

Article

A Hybrid Reactor System Comprised of Non-Thermal Plasma and Mn/Natural Zeolite for the Removal of Acetaldehyde from Food Waste

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Abstract: The degradation of low concentrations of acetaldehyde while using a non-thermal plasma (NTP)/catalyst hybrid reactor system was investigated while using humidified air at ambient temperature. A series of highly active manganese-impregnated natural zeolite (Mn/NZ) catalysts were synthesized by the incipient wetness method using sonication. The Mn/NZ catalysts were analyzed by Brunauer-Emmett-Teller surface area measurements and X-ray photoelectron spectroscopy. The Mn/NZ catalyst located at the downstream of a dc corona was used for the decomposition of ozone and acetaldehyde. The decomposition efficiency of ozone and acetaldehyde was increased significantly using the Mn/NZ catalyst with NTP. Among the various types of Mn/NZ catalysts with different Mn contents, the 10 wt.% Mn/NZ catalyst under the NTP resulted the highest ozone and acetaldehyde removal efficiency, almost 100% within 5 min. Moreover, this high efficiency was maintained for 15 h. The main reason for the high catalytic activity and stability was attributed to the high dispersion of Mn on the NZ made by the appropriate impregnation method using sonication. This system is expected to be efficient to decompose a wide range of volatile organic compounds with low concentrations.

Keywords: non-thermal plasma/catalyst hybrid reactor system; manganese-impregnated natural zeolite; acetaldehyde; odor from food waste

1. Introduction

The increase in volatile organic compounds (VOCs) has become an important environmental issue worldwide, because VOCs are typically odorous substances that can cause discomfort and have an adverse impact on human health [1,2]. In addition, VOCs that are emitted from food waste are considered to be a severe problem in Korea, and the government has been trying to reduce the levels of VOCs to improve health and quality of life. Especially, acetaldehyde is one of the main odorous components generated during food waste decomposition, and it is generally difficult to degrade than other components. Various methods, including adsorption [3–7], thermal and catalytic oxidation [8], and photo-catalysis [9,10], have been applied for the removal of high concentrations of VOCs in air.

On the other hand, conventional removal methods are unsuitable for removing low concentrations of VOCs because of their low efficiency and high cost [11]. Therefore, alternative technologies need to be developed to overcome the limitations of conventional methods, which cannot be applied effectively for the removal of low concentrations of VOCs.

Non-thermal plasma (NTP) techniques offer an innovative approach for the removal of VOCs [1,12,13]. The oxygen and other oxidative species generated by plasma are able to oxidize VOCs. On the other hand, the formation of highly toxic and reactive by-products, such as NO_x and ozone [14,15], during the removal of VOCs while using the NTP technology is considered to be a problem with this system. Since ozone is a powerful oxidant and residual ozone can damage facility or hurt life, ozone is the most undesirable by-products in the NTP discharge zone and is thermally stable above 250 °C [16]. The additional use of a catalyst for the removal of VOCs using NTP technology might remove VOCs and reduce the undesirable by-products of NTP technology. The removal efficiency of ozone depends on the position of the catalyst. A comparison of in-plasma catalysis (IPC) and post-plasma catalysis (PPC) processes has shown that PPC technology has higher performance for the removal of ozone [16]. The temperature and humidity of the PPC process are also very important for the removal of VOCs emitted from food waste. Stable activity of PPC under ambient temperature and humidity that is higher than 50% is necessary for the successful application to the removal of ozone and VOCs from food waste. Despite this, most of the experiments were performed at high temperatures, up to 200~700 °C [17], without considering humidity.

Many types of catalyst have been applied widely for the removal of VOCs while using the PPC process [17]. Several catalysts, such as $\gamma\text{-Al}_2\text{O}_3$, SiO_2 , TiO_2 , and zeolites, have been used for the complete oxidation of VOCs, and various types of metal, such as Ag, Cu, Pd, Pt, Ni, Co, Fe, and Mn, have been used as coating or impregnation materials on these catalysts to provide additional catalytic activity [18]. Among them, Mn has been widely used as an impregnated metal for the removal of VOCs [11,19,20]. On the other hand, its actual application is limited to vehicles and indoor air control because high temperatures are required to provide the high and rapid response for odor removal. The negative impact of humidity in air and the high cost of the catalyst limit the applicability of the catalytic process to the removal of VOCs from food wastes. In this aspect, the PPC technology has a potential application for the removal of VOCs. A successful approach for the removal of VOCs and ozone while using the cost-efficient PPC process needs to be tested under high humidity and ambient temperature, so that this process can be applied to food waste.

