal to those of p-xylene molecules by more than 25%, in terms of maximal adsorption capacity [44].

Another study by Chandak and Lin, [45] has compared the adsorption isotherm of ethanol, trichloroethane and trichloroethylene on dealuminated Y zeolite (DAY) and silicate at different temperatures. There, DAY zeolite has a 60% higher VOC adsorption capacity than silicate due to its large pore volume with higher acidity [45]. The removal of volatile organic compounds (VOCs) by adsorption at room temperature was accomplished using Mordenite and X- or Y-type Faujasite in the study [34] by Kim and Ahn. In this work, studies were conducted to determine the relationship between the adsorption and/or desorption behavior of several VOCs, including benzene, toluene, o-, m-, and p-xylene, ethanol, methanol, isopropanol, methylethylketone (MEK) [34]. It was demonstrated that the crystal structure of Mordenite zeolites with low surface area determined their adsorption behavior, whereas Faujasite zeolites had the highest adsorption capacity than Mordenite. Since HY(Si/Al = 80) has a greater mesopore volume than the other





Fig. 2 Adsorption of Phenol into high-temperature hydrothermal treated hydrophobic zeolite in a humid environment [41]

zeolites utilized in this investigation, it demonstrated the highest adsorption capacity. Additionally, it was discovered that the pore structure had a significant impact on the adsorption capacities of zeolites for many VOCs [34]. In another study by, Brodu and Sochard in [46] toluene adsorption has been studied experimentally and modelled on various hydrophobic high silica zeolites: Faujasite (FAU), ZSM-5 and Mordenite (MOR). Here again, as in the previous study, toluene adsorption in FAU zeolite is higher than in MOR or ZSM-5 [46]. Thus, it demonstrates a precise correlation between the VOC's molecular size and the pore and channel shape for adsorption. The functional group of the VOCs, which has the power to regulate the adsorption's strength, is also relevant. For instance, in the article [47], because o-xylene lacks a functional group, unlike isopropanol, its adsorption capability has been lowered [47].

Literature based on VOC abatement via other zeolites except FAU type is summarized below in Table 2. The references include information on the adsorption capacity (mg/g) and percentage removal of each volatile organic compound (VOC) removed by a specific zeolite catalyst, which is mentioned here. Variation in these values may depend on the catalyst surface as well as the properties of adsorbates. However, some limitations have been observed when VOCs are remediated with these zeolites.

This study revealed that FAU zeolites are better suited for larger VOC molecules, while ZSM-5, Beta zeolite, and clinoptilolite zeolites are effective for smaller VOC molecules. Additionally, MOR zeolites were found to offer a balance between different-sized VOCs due to their unique pore structure. However, the synthesis procedures for MOR zeolites are more intricate than those for FAU zeolites. Previous research studies as given in Table 2 have indicated that the selection of zeolite type for volatile organic compound (VOC) elimination via adsorption depends on the specific VOCs of interest and their molecular sizes. Also, important factors like temperature, humidity, and VOC concentration can impact the adsorption capacity and efficiency of zeolites in VOC elimination applications.

Table 2 Summary of VOC removal via various zeolite types (except FAU types)

Zeolite Type		Removed VOC	Removal efficiency		Limitation of the zeolite catalyst	Refs.
Type	Accessible Volumeª/Å <sup>3</sup>		Adsorption capacity /(mg/g)	Percentage removal/%		
Zeolite L	330.95	n-hexane, cyclohexane, benzene, toluene, ethanol, acetone, methyl ethyl ketone and trichloroeth- ane	1	8–12.5	<ul> <li>Lack of acid sites</li> </ul>	[39]
Cr-ZSM-5	511.0	ethyl acetate and benzene	1	50	<ul> <li>Smaller pore sizes compared to FAU zeolites</li> </ul>	[48]
Silicalite-1 (ZSM-5)	511.0	2-Chloro Phenol	1	25	and relatively low Si/Al ratios	[49]
Silicalite-1 (ZSM-5)	511.0	n-hexane	110.30	I	• Limited adsorption capacity	[20]
ZSM-5	511.0	Toluene	85.72	1	remediation	[ <mark>5</mark> 1]
Co-ZSM-5	511.0	Isopropanol		00	<ul> <li>Temperature limitations</li> </ul>	[ <mark>52</mark> ]
ZSM-5	511.0	BTEX	0.164, 0.220, 0.192 and 0.191	1	<ul> <li>Catalyst deactivation</li> </ul>	[23]
Co-ZSM-5	511.0	BTEX	2.23-3.33		• Water sensitivity	[54]
Rh <sub>1</sub> Cu <sub>3</sub> /ZSM-5	511.0	Toluene	1	00		[55]
Fe/ZSM-5	511.0	Toluene	I	97.6		[26]
Pt-HP MOR zeolite	346.86	Toluene	I	98	<ul> <li>Catalyst deactivation</li> <li>Synthesis of MOR is not as easy as FAU</li> </ul>	[57]
TiO <sub>2</sub> -Natural zeolite	I	Toluene	I	26	<ul> <li>Effect from impurities and less crystallinity</li> </ul>	[58]
TiO2_clinoptilolite zeolite	193.53	Toluene	1	80	<ul> <li>Smaller pore sizes compared to FAU zeolites</li> <li>Difficult in regeneration of the catalyst</li> </ul>	[58]
Ag-β-zeolite pellets	448.15	Acetone	62.14	1	Narrow pore size	[59]
Fe/Beta zeolite	448.15	Toluene	I	86.6	<ul> <li>Less stable under hydrothermal conditions compared to FAU zeolite</li> </ul>	[56]
<sup>a</sup> According to the IZA dat	abase (3956.1	8 Å3 for FAU). However, according to the sample pre	eparation procedures and Si/Al	ratio, these th	neoretical values can be varied	





### 4.2 In catalyst support

As mentioned above, the properties of porous materials are excellent for adsorption and catalytic performance, due to their high specific surface area. The support of catalysts can be inert or participate in the catalytic reaction mechanism. The most widely used catalyst supports are MOFs, carbon, alumina, silica, and zeolite [29, 30, 60]. Catalytic substances are typically applied to porous structures through ion exchange, impregnation or co-precipitation [61].

The type of support is a crucial factor in catalyst design, significantly impacting the activity and durability of supported metals [62]. Therefore, porous materials are used because a high reaction rate usually requires a large surface area, which the pores in porous materials help achieve. Furthermore, these catalysts are designed with a specific surface area and pore size to control the mass transfer of reactant molecules to the active site. Therefore, the discovery of ordered porous material has exposed large opportunities for new applications in heterogeneous catalysis. Clay mineral is a value-added porous material in environmental applications since it's available in local resources [62]. Among other porous structures, zeolite can selectively adsorb molecules based on their size as discussed above. Since there are a lot of pore structures of zeolites, some are selective for large molecules and others are for small molecules. Then zeolites are called "shape-selective catalysts" [63]. However, the selection of a suitable zeolite catalyst material for the reduction of a mixture of VOCs remains a significant challenge.

Moving on to zeolites, the key features of zeolite catalysis include acidity and shape selectivity. The inherent acidity of the OH groups is used to evaluate the acidity. In the article by Soscún et al. [64], the acidity is explained in terms of the topology of the charge density that was estimated at the location of the acid sites' essential OH bonds. The increasing acidity in zeolite structure is an important factor for successful use in catalysis [63]. Si/Al ratio is directly correlated with acid site density. As the density of the Al atom in the zeolite frame is increased, the strength of Brønsted acid sites decreases. Therefore, dealumination will be done to isolate Al–OH surrounded by silicon. The Brønsted acid sites are generated through ion exchange is another important method. Then the catalytic activity of zeolite can be used as a measure of its acidity [65]. However, for chemical processes, strong acidity is not required but weak acidity may be enough. The common zeolites have weak to strong acidity sequences, Y < ZSM-5 < MCM-22 < Mordenite [36]. These acid sites are particularly effective in breaking C-H and C–C bonds, leading to the activation and subsequent degradation of VOCs into less harmful compounds [66]. Moreover, the presence of acidic sites can improve the selectivity and efficiency of VOC conversion by promoting specific catalytic pathways. This enhanced catalytic activity is due to the strong acid sites acting as active centers for the chemical reactions necessary for the degradation of VOCs [32].

Another important factor is shape selectivity, which depends on the pore width or pore architecture of the solid catalyst. This is a unique feature in zeolite heterogeneous catalysis when the size of reactants is of the same order in magnitude as the pores and cavities of zeolite. The shape selectivity can be focused on the reactant and product shape selectivity and transition state shape selectivity [63].

