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Transition metals-incorporated zeolites as environmental catalysts for indoor air ozone decomposition

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ABSTRACT

The present study aimed to prepare catalysts of Fe- and Cu-loaded zeolite via ion-exchange technique using dilute solutions of metal nitrate precursors followed by calcination at 600°C in the air for 4 h. Commercial zeolite ZSM-5 with specific surface area of 400 m²/g and diameter particle of 1.2–2 mm was used as a parent support. The prepared catalysts were characterized by Fourier transform infrared spectroscopy analysis. The IR absorbed bands of Cu-ZSM-5 and Fe-ZSM-5 revealed a shift in the frequency and a reduction in the intensity framework. This indicates that both catalysts have a significant change in the number of the zeolite structure bonds. The catalytic activity of the prepared materials compared to the parent zeolite was evaluated for the catalytic ozone decomposition. The ozone stream of the initial concentration (13 g/m³) with air flow rate (Q) of 0.18 m³/h was passed through a glass jacket column reactor filled with a fixed bed of 40 g zeolites. It was showed that the ozone removal efficiency by Cu-ZSM-5 and Fe-ZSM-5 was obviously higher than that found with the parent ZSM-5. In terms of O₃ removal efficiency, zeolite samples could be ranked as follows: Fe-ZSM-5 > Cu-ZSM-5 > parent ZSM-5. The results revealed about 90% O₃ removal efficiency for Fe-ZSM-5 and 70% for Cu-ZSM-5 as compared to nearly 40% for the parent zeolite. Consequently, the incorporation of Fe and Cu metals onto the zeolite surface plays a key role for enhancing the gaseous ozone elimination.

1. Introduction

Among indoor air pollution problems, the presence of ozone in the ground atmospheric layers is a significant factor. Ozone is a toxic substance commonly found or generated in human environments as a result of its use. It is widely used in water disinfection, cleaning of contaminated gases, and sterilization in medical use [1]. The exhaust gases from these processes contain residual ozone, which could be above the acceptable value. Furthermore, in indoor working environments, several sources can be responsible for ozone formation such as photocopiers, laser printers, fax machines, and sterilizers [2]. The current Occupational Safety and Health Administration (OSHA) standard for ozone is 0.1 part per million (ppm) in air; ozone is highly toxic above this concentration and long-term exposure to ozone can cause lung damage [3,4]. Thus, the removal and decomposition of ozone from the human environment became an essential issue. The catalytic ozone decomposition using microporous materials is of great significance. Activated carbons are one of these

adsorbents which had been used for ozone elimination [5]. Using activated carbon for this purpose has many disadvantages; safety conditions have to be taken into consideration since activated carbon could be flammable [6]. Moreover, the activated carbon could be exhausted by the long-term use of AC, leading to deterioration of its physical and chemical surface properties [7]. Recently, low cost natural and synthetic zeolites appear as alternative materials for gaseous ozone removal from contaminated indoor air [8]. The zeolites framework of [SiO₄]⁻⁴ and [AlO₄]⁻⁵ tetrahedral bonded together via oxygen atoms [9]. Hence, they generate a high internal surface area available for adsorption and catalytic processes [10]. They possess well-defined uniform pores and crystal structure, thermal and chemical stability, and are easy to use in the ion-exchange method [11]. Zeolites have been applied as catalysts in the advanced oxidation processes in combination with ozone for the oxidation of volatile organic compounds from industrial emissions [12–16]. For gaseous ozone regression over zeolites at ambient conditions, there are only few reported investigations. Two mechanisms are proposed: decomposition

of ozone on strong Lewis acid sites and then its adsorption on weak acidic sites [17]. Nevertheless, there are still some doubts about the nature of chemical interactions between ozone and zeolite surface active sites.

On the other hand, the transition metals and their oxides have been found to be the most active substances for ozone decomposition [2]. Zeolite is characterized by its ability to participate in ion-exchange reactions [10]. The incorporation of various transition metal ions, such as iron, copper, and cobalt ions, into these materials can significantly change the chemical properties of zeolites making them active and efficient catalysts for several redox processes [18]. The crystal structure of ZSM-5 is composed of two types of channel systems with similar size and 10-membered oxygen ring. Straight channels have an oval cross-section of $5.3 \times 5.6 \text{ \AA}$ and sinusoidal channels with cross-section of $5.1 \times 5.5 \text{ \AA}$. These two types of channels are perpendicular to each other and generate microporous volume network of diameters of 8.9 \AA . Na ZSM-5 zeolite is basic and a typical catalyst, but its catalytic ability is poor. Through ion exchange, that is, Na^+ from the framework is substituted by H^+ and forms HY zeolite which has unselective acid sites located on the external surface. Furthermore, the hydrothermal stability of HY zeolite is very poor. The presence of protons gives the ZSM-5 zeolite the ability to exchange with transition metal ions. Modification of ZSM-5 including incorporation of transition metal ions leads to good catalytic activity and good hydrothermal stability. The catalytic properties of transition metal zeolites are strongly influenced by the composition, location, and structures of the reactive metal species introduced into the microporous space [19].