In this study, a post-NTP/catalyst hybrid system was developed for the removal of VOCs from food waste. To enhance economic feasibility, natural zeolite (NZ) was applied as a catalyst support instead of synthesized catalysts. Also, low cost NZ was applied to develop the economic removal process of VOCs from food waste. Because NZ has showed good catalytic activity for toluene oxidation activity [21,22], high catalytic activity of NZ for acetaldehyde oxidation could be expected. However, NZ has never been applied to the plasma/catalyst hybrid system for decomposition of acetaldehyde. Mn/NZ, which was prepared by the incipient wetness method with sonication, was used as a catalyst at the downstream of the NTP reactor, and acetaldehyde was used as a model food waste VOCs pollutant. A higher relative humidity with 60% and ambient temperature was applied to form a plasma at the discharge zone and the effect of humidity on the removal of VOCs and the formation of ozone in the NTP/catalyst hybrid system was evaluated by comparing the removal efficiency of acetaldehyde and ozone in the system.

2. Results and Discussion

2.1. Characterization of the Catalyst

The Mn/NZ by the incipient wetness method with sonication were characterized by Brunauer-Emmett-Teller (BET) surface area measurements and X-ray photoelectron spectroscopy (XPS). Table 1 lists the specific surface area and the surface atomic concentrations of the NZ or the

Mn/NZ. The Mn loading on the NZ had a significant effect on the specific surface area and surface atomic concentration. The specific surface areas of the raw NZ, 1 wt.% Mn/NZ, 3 wt.% Mn/NZ, 5 wt.% Mn/NZ, 10 wt.% Mn/NZ catalyst, and 10 wt.% Mn/NZ catalyst without sonication were 134.8, 29.3, 25.2, 21.4, 20.9, and 19.1 $\text{m}^2 \text{g}^{-1}$, respectively. The specific surface area of the Mn/NZ catalyst was much lower than that of raw NZ. The Mn atomic concentration increased with increasing Mn loading on the NZ. The 10 wt.% Mn/NZ showed a higher surface atomic concentration of Mn when compared to the 10 wt.% Mn/NZ calcined at 550 °C or the 10 wt.% Mn/NZ without sonication, despite their equal Mn loading. The surface atomic concentration of impregnated Mn on NZ is related to the dispersion of Mn [23]. Thus, this suggests that the introduction of Mn was well dispersed on the surface of the NZ when the Mn/NZ was treated by the incipient wetness method with sonication.

Table 1. Characteristics of the Mn-impregnated natural zeolite catalysts.

Catalysts	BET Surface ($\text{m}^2 \cdot \text{g}^{-1}$)	Surface Atomic Concentration (%)				
		O	Al	Si	Ca	Mn
raw NZ	134.8	65.3	4.54	22.32	0.65	0
1 wt.% Mn/NZ	29.3	65.6	4.80	21.96	0.67	1.04
3 wt.% Mn/NZ	25.2	64.22	4.23	19.86	0.75	3.10
5 wt.% Mn/NZ	21.4	62.15	3.49	17.76	0.84	7.37
10 wt.% Mn/NZ	20.9	55.73	1.47	7.72	1.05	20.14
10 wt.% Mn/NZ (550 °C)	-	59.71	2.77	13.95	0.85	14.61
10 wt.% Mn/NZ without sonication	19.1	54.65	1.49	7.06	2.87	17.09