Most of the time catalytic oxidation is coupled with adsorption when porous materials are used in catalyst support for oxidation of pollutants [67]. Porous materials play a significant role in influencing the activity and durability of catalysts used in VOC adsorption and degradation. Above mentioned properties, enhance the availability of active sites for adsorption and catalytic reactions. As a result, they contribute to increasing the overall efficiency of the process [27]. They also aid in the even distribution of catalytic components, preventing aggregation and ensuring consistent performance over time [68]. Furthermore, the incorporation of porous supports elevates the mechanical strength and thermal stability of the catalyst, thereby extending its operational lifespan [69].

Then the main reasons for using zeolite as a metal and metal oxide support in catalysis are its high surface area and controllable acid/base properties as described above Fig. 3 represents the basic (left) and acid (right) sites in the Na-zeolite structure. Loaded metals can cause zeolite structures to be electron-rich (basic) or electron-poor (acidic) in nature depending on the size of the metal, and it can result in new catalytic activity [36]. Since basic zeolites exhibit

**Fig. 3** Representation of the basic (left) and acid (right) sites in Na- zeolites [43]





greater catalytic conversion and acidic zeolites exhibit better adsorption, it indicates that the VOC conversion ratio is highly influenced by the acidic/basic sites of zeolites [47].

## **5** Faujasite zeolites

#### 5.1 Structure and properties

The Faujasite (FAU) structure is one of the most frequently employed in catalytic oxidation. It consists of three significant zeolites: Zeolite X (low-silica FAU), Y (high-silica FAU) and USY (Ultra-Stable-Y) [65]. Each with different frameworks and features, with Si/Al ratios of 1.25, 2.3, and 5.6, respectively [70]. Zeolites having between 96 and 77 Al atoms per cell (Si/Al ratios between 1 and 1.5) are referred to as Zeolites X, whereas zeolites with less than 76 Al atoms per cell (Si/Al ratios more than 1.5) are referred to as Zeolites Y [71]. Faujasite was the first molecular sieve to be used for catalytic purposes in 1959, with Zeolite Y acting as a catalyst for the isomerization reaction [71]. The Mobil Company employed zeolite X in the catalysis of cracking processes in 1962. Grace invented ultra-stable zeolite Y (USY) as a catalyst in 1969.

The secondary building unit (SOD) of FAU type has double 6-rings, a sodalite cage, and an extensive cavity with four 12-ring windows [72]. The 6-rings of adjoining SOD units face one other and are linked through oxygen bridges to create shared double 6-rings. This results in the formation of a diamond cubic lattice arrangement of SOD units. That is, SOD units are organized in the same way as FAU and LTA framework types [73]. This creates a large cavity of tetrahedral symmetry in FAU called the "super-cage" (which should be called a super-cavity with 0.74 nm) that is accessible by a 3D 12-ring pore system [74] (Fig. 4). While adsorption of pollutants, adsorbed molecules diffuse in 3D directions in the crystal interior. Only the super-cages are accessible to molecules bigger than water or ammonia so they are unable to enter the area inside sodalite cages. Therefore, all reactions and the majority of such adsorbed molecules are contained within the super-cages [70].

Multiple metals can be introduced to the structure to balance out the negative charge of the Faujasite framework, and their placement will depend on the available sites. The hexagonal prisms (S<sub>1</sub>), in the sodalite cages (S<sub>1</sub>) or the super-cages (S<sub>11</sub>, S<sub>111</sub>) are where these exchanged cations are most frequently seen. Fig. 4(b) presents those sites on the framework of the zeolite Y. The type, quantity, and hydration state of the cations are all factors that affect the cation locations. The position of the cations in the structure will have an impact on the catalytic ability of zeolite [76]. Some of the cations exchanged with FAU zeolite (Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Cs<sup>+</sup>, Rb<sup>+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, etc.) have been extensively studied by Sels and Kustov in [77].

Faujasite Y zeolites have been employed in a variety of chemical and catalytic applications including adsorption, separation, petroleum refining, aromatic alkylation, petrochemical, environmental protection and natural gas dehydration



Fig. 4 a Faujasite zeolite framework, b The Faujasite structure showing some of the cation positions [70, 75]



[78]. This is due to their superior characteristics, which include a huge surface area (over 900 m<sup>2</sup>/g) [67], large adsorption capacity [41], large pore volume (up to 0.5 cm<sup>3</sup>/g) [67], high porosity, great thermal stability (up to 800 °C) [67], 3D channel structure and a substantial ion exchange capacity [65]. The name "molecular sieves" refers to the capacity of zeolites to adsorb molecules smaller than their pores and channels while rejecting molecules that are too big based on the size exclusion principle [79].

Because of their homogenous pore size, FAU-type zeolites are employed in VOC adsorption as molecules greater than a particular size are prevented from entering the lattice. As a result, zeolites enable them to adsorb selectively. Fig. 5 depicts the pore size of several zeolites as well as the kinetic molecular diameter of chosen molecules [80].

An adsorbent for the elimination of phenol, a synthetic Faujasite (FAU-type zeolite NaY), has been tested by Mohammed [81]. In this study, they carried out seven adsorption experiments at different temperatures (293, 303, and 313 K) [81]. The preferred adsorption location for phenol and H<sub>2</sub>O molecules in the zeolite is represented by the density field maps given in that article with the caption "Density field for phenol in zeolite NaY computed by GCMC at different temperatures. Phenol (green) and water (red)". It's interesting to see how evenly dispersed the H<sub>2</sub>O molecules are within the channels over zeolite intersections. Based on density field maps four water molecules can be adsorbed more readily through the smaller zeolite apertures, but it's more difficult to move phenol molecules through the tiny aperture. The majority of phenol molecules are adsorbed at the core of wide junctions and big channels [81]. Due to their diffusional restrictions and slow transport, FAU zeolites can hinder the catalytic oxidation of very large volatile compounds. Numerous approaches have been successfully used to address this issue, including synthesis of larger micropores, recrystallization, decreasing zeolite crystal size, dealumination, desilication and use of ordered mesoporous materials and introducing a secondary pore system with increased microporosity. One of the most popular techniques for producing materials with suitable molecular transport capabilities is the fabrication



#### Effective pore size and Kinetic molecular diameter/ nm

Fig. 5 Correlation between effective pore size of industrially important zeolites and kinetic molecular diameter of some compounds [80]

of "hierarchical pore structures" [57]. By incorporating a secondary pore system of mesopores (2–50 nm) within the naturally microporous zeolite crystals, which should have additional intra- or inter-crystalline mesoporosity in addition to the natural microporosity of zeolites, which are able to have the most structural functions in a small amount of volume and space because of their high diffusion efficiency [82].

#### 5.2 Synthesis of initial structure of zeolite

Zeolite synthesis under hydrothermal conditions was established around 1950 [83]. They demonstrate that a final product can be obtained by heating aluminosilicate raw materials in the presence of alkaline solutions for a few hours or days, depending upon the type of raw materials and process parameters (temperature, pressure).

Zeolites X and Y are typically synthesized using the same chemical sources and under comparable circumstances as LTA (Si/Al = 1), but with a higher silica concentration. In most cases, zeolite manufacturing is done in batches, however, continuous procedures have also been created. The commercial synthesis of zeolite Y is accomplished in the absence of organic templates and with typical gel compositions of (8.0–10.0) SiO<sub>2</sub>: (1.0) Al<sub>2</sub>O<sub>3</sub>: (2.3–3.5) Na<sub>2</sub>O: (120.0–180.0) H<sub>2</sub>O [84]. The time-consuming ageing stage is currently eliminated by the use of seeding mixes, which are frequently colloidal. The gel is subsequently transferred to a reactor where crystallization occurs within 4 to 72 h at 85 °C to 100 °C [85]. Further, this type of zeolite can be synthesized using several procedures such as free template seeding, organic template, increasing the alkali treatment, and temperature control by hydrothermally or using microwave power [86–89].

FAU and LTA crystallizations are highly dependent on synthesis variables such as alkali concentration, Si/Al ratio in gel precursor, ageing duration and temperature, and crystallization temperature. Different crystal phases are formed as a result of a little variation in these properties. Therefore, it's essential to clarify the crucial factors that will control the FAU/LTA phase selection. FAU is aided by a high hydrothermal reaction temperature and a relatively low ageing temperature, however, the effects of these parameters on the phase selection are not as strong as those of ageing time [90]. In some cases, the Zeolite P phase can be formed during FAU synthesis. This can be prevented by adding inorganic salt like NaCl. The FAU crystals remained stable in the presence of NaCl for a considerable amount of time after FAU crystallization was complete but before sodalite was formed. The growth of  $(Na_4Cl)^{3+}$  clusters keeps the sodalite cages stable in sodium FAU zeolite [91]. Figure 6 summarizes the general flow chart of the synthesis of any kind of zeolite and the factors affecting gelation and crystallization steps.