Among several methods, aqueous ion exchanges are the most commonly used for preparing zeolite with transition metals. The resulting material contains aqueous metals in the pores and cavities of the zeolite. Upon high temperature treatment, water is removed and the metal coordinates to oxygen's surface of the exchange sites. Several authors have studied the performance of the transition metals in zeolites or on other supports for different organic compounds' catalytic oxidation [20–22].

In this paper, we will focus firstly on the preparation of transition metals Cu and Fe loaded on zeolite ZSM-5 (commercial zeolites) by the conventional ion-exchange method. These catalysts are thus able to work at a low reaction temperature and both Fe and Cu were used as active components for ozone decomposition. The prepared catalysts were then characterized by Fourier transform infrared (FT-IR) techniques and scanning electron microscopy (SEM) assays. The second objective of this work was to compare the activity of parent

zeolite ZSM-5 with the prepared catalysts Cu-ZSM-5 and Fe-ZSM-5 toward the decomposition of ozone. Understanding their structures and performance for ozone decomposition might lead to the development of novel active and selective oxidation catalysts.

2. Material and methods

2.1. Catalyst preparation

Commercial zeolite ZSM-5 with specific surface area of $400 \text{ m}^2/\text{g}$ and diameter particle of 1.2 mm was provided by Zeochem Co. and directly used as the parent zeolite in this study. The main characteristics of adsorbents are given in Table 1. The parent zeolite (40 g) was added to 500 mL of 0.1 M nitrate aqueous solutions of $\text{Cu}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ and the ion exchange was then carried out under vigorous stirring for 48 h at room temperature. After the ion exchange, the zeolite was filtered, thoroughly washed with deionized water, dried overnight at 100°C , and then calcined at 600°C for 4 h in the air and denoted as Fe-ZSM-5 and Cu-ZSM-5.

2.2. Material characterization

Characterization of the parent (ZSM-5) and modified zeolites (Fe-ZSM-5 and Cu-ZSM-5) was performed by FT-IR spectroscopy (Perkin-ElmerSpectrum, USA) to describe the surface functional groups. The information about solid surface morphology (size, shape, and pore distribution) was given by SEM assays (QUANTA-200, Philips).

2.3. Experimental setup

Figure 1 shows the schematic diagram of the experimental setup; the pilot reactor was composed of a glass jacket column of 45 mm inner diameter with a height of 160 mm . The experimental conditions are summarized in Table 2. The reactor was filled with a fixed bed of 40 g zeolites. An air stream of ozone was introduced into the reactor bottom. Ozone gas was generated by electrical discharge of the air (Labo5LO Trailigaz ozoner kind). The feed pipes were Teflon and stainless steel. Sampling

Table 1. Main characteristics of the parent zeolite ZSM-5 sample.

Parameters	Parent zeolite ZSM 5
Clay binder content (%)	20
Crystalline framework	Interconnected channels
Pore internal diameter (\AA)	($5.7 * 5.1$) and 5.4
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (mol/mol)	1880
Active porous volume (cm^3/g)	0.18
Na_2O (wt%)	<0.01
Bulk density (g/cm^3)	0.4–0.5
Pellet diameter (mm)	1.5–2