The surface elemental compositions, such as the Mn oxidation states and adsorbed oxygen species, were investigated by XPS. Figure 1 shows the XPS spectra in the O 1s and Mn 2p binding energy regions at different Mn loadings. Figure 1A shows the Mn 2p XPS spectra of the samples in the 633~660 eV range. The binding energies at the 640.0~650.0 eV and 650.0~660.0 eV regions were attributed to Mn 2p 3/2 and Mn 2p 1/2, respectively. The Mn loading of the Mn/NZ catalysts has a significant impact on the distribution of surface Mn. The O 1s spectra in Figure 1B show different features, which depend on both the chemisorbed lattice oxygen (O_2^-) and the adsorbed oxygen species (i.e., O_2^- , O^- , and O_2^{2-}). Overall, the peak at 529.7~530.1 eV corresponds to O_2^- , and the peak at 531.1~531.7 eV was assigned to O_2^- , O^- , and O_2^{2-} [24]. The XPS data show that the MnO_x of the 1 and 3 wt.% Mn/NZ had only adsorbed oxygen species, whereas the MnO_x of 5 and 10 wt.% Mn/NZ had both lattice oxygen species and adsorbed oxygen species. In the 10 wt.% Mn/NZ, the binding energy of the lattice oxygen species was stronger than that of adsorbed oxygen species. In particular, more oxygen lattices were observed in sonicated 10 wt.% Mn/NZ than 10 wt.% Mn/NZ without sonication. Figure 2 shows the Mn 2p and O 1s XPS spectra of the 10 wt.% Mn/NZ catalysts that were obtained at different calcination temperatures. The Mn 2p spectra of the catalyst can be assigned to three components corresponding to Mn^{2+} , Mn^{3+} , and Mn^{4+} species on the surface of the catalysts [25]. As shown in Figure 2A, the catalyst at different calcination temperatures showed peaks for Mn^{2+} , Mn^{3+} , and Mn^{4+} species, but no significant differences were observed in the surface Mn^{n+} content. The O 1s spectra in Figure 2B show that asymmetrical O 1s can be fitted with three components, such as the adsorbed lattice oxygen species, adsorbed oxygen species, and water. In the 10 wt.% Mn/NZ calcined at 350 °C or 550 °C, the MnO_x has lattice oxygen (O_2^-) and adsorbed oxygen species. The 10 wt.% Mn/NZ calcined at 350 °C shows that there is a higher content of lattice oxygen species than adsorbed oxygen species. Previous studies reported that the samples that were possessing larger amounts of surface lattice oxygen or adsorbed surface oxygen have higher catalytic activity for VOC oxidation [24,25].

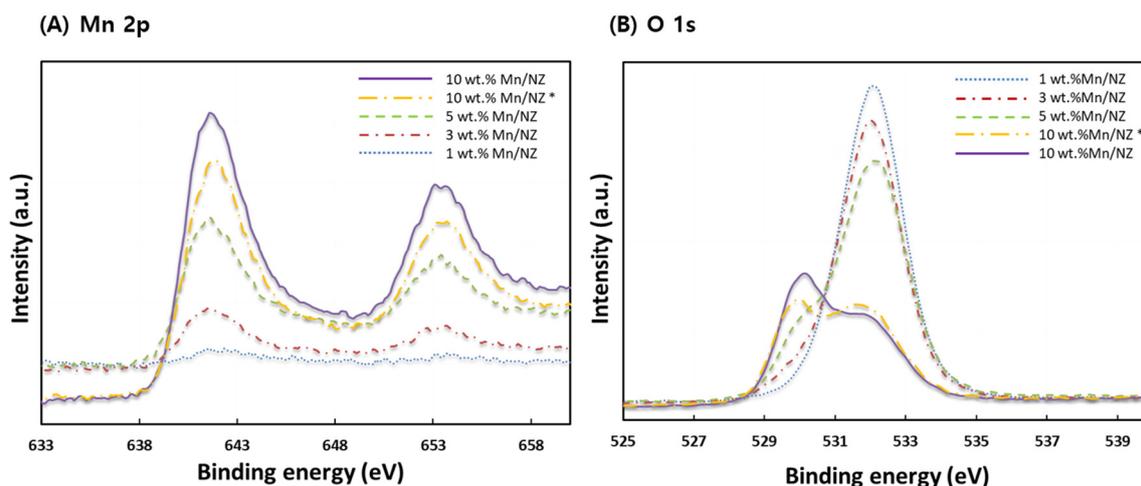


Figure 1. The Mn 2p and O 1s high resolved XPS spectra of 1, 3, 5 and 10 wt.% Mn/NZ (10 wt.% Mn/NZ*: without sonication).