Zeolite also can be synthesized from natural aluminosilicate minerals such as kaolin, fly ash, agriculture waste, waste porcelain, and so on, and can be used to remove VOCs [92]. Natural zeolites have been proven to be useful in the treatment of oilfield wastewater and the sorption of volatile petroleum hydrocarbons [93]. Zhou [94] has successfully synthesized zeolites from coal fly ash (CFA) as adsorbents for volatile organic compound (VOC) removal along with modified by acid solution and mixed alkali solution (NaOH and KOH). In this work, it has been discovered that the crystallinity of the synthetic products increased with increasing concentration of the mixed alkaline solution which enhances VOC adsorption.

The "kaolin conversion process" is another commercial path to zeolite Y synthesis [95]. The benefit of this approach is that the beginning material, clay mineral, may be shaped to the appropriate catalyst particles before being converted to the zeolite phase. But, to induce zeolite formation a silicon source has to be added. For instance, kaolin that has been tempered and hydrated, along with zeolite seed crystals and sodium silicate, is suspended and spray-dried to produce micro granules. These granules are then treated at 98 °C with sodium silicate and sodium hydroxide to produce a catalyst that contains > 40 wt% zeolites NaY. To create the active catalyst phase, this material is subjected to dealumination and ion exchange[63]. To improve the silica content of Zeolite Y, post-synthesis modifications are performed rather than direct synthesis. Because the decrease of  $N_2O$ , SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and H<sub>2</sub>O in the gel would necessitate a substantially longer crystallization time [65].

When determining the structure and composition of the final zeolite product, the Si/Al ratio in the parent mixture plays an important role. In most cases, the Si/Al ratio in the precursor gel is greater than that in the crystalline result. The excess silicon is left in the mother liquid [65]. For example, Zeolites with 4, 6, and 8-member rings, such as zeolites A, F, X, Y, and sodalite, are often created at low Si/Al ratios, but at rising ratios, Mordenite, beta, and ZSM-5, zeolites which with 5 rings are formed. The primary reason for this is that two aluminium atoms do not prefer to be in the same 5-ring unit, but can easily be present in a 4-ring unit [73].

Low-silica FAU (X, Si/Al = 1–1.5) and high-silica FAU (Y, Si/Al = 1.5–3) can only be crystallized within a narrow Si/ Al ratio from the Na<sub>2</sub>O–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–H<sub>2</sub>O system by varying the batch composition. However, little success has been

![](_page_12_Picture_12.jpeg)

![](_page_13_Figure_4.jpeg)

reported for the synthesis of Y zeolite with Si/Al > 3 from this synthetic system [65]. Zeolites cannot be made simply by changing the Si/Al ratio of the parent mixture. They require unique synthetic circumstances, such as particular side-directing agents or secondary synthesis techniques, as discussed above. The relationship between the Si/Al ratio in the parent gel and that in the crystalline result is quite complex [65].

Zeolites with high silicon content promote VOC catalytic applications [96]. High silica zeolites have a more uniform surface and possess hydrophobic characteristics which are beneficial for organic molecules. These high silica zeolites are employed in catalytic processes using water-inhibited acid sites [97]. When silicon content is further increased, the organophilic nature increases the conversion of polar oxygenated hydrocarbons to kinds of paraffin and aromatics. The hydrocarbon transformation of zeolites is increased by the strong acidity of zeolites prepared via certain pathways, including  $NH_a^+$  and multivalent cation exchange, and steaming [70]. When the synthesis of high silica zeolites, side-directing agents are used in most cases. A hexadecyl trimethyl ammonium (HDTMA) surfactant-modified synthetic zeolite was studied by Vidal [98] for its efficiency in removing BTEX from aqueous solutions. Here, more than 95% of BTEX was eliminated when zeolite was treated with surfactant levels at 100% of the exchange capacity. This remarkable efficiency was most likely brought on by the hydrophobic surfactant monolayer that formed on the surface of the zeolite, which made it easier for organic molecule adsorption [98].

Calcination is another step of the synthesis of purified zeolites with enhanced properties. During calcination by ammonium or polyvalent cation exchange "bridging hydroxyl groups" are usually formed [63]. These "bridging hydroxyl groups" are protons associated with negatively charged framework oxygen linked into alumina tetrahedra, which are the Brønsted acid sites, as demonstrated in Fig. 7. The protons are quite mobile at higher temperatures, as at 550 °C they are lost as water molecules followed by the formation of Lewis acid sites, as shown in Fig. 7. A Lewis acid

![](_page_13_Picture_8.jpeg)

Fig. 7 Formation of Lewis acid sites in zeolite when calcination [63]

![](_page_14_Figure_5.jpeg)

site occurs as threefold-coordinated aluminium or silicon ( $\equiv$  Al or  $\equiv$ Si<sup>+</sup>), or extra framework aluminium-containing species such as AlO<sup>+</sup>. Lewis site also forms upon de-hydroxylation and dealumination of zeolites [63].

The catalysts that were calcined at higher temperatures exhibit significantly higher stability of both active metal component and catalyst's support showing greater resistance to leaching and adsorption of intermediate products of the reaction. In a study on copper-bearing 13X zeolite as a catalyst for the catalytic wet oxidation process with hydrogen peroxide as oxidant by Valkaj et al. [99], been investigated that total degradation of phenol can be achieved under mild operating conditions after post-synthesis thermal treatment of catalyst at 1273 K for 5 h [99].

These synthesis methods for Faujasite-type zeolites significantly affect their properties and efficiency in eliminating volatile organic compounds (VOCs). Conventional hydrothermal synthesis produces high-silica faujasite with good stability and high adsorption capacity [100]. These characteristics are crucial for the adsorption of larger VOC molecules as described above. Microwave-assisted synthesis improves crystallinity and results in more uniform pore structures. These mesopore volume characterized by cylindrical mesopores offers specific advantages for the desorption of volatile organic compounds (VOCs) and the regeneration of zeolites [34]. Templating methods or post-synthesis treatments can be used to create hierarchical zeolite with enhanced mass transfer and increased accessibility to active sites, beneficial for catalytic VOC oxidation [57]. However, the choice of synthesis method directly impacts the physical and chemical properties of faujasite zeolites, affecting their adsorption capacities, catalytic efficiency, and stability in VOC remediation applications.

#### 5.3 Cation modification of FAU zeolite

Post-synthesis modifications are typically performed on synthesized zeolites in order to fine-tune their catalytic characteristics. The most important and widely used post-synthesis modification procedures are ion exchange in aqueous suspension, solid-state ion exchange, and framework dealumination/desilication [63].

Dealumination and desilication are processes used to modify the structural and chemical properties of zeolites. Dealumination is often achieved through acid treatment or thermal methods, creating additional acidic sites and enhancing hydrophobicity by removing the framework aluminium atom [101]. In contrast, desilication involves removing silicon atoms using alkaline treatments, which increases porosity by introducing mesopores [102]. These modifications are crucial for enhancing the adsorption and catalytic properties of zeolites, particularly for volatile organic compound (VOC) remediation. Introducing mesopores via desilication improves the diffusion and accessibility of VOC molecules to active sites, while the enhanced acidity from dealumination improves the catalytic breakdown of these compounds [101]. Compared to their non-modified counterparts, dealuminated or disilicate Faujasite zeolites show higher efficiency in VOC removal in many publications due to their improved structural properties that facilitate better adsorption and

![](_page_14_Picture_12.jpeg)

![](_page_15_Figure_4.jpeg)

Fig. 8 Metal-containing zeolites types [105]

catalytic degradation of VOCs [88, 103, 104]. Additionally, changing the surface polarity of zeolite provides another advantage by controlling water adsorption.

When moving on to the cation modifications, three typical types of metal species supported by zeolites have been noted by Chai et al. [105]. These are metal species loaded on the crystals' exterior surfaces, metal species contained inside the channels or cavities of zeolites and metal species integrated into the framework of zeolites as represented in Fig. 8.