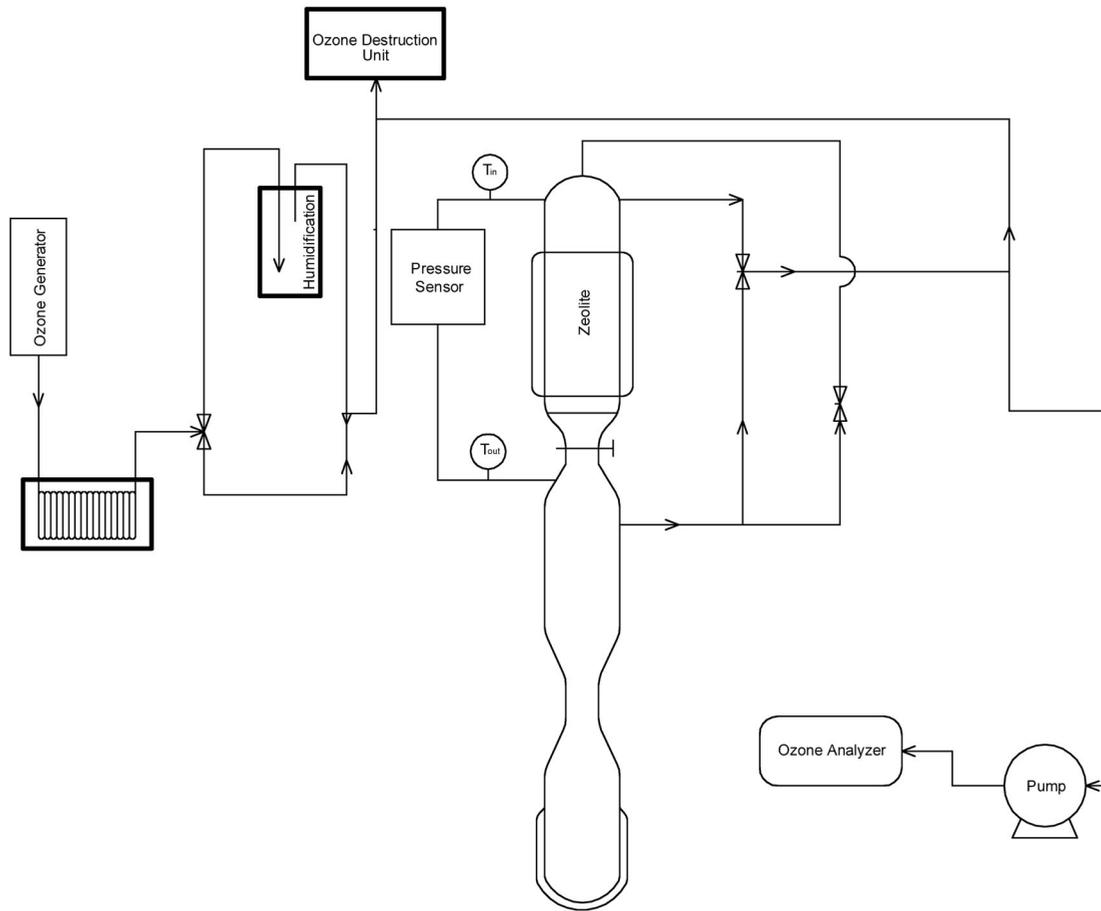


Figure 1. The schematic diagram of the experimental setup.

of the gas phase was performed in the inlet and outlet of the reactor and sent by a diaphragm pump to an UV ozone analyzer (MT 964 BT Messtechnik GmbH, Berlin Germany). The production of ozone is a function of the pressure (0.7 bar) and the air flow rate (Q), which was set at $0.18 \text{ m}^3/\text{h}$ with applied power of 90 W. Prior to the experiment, the ozone stream was passed for an hour to stabilize the ozone initial concentration. The inlet concentration of O_3 was adjusted to 13 g/m^3 . The output of the ozone generator and the ozone-containing air flow can be moistened with a sparging system in a water column. Ozone outlet concentration was recorded continuously by UV absorbance at 254 nm with an ozone analyzer. The device was connected to a continuous data

acquisition system with software (BMT link 964 V1.10). The moisture content of the effluent could be measured by a portable hydrometer. The temperature was measured continuously at the inlet and outlet of the reactor by Pt100 temperature sensors used to monitor the temperature by digital displays (WEST 6010) fixed on the control cabinet. During each experiment, the zeolite bed was weighed at the end to calculate the difference in weight of zeolite. The exhaust gas stream was sent to an ozone destroyer before discharging into ambient air. The amount of ozone consumed was calculated by integrating the difference between the ozone amounts of column input and output during the experiment. Calculating the amount removed (g/g) is expressed by the following equation (Equation (1)):

$$q = \int_0^t \frac{(C_0 - C) \cdot Q_v \cdot dt}{m}, \quad (1)$$

where Q_v is the volumetric flow rate (m^3/min), C is the gas phase concentration at the reactor outlet (g/m^3), m is the mass of the zeolites (g), C_0 is the reactor inlet ozone concentration (g/m^3), and t is the time needed for the zeolite to reach saturation with ozone.

Table 2. Experimental conditions during the ozone decomposition by zeolite catalysts using the pilot reactor.

Parameters	Values
Reactor internal diameter (mm)	45
Ozone air flow, Q (m^3/h)	0.18
Superficial velocity (m/s)	0.032
Ozone concentration (g/m^3)	13
Bed mass (g)	40
Ozone pressure (bar)	0.7
Ozone generator power (W)	90
Ozone flow (g/h)	0.9 3.6

The ozone removal efficiency (%) was calculated on the basis of equation (Equation (2)), where C refers to the concentration.

$$\text{Removal efficiency (\%)} = \frac{C_{\text{inlet}} - C_{\text{outlet}}}{C_{\text{inlet}}} \times 100. \quad (2)$$