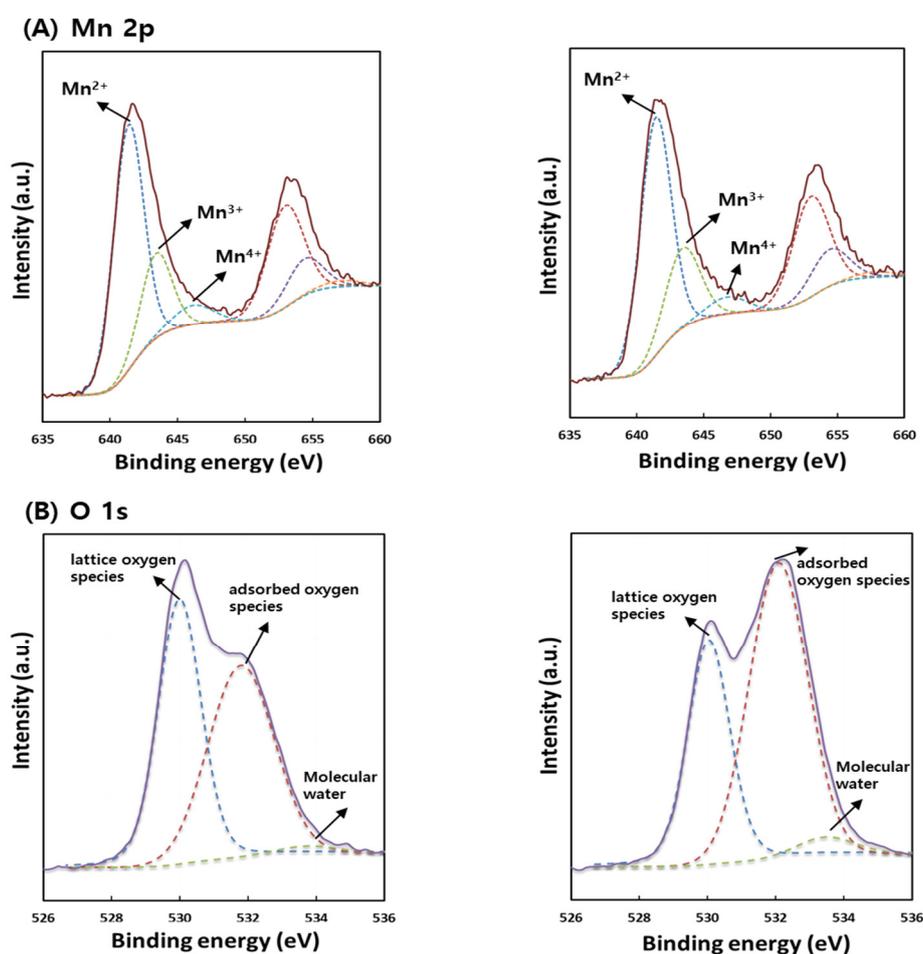


Figure 2. Curve fitting of the Mn 2p and O 1s XPS spectra. (A) Mn 2p of 10 wt.% Mn/NZ calcined at 350 °C and 550 °C, and (B) O 1s of 10 wt.% Mn/NZ calcined at 350 °C and 550 °C. Left: 10 wt.% Mn/NZ calcined at 350 °C; right: 10 wt.% Mn/NZ calcined at 550 °C.

Figure S1 shows the X-ray diffraction patterns of the sonication treated Mn/NZ and untreated Mn/NZ by the incipient wetness method. Because low or absent peak intensity of MnO_x implies high dispersion of MnO_x [26], it can be confirmed again that the sonicated Mn/NZ has a higher dispersion

of Mn than the Mn/NZ without sonication. This is consistent with data that a higher Mn surface atomic concentration of sonicated Mn/NZ is related to the high dispersion of Mn.