In Fig. 8 types (a), designated as metal/zeolites, are typically made by simple impregnation using zeolite supports and metal precursors. During the calcination processes, metal species always migrate and gather into larger fragments. In contrast, the metal species are effectively shielded by the zeolite frameworks in the samples of (b) indicated as metal at zeolites. Strong confinement effects may be produced by the intricate network of channels and micropores, and this can considerably reduce the development of particles into a given size region. While this is going on, guest molecules may freely reach the metal species that are contained in zeolites thanks to the interconnect channels of zeolites. Further extraction and reduction procedures are required to produce zeolite-supported metal particles in the samples of (c) designated as Me-zeolites, where metal species are integrated into the zeolite framework in the form of cations. In this case, depending on the specific extraction and reduction techniques, the samples of (c) can be converted to (a) or (b) [105].

Rare earth metals and transition metals have frequently been used to modify Faujasite zeolites. It has been noticed by Xu et al. [65] that the rare earth exchange activity of NaFAU (Na<sup>+</sup> as a counter-cation) is much higher than that of NaFAU and CaFAU, and its activation temperature is significantly lower. In this publication, they mentioned that upon rare-earth exchange, the surface acid sites in the Y zeolite are more broadly dispersed (even more extensively than in HY) and the acid strength of the acid centers is enhanced. Furthermore, after an exchange with Rare Earth (RE) 3p trivalent cations, the resultant RE-Y zeolite has greater thermal and hydrothermal stabilities than the Y zeolite exchanged with monovalent and divalent cations. To prepare a proper catalyst, re-exchange and calcination are required. The exchange degree is strengthened when the exchange-reaction temperature is raised to its optimum[65].

![](_page_15_Picture_10.jpeg)

There are still difficulties in the procedure, making it crucial to improve zeolite synthesis for the encapsulating of metal nanoparticles. Hauberg [106] introduced different approaches and their one synthesis method is centered on avoiding the usage of organic structure directing agents (OSDAs), which are harmful to the environment. A similar strategy was used to successfully encapsulate platinum nanoparticles with a size range of 1–2 nm in CHA zeolite by first encapsulating it to form CHA. Zeolites may be made without using any solvents, which lowers the amount of equipment needed for the process and increases reaction yields. Targeted alkenes exhibited full-size-selective hydrogenation by the produced platinum-containing zeolite[106].

Copper had been deposited on HY zeolite using three distinct methods by Singh in [107]; aqueous ion exchange  $CuY_{AIE}$ , wet impregnation  $CuY_{IMP}$  and precipitation-impregnation  $CuY_{PI}$  for oxidation of quinone. This study discovered that  $CuY_{AIE}$  and  $CuY_{IMP}$  had greater mineralization efficiencies and faster oxidation than  $CuY_{PI}$  [107]. In order to absorb VOC, silver-loaded zeolites were prepared using the ion exchange (IE) and incipient moist impregnation (IM) procedures in another study by Teng [108]. The impregnation approach of silver-loaded zeolites failed in the adsorption process. The outcome demonstrates a low VOC uptake capacity and an early breakthrough time. In comparison to AgZSM-5, AgY (IE) had the maximum VOC uptake capacity and adsorbent service time (IE). As a result, it can be seen that the ion exchange technique is the most effective way for cation modification of zeolites for VOC degradation.

Yi et al. [109] have noticed that the toluene adsorption capacity of regular 13X zeolite was outstanding, however, its catalytic capacity was poor. However, the catalytic performance was noticeably enhanced after adding Cu, Co, Ce, and Mg active compounds using the impregnation technique and the adsorption capacity was decreased. Co/13X demonstrated significant toluene adsorption capacity and excellent catalytic efficiency, with a carbon balance of 81.6% with 74.4% of CO<sub>x</sub> [109].

To remove toluene at low temperatures, Romero and his team have been working to create a bifunctional material that can be employed as both a catalyst and an adsorbent. Aqueous solutions of  $Cu(NO_3)_2 \cdot 2.5H_2O$  has used to synthesize copper zeolites for the sodium present in the parent NaX zeolite [110]. According to their study, the oxidation of toluene has been accelerated by the presence of evenly distributed CuO species. By measuring the adsorption isotherms at different temperatures, Benmaamar and Bengueddach [111] investigated the ability of NaY, BaY, KY, NaX and BaX zeolites to adsorb m-xylene and toluene. Comparing the NaX and NaY zeolites to the other samples, they showed the highest capacity for the adsorption of toluene and m-xylene. The order in which the adsorption affinities of m-xylene and toluene declined was NaY > NaX > BaX > KY > BaY. These findings highlight the great ability of the faujasite zeolites to eliminate m-xylene and toluene vapors at extremely low concentrations [111]. From this study, it's understandable that adsorption is influenced by the nature and position of cations inside the zeolite structure. According to cations used for this study, sodium (Na) ions form stronger adsorption sites than potassium (K) and barium (Ba) ions. This may be because the greater charge density of Na<sup>+</sup> ions improves their interaction with the molecules of the adsorbate. Not only cations but also adsorption is influenced by the zeolite framework's structure. Faujasite zeolites such as NaY and NaX have bigger pore sizes and higher surface areas, which often translate into more adsorption sites. But compared to NaX, NaY has a larger Si/Al ratio, which has an impact on its adsorption characteristics.

#### 5.4 Regeneration of the zeolite

Zeolites require less frequent regeneration than activated carbon, reducing costs and downtime. Regeneration after VOC adsorption is crucial for maintaining efficacy and extending operational life. Saturation diminishes adsorption capacity, necessitating efficient regeneration without damaging the zeolite structure. Several methods have been explored for regenerating VOC-saturated zeolites such as thermal regeneration, solvent regeneration, non-thermal plasma (NTP) regeneration and photocatalytic regeneration [112].

Thermal Regeneration involves heating the zeolite to high temperatures to desorb the VOCs. While effective, it can lead to the loss of adsorptive capacity and structural degradation over time [113]. Non-thermal plasma (NTP) has gained attention for its ability to regenerate zeolites at lower temperatures, thus preserving their structure and capacity. It can also enhance the catalytic activity of zeolites by activating adsorbed species, facilitating VOC degradation into harmless products [32]. Integrating photocatalysts like  $TiO_2$  with zeolites enables the use of UV light to degrade adsorbed VOCs in photocatalytic regeneration [114]. This method has shown promise, particularly in the decomposition of formaldehyde and other hazardous compounds, while also allowing for multiple regeneration cycles without significant loss in efficiency [114]. Solvent regeneration is a crucial aspect of managing VOC (volatile organic compound) remediation processes, especially in systems where solvents are used to extract or absorb contaminants. Effective solvent regeneration methods ensure the sustainability and economic feasibility of these systems by allowing the repeated use of solvents [115].

While thermal regeneration is energy-intensive and effective, it could damage the zeolite structure. Even though solvent regeneration uses less energy, it still has drawbacks including solvent management and possible secondary

![](_page_16_Picture_12.jpeg)

pollution. Low temperatures are used in non-thermal plasma regeneration to maintain the structural integrity of zeolites, although this process may result in undesirable byproducts. The best zeolite regeneration technique is determined by the particular application requirements, taking into account operational costs, environmental impact, and effectiveness. Nevertheless, non-thermal plasma regeneration provides a more balanced approach because it performs at lower temperatures while protecting the zeolites' structural integrity. It is particularly effective when combined with photocatalytic techniques to enhance VOC degradation without significant energy costs or structural damage.

The ongoing research focuses on improving the stability and adsorption effectiveness of zeolites during the regeneration process [44, 109, 116–120]. This involves the development of hybrid materials and refining the regeneration parameters. It can be suggested for future studies to integrate different regeneration techniques to take advantage of their benefits, for example, using non-thermal plasma (NTP) alongside photocatalysis to optimize the degradation of volatile organic compounds (VOCs) and extend the lifespan of zeolites.

# 6 Catalytic oxidation of VOC

#### 6.1 Heterogeneous catalytic oxidation for VOC removal

A catalyst is a material that participates in a chemical process in order to accelerate the process of reaching chemical equilibrium without reacting with the reactants in that particular reaction [61]. There may be several chemical reactions going on at once, but a correctly designed catalyst will decrease the barrier for the desired reaction, leading to much greater selectivity and, as a result, a proper product [121] (\\* MERGEFORMAT Fig. 9). The majority of catalysts are complex solid materials where the process occurs on the surface. This is known as heterogeneous catalysis, and it's available in both bulk and supported forms. Most are supported catalysts, with the active site supported on a large surface area, such as zeolites, and activated carbon, as discussed above. This aids in the dispersion and stability of the active phase, as previously described [80].

Heterogeneous catalysts are used in many industries since there are many advantages compared to homogeneous catalyzes such as easy separation of catalyst from the reaction mixture, high activity and selectivity etc.