3. Results and discussion

3.1. Fourier transform infrared spectrometry

Figure 2 depicts the FTIR spectra for the parent zeolite ZSM-5, Fe-ZSM-5, and Cu-ZSM-5. The absorption features of zeolite samples resulted in different absorption peaks at a range of 400–4000 cm^{-1} . Based on the literature, peaks at 3640 cm^{-1} can be assigned to O–H groups attached to extra-framework alumina species [23]. The peak at 3744 cm^{-1} represents the stretching silanol groups (Si–OH) and the vibration at 1660 cm^{-1} can be assigned to the deformation band of adsorbed water [24]. Hassan and Hameed [25] reported that the region from 1600 to 3700 cm^{-1} is ascribed to the existence of zeolite water molecules. The zeolite framework also revealed peaks at a range of 1203–1077 cm^{-1} which are assigned to the complex of Si–O–Si asymmetric stretchings whereas the bands of 796–580 cm^{-1} could arise due to Si–O–Si symmetric stretchings. Moreover, the bands of 580 and 460 cm^{-1} could be assigned to Si–O–Si linkages of the alumino-silicates framework [26]. The peak at 800 cm^{-1} could be ascribed to the vibration of Al–O–Si [27]. Comparison between the band intensities of the individual samples before and

after introducing Fe and Cu into zeolites allowed investigating the structural changes with respect to Fe-, Cu-, and Al-related acid sites. The coordination of Fe and Cu ions with the framework bridging oxygen atoms was documented by an intensity decrease in the stretching vibration band of OH– groups at 3640 cm^{-1} . This decrease in hydroxyls concentration is consistent with the removal of Al from the framework leading to the formation of an extra-framework Al species and condensation of silanol groups. The bands of Cu-ZSM-5 and Fe-ZSM-5 demonstrated a significant change in the frequency shift or a reduction in the intensity framework. Thus, Cu-ZSM-5 and Fe-ZSM-5 catalysts have a significant effect on the number of the zeolite framework bonds.

3.2. Scanning electron microscopy

To study the morphology of zeolites, the solid samples were characterized by SEM before and after the ion exchange treatment. The SEM photographs are shown in Figure 3. It can be observed that the parent ZSM-5 zeolites (Figure 3(A)) have coffin-shaped particles of an average size of about 3–5 μm . Similar morphology and particle size were observed for the modified zeolites; Fe-ZSM-5 and Cu-ZSM-5 (Figure 3(B) and (C), respectively). Therefore, it can be concluded that the morphology of ZSM-5 zeolite remained practically unchanged after the ion exchange treatment. The only detectable difference between these catalysts is that the modified zeolites have metallic (Fe–Cu) particles dispersed as aggregate clusters located at the surface of ZSM-5 and the presence of these metals

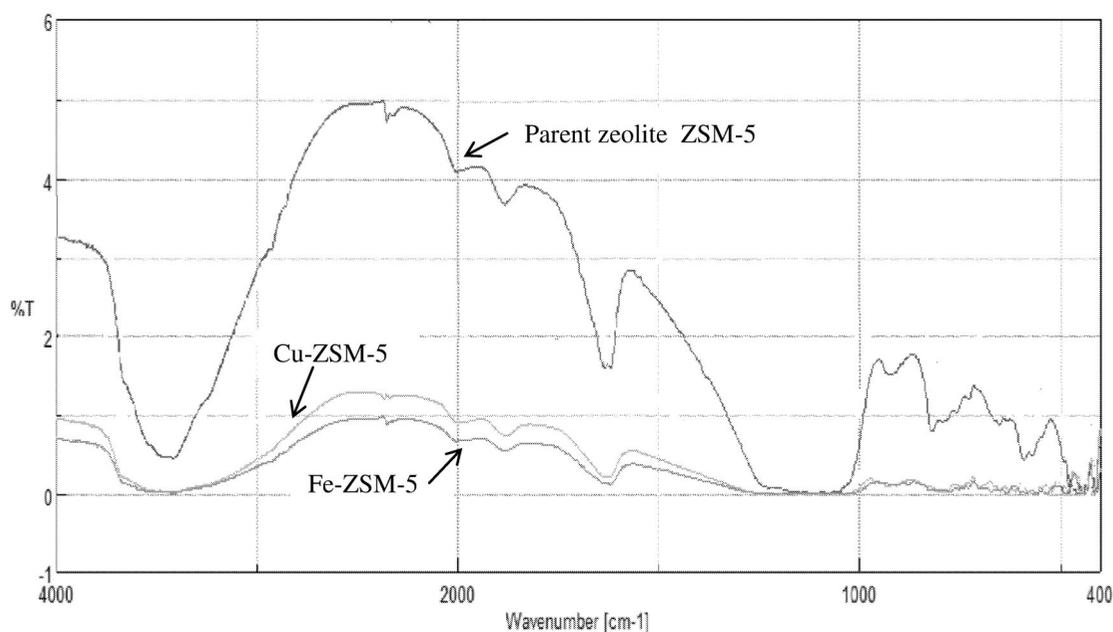


Figure 2. FTIR spectra for the parent zeolite ZSM-5, Fe-ZSM-5, and Cu-ZSM-5.