2.2. Acetaldehyde Removal Activity

Figure 3 shows the concentration of acetaldehyde removed after 5 min of the NTP/catalyst hybrid reaction while using the NTP and 1 g of the Mn/NZ catalyst at 60% relative humidity. First, acetaldehyde adsorption efficiency of the catalyst was evaluated, but there was no adsorptive removal of acetaldehyde. Although additional adsorption was performed for 1 h, the adsorption of acetaldehyde in high relative humidity atmosphere was not proceeded at all over all the catalysts (data not shown).

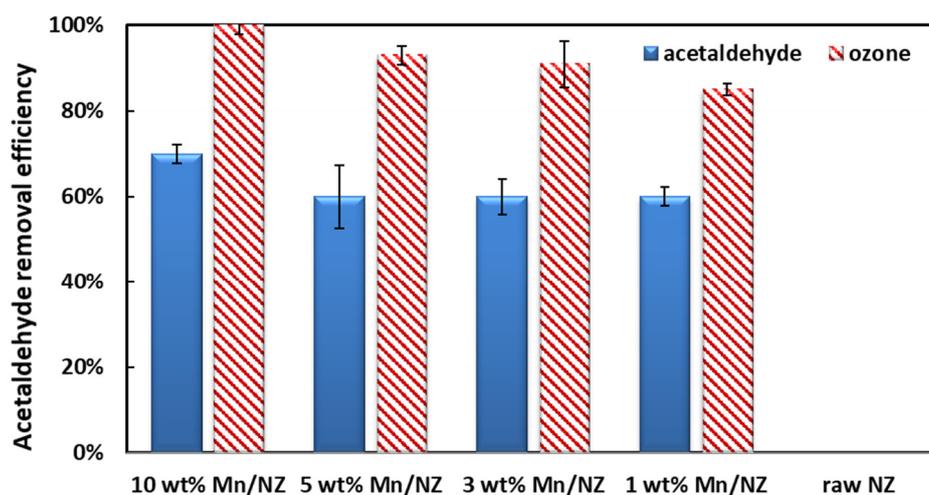


Figure 3. Acetaldehyde and ozone removal efficiencies of the Mn loaded NZ catalysts (1, 3, 5, and 10 wt.% Mn/NZ). Relative Humidity: 60%, The amount of catalysts: 1 g.

The NTP/catalyst hybrid system using the raw NZ catalyst did not decompose acetaldehyde, whereas the removal efficiency of acetaldehyde was increased by applying a catalyst with Mn. The NTP/catalyst hybrid system using the 1, 3, and 5 wt.% Mn/NZ catalysts decomposed 60% of acetaldehyde present. The acetaldehyde removal efficiency was increased further to 70% using the 10 wt.% Mn/NZ catalyst. In addition, 100% ozone decomposition was also achieved after 5 min of using the 10 wt.% Mn/NZ together with the NTP. This indicates that the Mn content in the Mn/NZ catalyst is very important for the decomposition of acetaldehyde and ozone. In addition, the removal of acetaldehyde was strongly related with the decomposition efficiency of ozone. When the decomposition efficiency of ozone was increased using the 10 wt.% Mn/NZ, that of acetaldehyde was also increased. This suggests that the newly generated oxygen species from ozone on the catalyst surface can allow for the additional decomposition of acetaldehyde [16]. Although the catalytic activity of the Mn-impregnated catalyst was reported to decrease at high Mn contents [27], in this study, the highest activity for the removal of acetaldehyde was achieved when the 10 wt.% Mn/NZ was applied.

To determine the effect of the catalyst amount on the removal of acetaldehyde, the catalytic decomposition of acetaldehyde using the NTP or the NTP/catalyst hybrid system was also performed, and the results are shown in Figure 4. The removal efficiency of acetaldehyde was extremely low, with almost no decomposition, when the acetaldehyde removal reaction was performed while using the NTP system without the Mn/NZ catalyst at ambient temperature under a humidified atmosphere. In contrast, the NTP/catalyst hybrid system showed much higher efficiency on the removal of acetaldehyde than a single reaction system using plasma only. The removal efficiencies of acetaldehyde were also increased gradually while using a larger amount of catalyst during the reaction using the NTP/catalyst hybrid system and approached 100% removal when 5 g of the catalyst was used.