The reaction takes place either on the external or internal surface of a porous solid. Heterogeneous reactions proceed via seven sequential processes (Fig. 10) [122]:

1. Mass transfer of reactants

2. Mass transfer of reactants

**Fig. 9** Simple energy profile diagram of VOC oxidation reaction with and without catalyst [121]

![](_page_17_Figure_13.jpeg)

![](_page_17_Picture_14.jpeg)

Fig. 10 Steps in a heterogeneous catalytic reaction

![](_page_18_Figure_3.jpeg)

- 3. Diffusion of the reactants to the internal catalyst surface
- 4. Adsorption of the reactants onto the catalyst surface
- 5. Reaction on surface
- 6. Desorption of the products
- 7. Diffusion of the products from interior pore
- 8. Diffusion away from the external surface

Then there are two ways of reaction steps, mass transfer-related steps (external diffusion and internal diffusion) which are fast and reaction kinetic-related steps (adsorption, reaction and desorption) which are slow. The rate of reaction is determined by the slowest step [122].

Heterogeneous catalytic oxidation is a promising technology that has been directed toward VOC degradation by a significant number of researchers in recent years [35]. This selectively converts VOC into harmless molecules and this technology is under the destruction category. In this method, VOCs oxidize in the presence of an appropriate catalyst at a temperature that is considerably lower than thermal oxidation, which may be approximated to be between 250 and 700 °C (thermal oxidation operates at nearly 760 to 1000 °C) [6]. As a result, heterogeneous catalysis consumes little energy and thus has a lower operating cost than other methods such as plasma catalysis and thermal oxidation. Furthermore, if used in recuperative mode, coupled with a heat exchanger after the catalytic combustion chamber, this can be more efficient [17].

The recent developments in catalytic combustion of VOCs over noble metal catalysts, non-noble metal catalysts, perovskite catalysts, spinel catalysts and dual functional adsorbent catalysts have been reviewed by Zhang and co-authors [121]. In that review, they discussed the effects of supports, coke formation, and water effects. Noble metals of Pt, Pd, Ag, Au, Ru, and Rh are mostly used as catalysts for VOC decomposition. Metal oxides employed as VOC oxidation catalysts are mostly derivatives of elements in periodic table groups III-B through II-B, such as Al, Ti, Mn, Fe, Co, Cu, Ce, and so on [121–123]. Regarding their review, it was determined that developing hybrid treatment technologies that are most effective in controlling VOC pollution [121]. Further research in catalytic oxidation is required to strengthen the understanding of the catalytic mechanisms involved in developing efficient and cost-effective catalysts for VOC removal [124].

![](_page_18_Picture_13.jpeg)

Urashima and Jen-Shih Chang [6], have provided brief characteristics of VOC removal technologies by demonstrating the application range concerning the relationship between concentration and gas flow rate for various VOC removal technologies. Catalytic oxidation is useful at moderate VOC concentrations (10–1000 ppm), but it's dependent on the gas flow rate [6].

Catalytic oxidation is simple to use in a small facility with short exhaust gas residence times. It's best suited for end-ofpipe VOC pollution control, and it's more effective with low-concentration effluent gas streams [23]. The disadvantage of catalytic technology is its lifetime is short and therefore catalyst replacement is required. If the target VOC is a mixed gas, catalytic activity is only effective for a specific type of catalyst. Due to the enormous diversity and nature of VOC mixtures, another challenge is selecting the appropriate catalyst from a huge number of available catalysts for catalytic VOC degradation [23].

## 6.2 Metal catalyst in zeolites for VOC abatement

The technique of catalytic oxidation of VOC includes bond dissociation or molecular rearrangement, which produces intermediates and products and is more practical and compatible with removal efficiency. There are numerous reports and patents on catalytic processes for VOC oxidation [17, 26, 48, 121, 124–126]. In the zeolite structure, acid–base pairs occur between the exchanged cations and oxygen atoms [127]. The more electropositive the cations, the higher the basicity of the zeolite. As discussed in previous sections, adsorption is commonly associated with catalytic oxidation using zeolites since it's the first stage in the oxidation process [35]; the VOCs can then be oxidized by the catalyst.

Metal oxides can provide improved thermal stability by selecting the appropriate catalyst composition. As a result, several studies have been carried out to eliminate VOCs by oxidation employing metal oxides such as  $MO_x$ , M = Ce, V, Cr, Mn, Co, Ni or Cu. Many studies have been conducted on catalytic oxidation processes using either noble metals (eg: Au, Pt, Pd, and Ag) or non-noble transition metal oxides. Noble metals are more active, but they are more expensive, toxic and thermally unstable due to sintering [80]. Because noble metals like platinum, palladium, and gold are expensive, hence significantly increase the initial investment for catalyst preparation. The sophisticated methods needed to incorporate these metals into zeolites also add to the cost. Additionally, the environmental impact of mining and refining these materials, including habitat destruction and pollution, raises concerns about the use of noble metals [128]. Also, by Nobel metals poisoning of active sites can occur [129].

However, noble-metal-based catalysts are extensively employed due to their efficacy in low-temperature VOC oxidation [130]. The noble metals most frequently used to oxidize VOCs are Pt and Pd. In terms of overall VOC oxidation activity, platinum is generally more active than palladium [131, 132]. In [131], AgY was shown to be the superior catalyst for the catalytic oxidation of butyl acetate over silver-loaded (HY and HZSM-5) zeolites due to greater metal dispersion, surface properties, acidity, and its pore structure. Methyl-isobutyl ketone (MIBK) was catalytically oxidized at low concentrations over numerous Pt/zeolite catalysts, including Pt/HFAU (Si/Al = 5 and 47) and Pt/HBEA (Si/Al = 50). In this investigation, Pt/HFAU(47) was likewise chosen as the catalyst with the highest activity over BEA zeolite. The temperature required to convert all of the MIBK decreases with increasing platinum concentration. Additionally, less platinum should be used in catalysts for improved performance [132].

Some researchers have concentrated on the incorporation of noble metals such as Au, Pt, Pd, Ru, and Ag into other metal oxides, which can improve catalytic activity due to their high electron transfer capabilities. However, this is dependent on the noble and transition metal composition and ratio [80, 123]. Additionally, synthesis methods, support, acidity, relative humidity, and physical characteristics all have an impact on the catalytic activity for VOC degradation. As a result, there has been a lot of interest in the catalytic activity-related preparation technique, the features of the support, and the physical structure, including the morphology, surface area, pore size, pore volume, and oxidation state[125]. Transition metal oxides such as copper, chromium, manganese, and nickel may withstand larger concentrations of toxins. However, their activity is often less than that of noble metal-based catalysts.

Auerbach [70] experimented with several zeolite structures, such as material (HY, FAU, HMOR, MOR, HZSM-5, MFI, and H-Beta BEA). Hydrophobic HY zeolite was shown to be the best adsorbent among the investigated zeolite adsorbents in this experiment, and its characteristics have been extended to the catalyst support by the addition of different transition metals (Fe, Co, Ni, Cu, Zn, Ag) and precious metals (Pt, Pd). Silver outperforms all other transition metals in the temperature-programmed surface reaction (TPSR) of toluene and methylethylketone (MEK). Temperature-programmed reductions (TPR) and O<sub>2</sub>-temperature programmed desorption (O<sub>2</sub>-TPD) on Ag/HY catalysts have been made to explain the nature of the Ag catalyst's active center for toluene oxidation. A possible active redox site during the oxidation

reaction was proposed to be a silver oxide species or partially oxidized metallic silver on the surface of the metallic silver phase [70].

The Cr-NaY zeolite produced after Cr(VI) biosorption was effectively reutilized as a catalyst in the oxidation of ethyl acetate, ethanol, and toluene in the study by Silva et al. [133]. There, XPS examination demonstrated that chromium is exchanged by the zeolite as Cr(III), and during calcination, the trivalent chromium was oxidized to Cr(VI), as validated by Raman and H<sub>2</sub>-TPR. In comparison to the beginning zeolite NaY, the introduction of chromium in the zeolite changed the chemical pathways, enabling a significant increase in activity and selectivity to  $CO_2$ . The following sequence is provided for VOC conversion: Toluene > ethanol > ethyl acetate [133]. Due to its several oxidation states, chromium among the transition metals is a fascinating metal to utilize in catalytic oxidation processes. In the oxidation of numerous contaminants, chromium catalysts have been extensively researched [133].