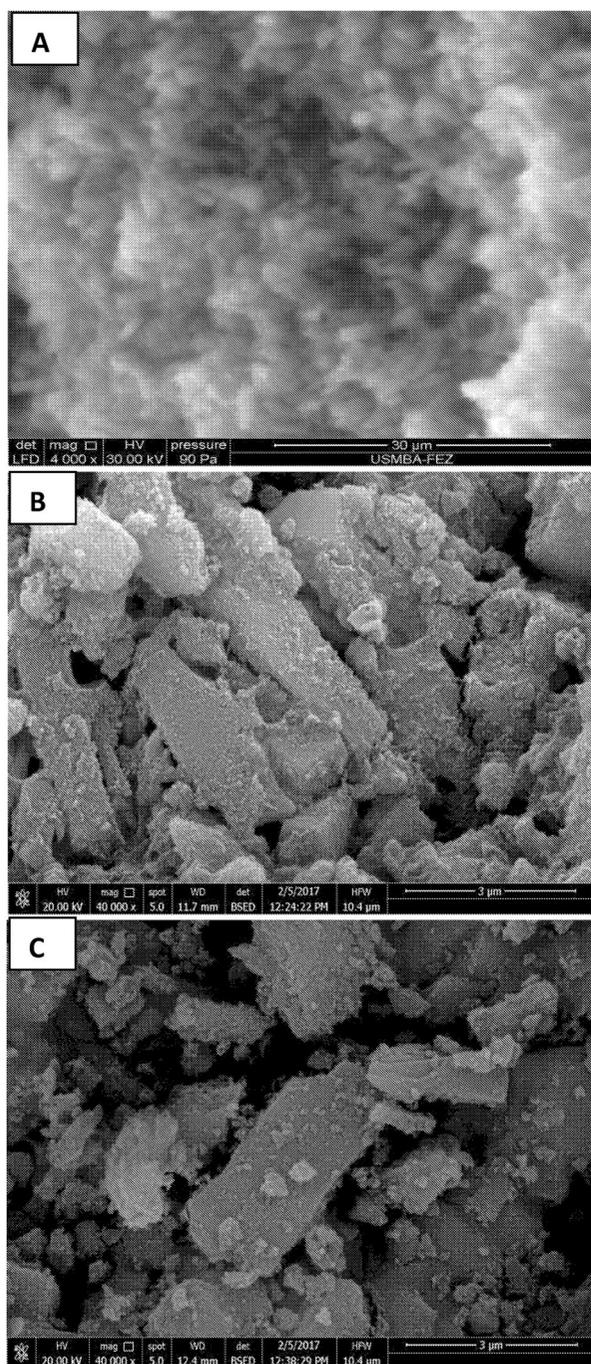


Figure 3. SEM photographs of the parent ZSM-5 (A), Fe-ZSM-5 (B), and Cu-ZSM-5 (C).

(Fe and Cu) on the modified zeolites is confirmed by the EDX analysis. The size of the metal particles varies at a range of 20–50 nm.

3.3. Catalytic performances of parent and transition metals-loaded zeolite

Figure 4 shows the catalytic activity of O_3 elimination over parent zeolite ZSM-5, Fe-ZSM-5, and Cu-ZSM-5.

The behavior of parent zeolite ZSM-5 toward the ozone decomposition was very dissimilar to that of Fe-ZSM-5 and Cu-ZSM-5. As shown in Figure 4, for the parent zeolite ZSM-5, a classical adsorption breakthrough curve was obtained. It was clear from the results that the physical adsorption of ozone took place onto the parent zeolite during the breakthrough time of 300 min, and its slope was increased as the ozone concentration increased.

The presence of low Lewis acid sites' concentration could be explained by these results, where the molecular ozone could be adsorbed via coordinative bonding with weak Lewis acid sites. A similar observation was reported by Izumi et al. [28] who only observed reversible physical adsorption of ozone gas stream on different ZSM-5 for temperatures below 0°C due to the high aluminum content of ZSM-5. Furthermore, ozone could be transformed immediately after adsorption on strong Lewis acid sites and decomposed into O_2 and an active atom of oxygen that could participate in catalytic removal of ozone [17]. The structure of zeolite is another factor that could play a fundamental role in ozone removal. The ratio of ozone molecular size (5.8 \AA) to zeolites pore diameter is defined as λ ; it is 1.05 in the case of ZSM-5 and ozone diffusion could then be hindered [29].