These results suggest that the NTP process is essential for the removal of acetaldehyde and the additional use of the 10 wt.% Mn/NZ catalyst as a post plasma reaction can increase the overall efficiency for the removal of acetaldehyde and ozone.

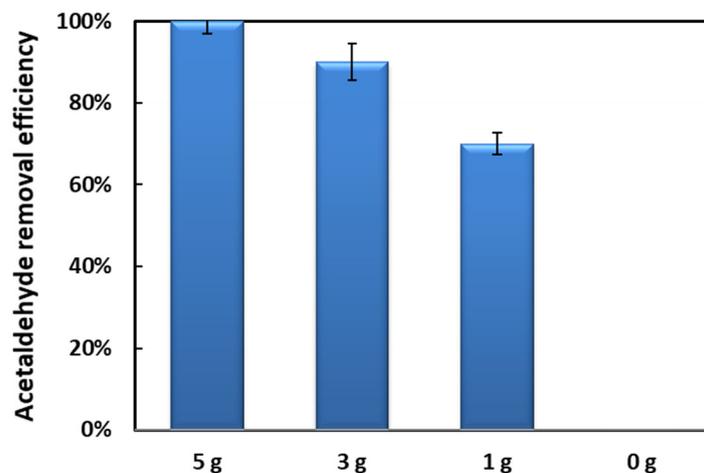


Figure 4. The effect of amount of catalysts (10 wt.% Mn/NZ) on the acetaldehyde oxidation in relative humidity 60%.

Also, the removal activity of acetaldehyde over a sonicated Mn catalyst was compared with that over Mn impregnated on the NZ without sonication. The catalytic activity of the sonicated 10 wt.% Mn/NZ was much higher than that of the 10 wt.% Mn/NZ without sonication (Figure 5). This can be explained by the high dispersion efficiency of Mn on the NZ catalyst, which was enhanced by the highly dispersed impregnation or surface atomic concentration of Mn via sonication during the incipient wetness method (Table 1) [28,29], and this leads to high catalytic activation for acetaldehyde removal.

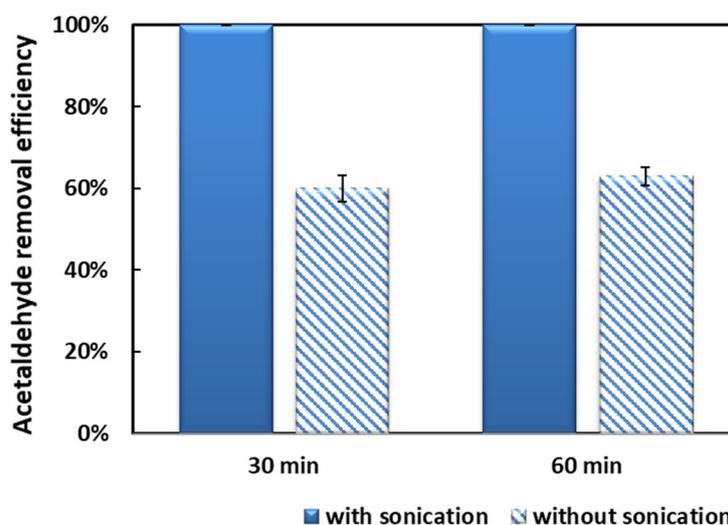


Figure 5. The effect of sonication on the catalytic activity of the 10 wt.% Mn/NZ for the acetaldehyde oxidation. Relative Humidity: 60%, The amount of catalysts: 5 g.

The effect of the calcination temperature of the Mn/NZ catalyst on the removal of acetaldehyde was also evaluated. For this, 5 g of the 10 wt.% Mn/NZ calcined at 350 °C and 550 °C were applied for the removal of acetaldehyde while using the NTP/catalyst hybrid system under a high humidity atmosphere. As shown in Figure 6, the removal efficiency of acetaldehyde using the Mn/NZ calcined at 550 °C was approximately 60%. On the other hand, that of the Mn/NZ catalyst calcined at 350 °C was 100%. This suggests that 350 °C is a more appropriate calcination temperature of the Mn/NZ