Therefore, the addition of two metals in the zeolite framework can significantly improve catalytic activity. According to research by Soares [76], ethyl acetate was entirely converted into carbon dioxide using duel metal catalysts based on NaY zeolite. Here copper served as the common cation in all  $M_1M_2$  catalysts, and NaY zeolite was ion-exchanged with copper, palladium, zinc, and silver as metal ions. Palladium significantly improves the parent zeolites' functionality, enabling the complete conversion of ethyl acetate to carbon dioxide (CO<sub>2</sub>). Then, the catalyst CuPd-Zeolite-Y has proven to be the most effective for this application among the examined metal phases [76]. Navlani-García[134] investigated preferential formic acid oxidation utilizing Pd and Cs nanoparticles supported on ion-exchanged ZSM-5 and Zeolite Y. The results reveal that catalytic performance is affected by the type of zeolite, its content, and the cation. They investigated a promising catalytic performance in all other samples except Pd/H-Y due to cation pore blockage and weak interaction. However, in long-term stability tests, Pd/Na-Y is appropriate for high formic acid conversion [134]. Shi et al. have introduced Ce species to USY zeolites and then Pt has loaded. These Pt/Ce-USY catalysts showed good catalytic activity for the elimination of non-chlorinated volatile organic compounds (VOCs) such as ethyl acetates, benzene, and n-hexane at low temperatures. By overcoming the issue of Zeolite's lack of active sites resulting from this dual metal ion substitution, they were able to develop a catalyst which has a strong oxidizing ability for the degradation of volatile organic compounds [135].

In another study, palladium was incorporated into zeolite FAU and BEA with different alkali metal cations (Na<sup>+</sup>, Cs<sup>+</sup> and H<sup>+</sup>) to investigate the impact of the type of alkali metal cations on palladium-based catalysts for propene and toluene oxidation [127]. The catalytic experiment was performed at temperatures between 25 and 300 °C (1 °C/min) for 100 mg of catalyst. In this work, total oxidation of propene and toluene was obtained since the reaction products include CO<sub>2</sub> and H<sub>2</sub>O. The catalysts based on zeolite FAU are more active than the BEA zeolites. Pd/CsFAU > Pd/NaFAU > Pd/HFAU is the activity order for FAU catalysts. Here, the catalytic activity is described in terms of VOC adsorption energies, cation electronegativity on Pd particles, Pd dispersion, and PdO reducibility [127].

A duel function adsorbent-catalyst process has been discussed in [136] with uncommon temperature swing oxidation of benzene, toluene and o-xylene (BTX) using CuO-CeO<sub>2</sub>/NaX as the catalyst. This procedure includes two steps: the adsorption of VOCs from the effluent gas flow, and the regrowth of the adsorbent-catalyst with temperature swing catalytic oxidation of the VOCs into CO<sub>2</sub> and H<sub>2</sub>O. The greatest rates of conversion of toluene, o-xylene, and benzene, respectively, are 99.3, 99.8, and 77.5% [136].

The prevailing preference for noble metal-supported catalysts for VOC catalytic oxidation can therefore be shown in several papers [16]. But concerning its negative impacts as discussed above researchers tend to use transition metals and metal oxides. Catalytic oxidation with transition metals can be improved by altering dual cations or dual metal oxides modification.

#### 6.3 VOC adsorption and oxidation in a mixture

In the real case scenario, the atmosphere contains a mixture of VOCs and other inorganic gasses. Therefore, it should be studied how a mixture of VOCs catalytically oxidized using the zeolite catalyst. Publications regarding VOC mixture oxidations with Zeolites are not abundantly available. However, in this section, a few selected publications are taken into account and to discuss mixture effects, articles with non-zeolite substrates have also been considered.

However, there is a significant research gap in the field of zeolites used for polluted gas remediation because some zeolites lack active sites with sufficient oxidizing activity, which leads to the oxidation of combinations of volatile organic compounds. This issue has been addressed by Shi et al. [135] who synthesized a Pt/Ce-USY zeolite catalyst using ethylene glycol reduction (r) and ion exchange (ex) methods. They examined the degradation of dichloroethane (DCE) in the presence of benzene. The Pt/Ce-USY-ex catalyst showed minimal influence and was characterized

![](_page_20_Picture_13.jpeg)

as having greater oxygen mobility caused by the  $Pt-CeO_2$  interaction. However, the DCE conversion rate decreased in the presence of benzene compared to single DCE over both catalysts. The decrease in DCE degradation could be due to the accumulation of carbon species on the zeolite surface as a result of the oxidation of non-chlorinated hydrocarbons [135]. So, these carbons may cover the active sites of the zeolite catalyst.

Numerous studies have clearly demonstrated that there is a notable difference between the oxidation of a single volatile organic compound (VOC) versus a mixture of VOCs. The latter typically exerts an inhibitory effect, primarily due to competitive processes such as adsorption competition and reaction competition with the chemisorbed oxygen present on the catalyst's active sites [47, 137] and also reaction intermediates or by-products may cover the active sites [138]. Takeuchi et al. have proposed that the surface area plays a critical role in toluene or benzene adsorption, as opposed to other surface characteristics [139].

The interactions of various species with the catalyst lead to significant variations in the oxidation of VOC mixtures when compared to single VOCs. Predicting the effects of VOC combinations is a challenging task. Although changes in selectivity to by-products during the oxidation of VOC mixtures have been noted, promoting effects are rarely observed [140, 141]. Promotion effects perhaps because the entire oxidation cycle is exothermic, raising the temperature of the catalyst surfaces [137]. However, obtaining a beneficial effect in the oxidation of VOC mixtures is highly dependent on various factors such as the type of catalysts used, the appearance of the reaction mixture, and the operating parameters. However, predicting the catalyst's behavior is challenging due to the complex nature of the process involved [138]. Furthermore, in a VOC mixture, predicting the catalytic oxidation of a componentbased only on its single-component behavior is not accurate. Therefore, the interaction between the VOCs must be considered [142].

The majority of articles state that volatile organic compounds (VOCs) are ordered as follows: alcohols > aldehydes > aromatics > ketones > alkenes > alkanes [47]. The order in which VOCs degrade is determined by the strength of the substrate's weakest C-H bond. It has been noted in many studies that, aromatic compounds hinder aliphatic hydrocarbons from oxidizing. Barresi and Baldi [143] investigated the deep catalytic oxidation kinetics of several aromatic hydrocarbons using a commercial platinum catalyst. According to this research, they found that the order of reactivity of the component mixtures was styrene > o-xylene > ethylbenzene > toluene > benzene. Here it can be seen a pattern with the substituted group to the benzene. The  $\pi$ -complex that forms are stable and oxidation is favored if there are methyl groups on the aromatic ring. The inhibitory effects grew stronger as the adsorption strength increased [143]. According to a study by Colman Lerner et al. [137], the order of VOC degradation over Pt/Mn catalysts supported on ceramic monoliths was MEK > Xylenes > Toluene. This is different from the prior sequence, and the increased conversion of MEK compared to toluene and xylene can be attributed to the different reactivity of these reactants with the same lattice of oxygen on the catalyst. The study also suggests that the size, polarity, and dipole moment of the reactant molecules may be related to their degradation [137]. The same sequence is obtained by Burgos et al. [144], and they also investigated, the order of adsorption on Pt-impregnated metallic monoliths is 2-propanol > MEK > toluene. Here again, the polarity of volatile organic compounds (VOCs) is a critical factor in their adsorption preference on the support. However, the complete oxidations of toluene and MEK were not affected by other VOCs, suggesting that these compounds undergo direct oxidation from the gas phase while oxygen atoms chemisorb on Pt. The relative reactivity of the compounds does not seem to be influenced by their competition for oxygen atoms. Therefore, it's accurate to describe potential toluene or MEK adsorbed on the support as mere observers of the oxidation process [144].

The inhibitory effects are mostly observed in many mixtures of VOCs in research publications. In the study by Ordóñez et al. [145], the use of a commercial Pt on gamma-alumina catalyst to catalytically oxidize benzene, toluene, and n-hexane in air, was examined both individually and in binary combinations. The findings revealed that n-hexane did not impact the conversion of benzene and toluene; however, the presence of either substance hindered hexane from combusting. Furthermore, when aromatic chemicals are in a mixture together, they inhibit one another [145]. This behavior may be qualitatively explained considering the higher affinity of the aromatic compounds for the catalyst surface. Concerning the benzene–toluene mixture. All these results also suggest that the toluene-surface interaction is stronger than in the case of benzene due to the presence of the methyl group. The same results have been obtained by He et al. [146] and they investigated the catalytic oxidation of benzene, toluene, and ethyl acetate over a Pd/ZSM-5 catalyst. However, promoting effect has been observed in toluene oxidation when ethyl acetate was added, due to the exothermic nature of the entire oxidation reaction, which raised the surface temperature of the catalyst. But, in the presence of ethyl acetate, benzene-surface interaction, resulting in the inhibition of benzene on the oxidation of toluene being stronger than that of toluene on the oxidation of benzene [146].