However, when Fe-ZSM-5 and Cu-ZSM-5 samples were used, a very high catalytic ozone conversion was observed after 30 min from the beginning of the reaction. Then, the catalyst activity decreased after

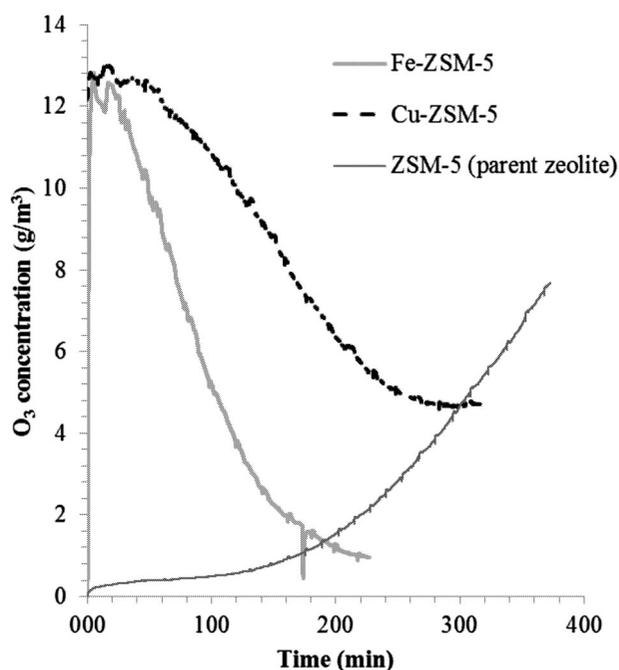
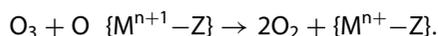
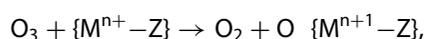


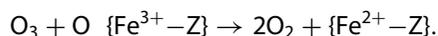
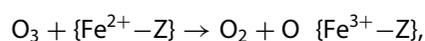
Figure 4. Catalytic performances of parent zeolite ZSM-5, Fe-ZSM-5, and Cu-ZSM-5 samples toward ozone decomposition.

150 min and remained finally stable for the remaining duration of the reaction. In this case, the reaction started with very high activity for ozone conversion to oxygen due to the presence of free metals catalytic centers. These results could be related to the fact that the transition metals' ions preferably occupy exchange sites in six-membered oxygen rings where the transition metals coordinate with the oxygen atoms of Al tetrahedra. Moreover, removal of the extra-lattice oxygens during high temperature pre-treatments could result in auto-reduction. Oxidation of reduced transition metals' sites often results in the formation of highly reactive oxygen species [30].

When the ozone streams are made to flow over the catalyst and when the new free centers are accessible, the catalyst then converts the O₃ molecules. Therefore, Fe and Cu metals loaded to the parent zeolite ZSM-5 increase the number of decomposition-active sites by modifying the surface. The difference in zeolites' activities could be related to the formation of metals-containing active sites. According to the literature [31–32], ozone decomposition on the M-ZSM-5 catalyst (M: Cu or Fe) follows this mechanism:



Transition metal oxides with several oxidation states could potentially show good catalytic performance in ozone decomposition. In the case of Cu-Z and Fe-Z catalysts, we have redox couples including Cu⁺/Cu²⁺ and Fe²⁺/Fe³⁺. These couples could be represented by the following reaction mechanism:



Panov et al. [33] reported the formation of the so-called α -sites core in Fe-ZSM-5 by reacting the zeolite with N₂O. Several studies evaluated the possible bi-nucleate metals' species formed in zeolite upon calcination in O₂; from the calculations of Yumura et al. [34], both sides-on peroxo and bis (μ -oxo) di-metal cores were found to be energetically favorable in ZSM-5. In previous study, many oxygen bridged bi-nuclear metal sites were reported in zeolite reaction with N₂O [35–37]. In the work of Costa et al. [38] and Palomino et al. [39] and Xamena et al. [40], an oxygen bridged metal dimer was proposed to be formed during the auto-reduction of two hydrated metal cores.

The reaction speed of the ozone conversion decreased gradually due to deactivation of the active sites with time. Furthermore, it was noticed that the

rate of O₃ decomposition by Fe-ZSM-5 catalysts was faster than that found by Cu-ZSM-5. This result suggested that Fe metal oxide could increase the catalytic activity of parent zeolite more than Cu metal oxide. These results could be explained by the higher activity of Fe ions than Cu ions according to the electrochemical series. Thus, Fe reacts with ozone faster than Cu, leading to ozone decomposition. Bataklijev et al. [2] investigated catalysts based on metals and their oxides in different oxidation levels and found that the catalytic activity of these metal oxides was increased by increasing the metal oxidation state. The catalytic activity degree of a number of elements to the decomposition of ozone was in the order Cu < Ag < Ni < Fe < Au < Pt. Similarly, Sugasawa and Ogata [41] found that the order of catalytic activity in the case of O₃ decomposition was Fe = Ni = Ag = Co = Mn > non-supported ZSM-5.