![](_page_21_Picture_8.jpeg)

According to research conducted by Sahraoui et al. [140], for aliphatic compounds it was discovered that the inclusion of ethyl acetate in the reaction mixture resulted in a decrease in the rate of butanol oxidation. This outcome may be attributed to a potential competition between butanol and ethyl acetate molecules for the adsorption sites or oxygen atoms, leading to this inhibitory effect [140].

The research conducted by Aguero et al. [141] aimed to determine the catalytic efficiency of a manganese oxide catalyst supported by alumina towards mixtures of VOCs. The study focused on ethanol, ethyl acetate, toluene, and mixtures of them. The research revealed that toluene was the most reactive compound as in the previous studies, followed by ethanol and ethyl acetate. Competition for adsorption sites between polar molecules, ethyl acetate and ethanol, occurs during oxidation. Ethyl acetate inhibits ethanol oxidation due to weaker adsorption on the surface [142]. However, toluene influences acetaldehyde production, promoting ethanol and ethyl acetate partial degradation. Toluene is the one that reacts with the chemisorbed oxygen on the catalyst most readily, and the competition is mostly for the chemisorbed oxygen atoms on the catalyst rather than for the adsorption sites. The same results have been obtained by Santos and co-workers [141] for the same compounds of mixtures.

It has been observed by Z. Wang et al. [147] that the presence of toluene does not affect the catalytic mechanism for the oxidative removal of toluene and acetone from a mixture. However, the presence of toluene can greatly inhibit the oxidation of acetone. The reaction pathway for the oxidative removal of toluene and acetone from the mixture may correspond to that of the oxidation of individual toluene or acetone. So the author claims that the conversion of these compounds is also dependent on the adsorption capacity [147].

Researchers López-Fonseca et al. [148], have studied the oxidation of 1,2-dichloroethane (DCE), dichloromethane (DCM), and trichloroethylene (TCE) in binary mixtures over three protonic zeolites, H-ZSM-5, H-MOR, and chemically dealuminated H-Y zeolite. The findings indicated that H-MOR and chemically dealuminated H-Y zeolites had the highest degradation activity for the binary mixes. The reason for this could be that coke has a mild deactivation impact because interconnected channel systems of H-ZSM-5 and H-Y offer multiple pathways to the active sites. It has been observed that the degradation of these chlorinated mixtures inhibits the reactivity of each other because of the competition for adsorption sites [148].

In a report by Brunchi [149], 21 commercial adsorbents of various classes were tested in batch adsorption experiments for their adsorption capacity toward a six-component mixture containing butanal, 2-ethyl-2-hexenal, 2,6-dimethylcyclohexanone, 2,4,6-trimethylanisole and 2,4,6-trimethylphenol as impurities and toluene as the solvent. The Na version of FAU-type zeolite functioned well. However, this work demonstrates that, in theory, if an appropriate force field is provided, simulations may be used to predict the adsorption behavior of the analyzed six-component combination. The binary systems with toluene were explored since the IAST (Ideal Adsorption Solution Theory) predictions were away from the experimentally obtained isotherm. IAST predicted the adsorption behavior of the six-component combination in NaY at low concentrations. Deviations were noticed at high concentrations [149]. There are two plausible explanations for this result: (1) non-ideal behavior of the adsorbed phase, or (2) improper fitting of the pure-component adsorption data over the range of high concentrations [150].

Becker and Förster conducted a study comparing the effectiveness of four different catalysts—NaY, CuY, PdHY, and PdY—in deep oxidation reactions of various aromatics, including benzene, toluene, and xylene. Their results revealed that PdY is the most active catalyst even at low concentrations. In contrast, CuY only showed detectable effects when copper content was no more than 1 wt%. The researchers hypothesized that the differences in activity between PdY and CuY are primarily due to the various states in which copper and palladium exist in the zeolite matrix. Additionally, benzene oxidation was found to be enhanced when the reaction with toluene occurred over PdY [151].

Over basic zeolites (CsX and NaX) and an acidic zeolite (HY), the catalytic oxidation of isopropanol and o-xylene in combination was studied by Beauchet and coworkers [47]. The basicity of the zeolite enhances the conversion of the VOC mixture into CO<sub>2</sub> for a given temperature. The results show that VOCs oxidize over NaX via a basic process and over HY via an acidic mechanism. Due to the formation of isopropyldimethylbenzenes via an acidic process, isopropanol increases the oxidation of o-xylene over HY. Isopropanol completely decomposed over HY zeolite between 200 and 300 °C, whereas o-xylene did so between 250 and 300 °C. Additionally, they discovered that adding platinum to zeolites accelerates the rate of VOC oxidation; this behavior is more pronounced when using PtHY, probably because of a higher Pt dispersion [47].

Over platinum-assisted catalysts, the catalytic oxidation of ethanol/toluene mixtures was also investigated by Ostrovsky [152]. Here, mutually inhibiting occurrences were noted, with ethanol providing a considerably clearer example. It was suggested that the competition for the oxygen atoms chemisorbed on the Pt particles is what causes the inhibitory effect.

![](_page_22_Picture_11.jpeg)

Beauchet et al. [153] have investigated the catalytic oxidation of isopropanol and o-xylene via basic NaX zeolite as single components and in a mixture. According to the results, o-xylene inhibits the degradation of isopropanol whereas isopropanol has no impact on o-xylene. The inhibitory impact of o-xylene appears to be caused by the adsorption of these aromatic VOCs close to the apertures of the NaX super-cages, which restricts isopropanol's access to the basic active sites of this zeolite, according to adsorption tests and molecular modelling. Additionally, the synthesis of secondary products (propene, coke) as a result of the isopropanol transformation is influenced by the adsorption of o-xylene close to the sites that might start its degradation is restricted by the adsorption of o-xylene close to the super-cage apertures of the NaX zeolite. Additionally, due to the simple dehydration of isopropanol, o-xylene competes with propene on the oxidation sites, increasing the selectivity towards propene and decreasing CO<sub>2</sub> production while increasing coke formation [153].

Guo et al. [129] have also pointed out in their review article that there is a mutual effect on the catalytic oxidation of mixed volatile organic compounds (VOCs). Therefore, it's crucial to consider this. By gaining a better understanding of how these catalysts interact with each other, researchers may be able to produce more affordable catalytic reactors and effective catalysts for industrial applications [129].

These indicate that zeolite catalytic oxidation of mixtures of VOCs remains difficult to discover. The inhibiting impact is the usual problem with this. Therefore, in this review, we recommend for future experiments, the modification of the zeolite structurally such that it has a variety of sites and channels that let a wide range of VOCs enter the inner surfaces and quickly oxidize them there before further VOCs arrive in the mixture. This idea can be related to size-exclusive chromatography.

#### 6.4 Advanced oxidation processes

Advanced oxidation processes (AOPs) have been identified as extremely effective and environmentally acceptable methods for removing hazardous organic contaminants from industrial effluent. It's being studied as a direct method for treating water or gas streams, and intriguingly, adsorbents can offer a favorable environment for oxidation reactions [154]. APOs rely on the usage of strong oxidizing species for example hydroxyl radicals ( $\cdot$ OH) or sulfate radicals (SO<sub>4</sub>-), produced by various modes of operation. Hydroxyl radicals are highly reactive and efficient at breaking down organic molecules, creating an oxidative environment that effectively attacks and decomposes VOCs. Sulfate radicals are particularly useful in environments where hydroxyl radicals may be less effective, providing an alternative for VOC degradation [155].

Numerous technologies have been explored as AOPs, including conventional and catalytic ozonation processes,  $O_3/Hydrogen peroxide (H_2O_2)$ , photocatalytic processes, electrochemical processes, ozonolysis, etc. [154]. Then, it can be seen that advanced oxidation processes (AOP) combine catalysts (such as transition metal ions), semiconductor materials, and sources of ultrasound or radiation with powerful oxidants like ozone, oxygen, or hydrogen peroxide. The oxidative capacity of advanced oxidation processes (AOPs) is used to start a series of chemical reactions that break down pollutants. Radicals can remove electrons from organic molecules, breaking the chemical bonds in pollutants. This process can alter the molecular structure of volatile organic compounds (VOCs), creating intermediate compounds that are further oxidized until they are completely mineralized [156].

Singh [107] reported that catalytic wet peroxide oxidation (CWPO) is a potential choice due to its capacity to degrade pollutants to  $CO_2$ ,  $N_2$ , and inorganic ions at low operating temperatures (about 100 °C) and atmospheric pressure [107] (Fig. 11).

In research by Ramakrishna [157], advanced oxidation methods utilizing ozone have been examined for the treatment of dioxane. In order to do this, wet impregnation was used to synthesize Fe-supported Zeolite-13X (Fe/zeolite-13X) catalysts with varying Fe concentrations. The primary byproducts of the catalytic oxidation of dioxane by air are CO and CO<sub>2</sub>, while small traces (less than 3%) of acetaldehyde, ethylene glycol mono format, ethylene glycol diformate, 1,4-dioxane-2-ol, 1,4-dioxane-2-one, and 2-methoxy-1,3-dioxalane are also formed. At 400 °C the Fe/zeolite-13X catalyst with 6 wt% Fe had the greatest catalytic activity, with 97% dioxane conversion and 95% selectivity for the production of carbon oxides (CO and CO<sub>2</sub>) [157].

In another experimental study by Monneyronet al. [154], the catalytic ozonation process was employed on a laboratory scale to treat the air polluted with BTEX chemicals as indicators of VOCs. This procedure was carried out in the presence of ZnO nanoparticles coated on a zeolite medium. The catalytic ozonation process in this scenario consists of several sub-processes, including the catalytic ozonation itself (ZnO/zeolite), adsorption, and simple ozonation. Additionally, they discovered that catalytic ozonation was more effective than simple ozonation and adsorption procedures. This method could bring the concentration of BTEX pollutants below the recommended limit [154].

 $H_2O_2$ -based AOPs are capable of providing more active species to the reactant and can effectively eliminate the pollutants in the reaction medium because of the homogeneously produced  $\cdot OH$  from  $H_2O_2$  in the solution. Numerous

![](_page_24_Figure_4.jpeg)

Fig.11 Proposed mechanism of CWPO of VOC on CuY<sub>IMP</sub> [107]

experiments have been conducted using appropriate metal catalysts that suggest that this approach may be suitable for the degradation of VOCs. The Fenton reaction, which produces hydroxyl radicals (OH) by the catalytic reaction of Fe(II)/Fe(III) in the presence of hydrogen peroxide, is one of the most studied AOPs. Fe and Cu cations have been utilized in the majority of situations for reactions of the Fenton type [107, 158–164]. The general Fenton mechanism is represented below with Fe cation [165].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$
(1)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H + H^+$$
 (2)

$$Fe^{2+} + \cdot O_2H \rightarrow Fe^{3+} + O_2H^-$$
 (3)

$$Fe^{3+} + \cdot O_2H \rightarrow Fe^{2+} + O_2 + H^+$$
 (4)

$$H_2O_2 + \cdot OH \rightarrow O_2H + H_2O \tag{5}$$

One of the numerous varieties of Fenton processes is the heterogeneous solid catalyst that we discussed in this article. The Fe(III) species are "immobilized" in the structure, pore, and interlayer space of such catalysts, which explains why zeolite mediates Fenton-like reactions throughout a wide pH range. This allows the catalyst to continue producing hydroxyl radicals from  $H_2O_2$  and prevents the precipitation of iron hydroxide. The catalysts continue to work throughout successive processes and have less iron ion leaching in addition to being easy to recover after the reaction.

As  $H_2O_2$ -based advanced oxidation processes (AOPs) may make it easier to remove VOCs,  $UV/H_2O_2$  was used [164] to degrade continuous-flow gaseous toluene in the batch system for the first time. However, several organic intermediates were produced in the UV/Fenton and Fenton solution processes, which oxidized the majority of the removed toluene into  $CO_2$ . The continual production of  $\cdot$ OH was primarily attributed to the better performance of the  $UV/H_2O_2$  process. This study shows that the  $UV/H_2O_2$  process may be used to treat VOCs in an effective and environmentally safe manner [164].

Advanced Oxidation Processes (AOPs) are highly valued for their ability to degrade a broad spectrum of VOC contaminants without producing secondary pollution. This makes them a sustainable choice for environmental purification efforts. The effectiveness of these processes depends on factors such as the concentration of pollutants, the presence

![](_page_24_Picture_15.jpeg)

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Table 3 Summary table	of FAU-type zeolite catalysts and metho	ods used in VOC removal		
Zeolite Type	Modification on Zeolite	Remediated VOC	Removal mechanism	Refs.
NaX	Pt	Tetrachloroethylene (PCE) and Methylethylketone (MEK)	Adsorption/Catalytic oxidation 94% conversion CO <sub>2</sub> of PCE, 92% conversion of MEK	[126]
HY (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 80)	Ag	Toluene	Catalytic oxidation (95% removal)	[166]
HY (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> =80)	Silver metal	Butyl acetate (BA)	Adsorption/Catalytic oxidation	[108]
NaY	Cr(VI)	Ethyl acetate, ethanol and toluene	Oxidation Ethyl acetate 100% Ethanol 39% Toluene 70%	[133]
NaY (Si/Al=2.556)	I	Butanal, 2-ethyl-2-hexenal, 2,6-dimethylcyclohexanone, 2,4,6-trimethylanisole, 2,4,6-trimethylphenol	Adsorption (total 215.7 mg/g)	[149]
TiO <sub>2</sub> /Y-zeolite	TiO2	Toluene and Benzene	Hybrid photocatalysts	[139]
H-Y zeolite	dealumination via ammonium hex- afluorosilicate treatment	1,2-dichloroethane (DCE), dichloromethane (DCM) and trichloroethylene (TCE)	Adsorption (DCE > DCM > TCE ~ 100%	[103]
NaX and USY	Dealumination	Toluene and dichloromethane	Adsorption	[167]
Zeolite HY	Silver-loaded	Butyl acetate	Catalytic oxidation	[131]
M-13X-Zeolite	Acid and steam treatments	Toluene	Adsorption	[168]
Commercial Zeolite	TiO2	Toluene	Advanced oxidation processes (80%)	[164]
Zeolite-Y (DAY and PtY)	Dealumination and Pt supported (IE)	n-Hexane	Microwave-heated adsorption and catalytic oxidation (67%)	[169]
13X zeolite	Zeolite coating	n-Hexane	Adsorption (131-175 mg/g)	[170]
Zeolite-Y	HDTMA-modified	BTEX	Adsorption (95%)	[98]
NaX zeolite	CuO-CeO <sub>2</sub> Co-impregnated	ВТХ	Adsorbent/catalyst Total oxidation = 77.5%-B, 99.3 -T, 99.8%-X	[136]
Zeolite13X	Ozone environment	Toluene	90% conversation	[171]

![](_page_25_Picture_5.jpeg)

of radical scavengers, and the method used for radical generation. As a result, AOPs play a critical role in modern air purification technologies, addressing the pressing need for efficient and eco-friendly pollution control methods.

In Table 3, an overview of previous research on volatile organic compound (VOC) depletion using a variety of modified Faujasite zeolite catalysts through different remediation mechanisms is provided, as briefly discussed in the present review study.

# 7 Conclusion

Zeolite has a wider range of pore sizes and the hydrophobicity of its surface increases by dealumination. The acidity of zeolite is the major feature influencing the catalytic oxidation of organic contaminants. Because of their higher acidity and accessibility of simple synthesis techniques, FAU zeolite catalysts have been used for the majority of VOC remediation. Numerous studies have shown that the best method for cation modification of zeolites for VOC degradation is the ion exchange method. In order to remediate VOCs, Faujasite zeolites have regularly been modified using rare earth elements and transition metals. Zeolites with a high pore size are more beneficial for the elimination of VOC because they have better sorption characteristics. Therefore, it's important to select the appropriate process parameters since the morphology of the microstructures of materials created under various circumstances changes. When compared to other traditional techniques for removing VOCs, catalytic oxidation is the most effective one. In certain papers, simulation-based prediction models have been investigated to better understand the adsorption of VOC mixtures. Studies on the remediation of VOC mixtures using zeolite catalysts are still lacking. Due to their increased oxidation activity toward VOC oxidation, FAU and MFI-type zeolite catalysts containing metal cations such as Pt, Pd, Fe, and Cu are the most often utilized. The oxidation of VOC mixtures differs significantly from that of single VOCs due to complex interactions with catalysts, leading to inhibitory effects and variations in oxidation efficiency and product formation. Further research in this area is essential for developing improved catalytic systems for environmental and industrial applications. However, because of its rapid reactions, advanced oxidation is also receiving a lot of attention in this scenario. Then, by taking into account all relevant factors, cation-modified FAU-type zeolite can be employed in VOC remediation, and by enhancing the oxidation process by AOP, interesting results would be obtained.

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