Generally, the reactivity of Fe-ZSM-5 and Cu-ZSM-5 toward O₃ decomposition is directly related to the presence of specific extra framework metal-containing cationic species in the micropores of ZSM-5 zeolite. Several studies demonstrated that the mononuclear oxygenated metal species for zeolites modified with Fe, Zn, Al, and Cu tend to self-organize into bi-nucleate oxygenated active cores [42–44].

Figure 5 shows the effect of metal oxide loaded onto zeolite ZSM-5 on the O₃ removal efficiency. It was showed that O₃ removal efficiency was obviously higher with Fe-ZSM-5 and Cu-ZSM-5 than that with the parent zeolite ZSM-5. In terms of O₃ removal efficiency, metal oxide catalysts could be ranked as follows: Fe > Cu. It was found that, O₃ removal efficiency reached 90% by Fe-ZSM-5 compared to zeolite ZSM-5 alone (40%); however, O₃ removal efficiency was 70% by Cu-ZSM-5. A similar observation was reported by Huang et al. [45] who found that Metals/ZSM-5 catalyst activity toward ozone decomposition was increased to 80% and kept stable after a long run. Kumar et al. [46] reported that for Ag-modified aluminosilicates, Beta and MCM-41 zeolites showed a very high decomposition of ozone (98% conversion for Ag/MCM-41 catalyst and almost 44% for Ag-modified Beta zeolite). Genov et al. [1] also cited that Ag loaded onto Bulgarian natural zeolite allowed decomposition of O₃ to O₂ at room temperature with a relatively high activity of 85%.

Figure 6 shows the evolution of temperature difference (ΔT) between the inlet and outlet of the adsorbent bed reactor as a function of time during ozone removal by Fe-ZSM-5, Cu-ZSM-5, and parent zeolite ZSM-5. The temperature profiles enabled us to explain the ozone removal mechanism. By using Fe-ZSM-5 and Cu-ZSM-5 catalysts, the concentration of ozone in the output decreased and the reaction temperature increased. The

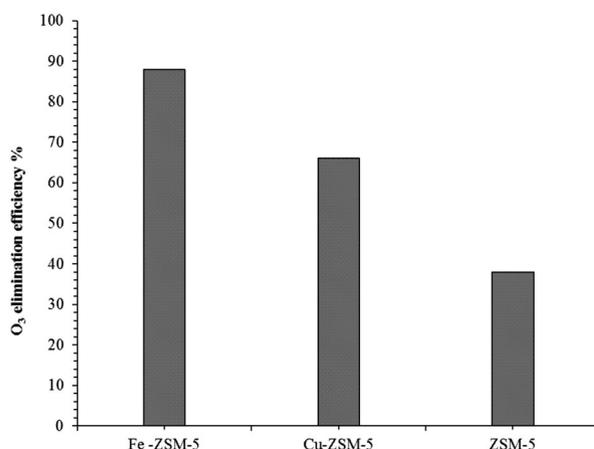


Figure 5. Ozone removal efficiency of ZSM-5 (parent zeolite), Fe-ZSM-5, and Cu-ZSM-5 samples.

full decomposition of ozone was almost completely at nearly 150 min with a rapid increase in the temperature (Figure 6). After 150 min, the temperature slowly increased and the decomposition of ozone was less effective and the behavior of ozone output concentration was very similar. For the parent zeolite ZSM-5, the temperature at the first few minutes (10 min) was increased and at the second part of the curves, the temperature was approximately stable. The temperature profile of parent zeolite ZSM-5 is thus an indicator of the ozone adsorption mechanism. With all zeolite samples, the temperature was increased by ozone decomposition. The increase in temperature in both Fe-ZSM-5 and Cu-ZSM-5 was much higher than that found in case of the parent zeolite ZSM-5, indicating that the ozone decomposition is an exothermic reaction. The temperature was rapidly increased in case of parent zeolite ZSM-5, then stabilized, and finally it decreased

gradually when the ozone concentration increased. According to this point, a significant oxidation of adsorbed compounds could be deduced. Ozone adsorption was predominant in the parent zeolite ZSM-5; however in the case of Fe-ZSM-5 and Cu-ZSM-5, the ozone decomposition was predominant. Similarly, Imamura et al. [47] found that the oxides of transition metals exhibit higher catalytic activity for the decomposition of ozone; moreover the conversion degree of ozone and their catalytic activity was arranged as follows: MnO₂ (42%) > Co₃O₄ (39%) > NiO (35%) > Fe₂O₃ (24%) > Ag₂O (21%) > Cr₂O₃ (18%) > CeO₂ (11%) > MgO (8%) > V₂O₅ (8%) > CuO (5%) > MoO₃ (4%).

Figure 7 shows that the quantity of ozone eliminated varies linearly from input ozone concentration for both Fe-ZSM-5 and Cu-ZSM-5. It may be supposed that in this case the decomposition was initiated by the Fe

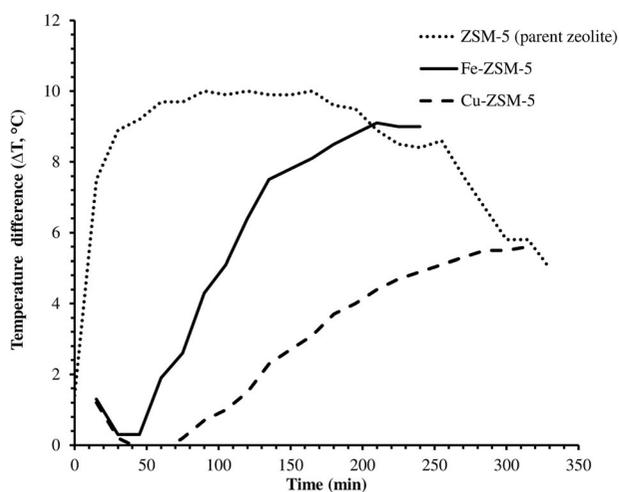


Figure 6. Comparison of temperature difference (ΔT , °C) between the inlet and outlet of the adsorbent bed reactor during ozone decomposition by Fe-ZSM-5, Cu-ZSM-5, and parent zeolite ZSM-5.

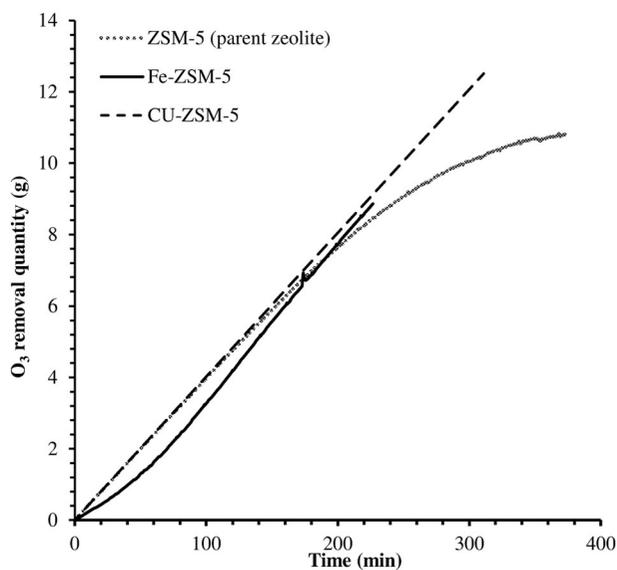


Figure 7. Quantity of ozone eliminated with the time using Fe-ZSM-5, Cu-ZSM-5, and parent zeolite ZSM-5.

and Cu metals' oxides on the zeolite surface leading to a high ozone decomposition rate. In the case of parent zeolite ZSM-5, O₃ elimination was firstly increased gradually by increasing the quantity of input ozone, and then O₃ elimination was constant and reached a steady state indicating the saturation of the parent zeolite ZSM-5. The decomposition was initiated by the hydroxyls groups or by the local heterogeneity of the zeolite framework [48]. During the ozone decomposition, very reactive species involved in some complex radical chain reactions leading to a total decomposition of the inlet ozone [49]. Investigation into the O₃ decomposition mechanism shows that the incorporation of metal into zeolite ZSM-5 reduces the activation energy for desorption of chemisorbed oxygen, then the rate-determining step, and thus improves the catalytic performance.

4. Conclusion

In this research, we found that transition metals Fe and Cu loaded onto zeolite ZSM-5 significantly enhanced the O₃ decomposition activity in comparison with the parent zeolite. As derived from FTIR spectra, the incorporation of Cu and Fe metals in zeolites causes a significant change in the number of zeolite framework bonds. It was found that, O₃ removal efficiency reached 90% by Fe-ZSM-5 compared to the parent zeolite ZSM-5 (40%); however, O₃ removal efficiency was 70% by Cu ZSM-5. These excellent properties of metal oxide catalysts could be attributed to the good dispersion of metals on the zeolite framework, the formation of framework Al O metal species, as well as the possible synergy between the active sites (zeolite and metal sites), making this catalyst a cost-effective candidate for catalytic O₃ elimination. Consequently, the deposition of transition metals in zeolite ZSM-5 improves the catalytic performance.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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