than 550 °C for the removal of acetaldehyde via the NTP/catalyst hybrid system. The effects of the Mn calcination temperature on the catalytic activity have also been reported elsewhere [30]. In addition, it was reported that the partial oxidation of MnCO_3 could be achieved at calcination temperatures between 300 and 400 °C, which allows for the co-existence of MnCO_3 and MnO_x that can increase the performance of the catalyst [24,25]. Furthermore, the best reducibility and abundant active lattice oxygen in the catalyst were associated with the excellent performance of VOC oxidation [25]. Tian et al. also reported that the lattice oxygen contributed to the catalytic activity [31]. Jin et al. also reported that the high activity of the mesoporous $\alpha\text{-Mn}_2\text{O}_3$ calcined at 300 °C might be due to its high oxygen mobility or oxygen vacancies and lattice oxygen. In addition, the low activity of commercial Mn_2O_3 seemed to be contributed to its lower oxygen mobility and surface area [32]. This is consistent with the data showing that more lattice oxygen species (XPS Figure 2B) and surface atomic concentration of Mn (Table 1) after calcination at 350 °C resulted in the best performance for the acetaldehyde decomposition.

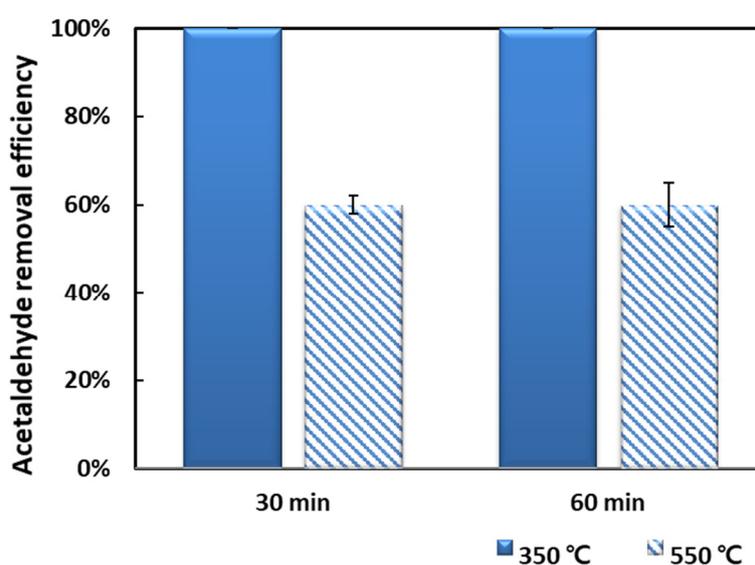


Figure 6. The effect of calcination temperature for the 10 wt.% Mn/NZ on the acetaldehyde oxidation. Relative Humidity: 60%, The amount of catalysts: 5 g.

To check the removal efficiencies of acetaldehyde and ozone under a high humidity atmosphere, the humidity of the system was also evaluated by the NTP/catalyst hybrid system using 5 g of the 10 wt.% Mn/NZ catalyst (Figure S2). Acetaldehyde and ozone were removed completely under both dry and humidified atmospheres. Even under the highly humidified atmosphere (RH = 80%), 100% of acetaldehyde was removed after 5 min reaction while using the NTP/catalyst hybrid system. This suggests that high humidity does not influence the removal efficiency of acetaldehyde when the NTP/catalyst hybrid system using the Mn/NZ catalyst is applied. This result is superior to previous results that were obtained with a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst for VOCs decomposition using post-plasma catalytic technology [33]. They indicate that VOC sorption to the catalyst determined by Van der Waals and H-donor interactions is the most critical parameter of VOC removal efficiency, and humidity affects those interactions. Hydrogen donor interactions are more independent to humidity than Van der Waals force. In the case of polar compounds, such as acetaldehyde tested in this study, both the Van der Waals and hydrogen donor interactions are an important sorption mechanism, which reduces the dependency of humidity on the removal of acetaldehyde. However, further research will be necessary to investigate this phenomena in depth.

2.3. Long Term Reaction Stability Test

To examine the decrease in acetaldehyde removal due to catalyst poisoning, a long term reaction test using the NTP/catalyst hybrid system was also performed under a humidified atmosphere. The VOCs removal efficiency on the catalytic reaction can be decreased when a large amount metal is impregnated, because high metal contents can make an extremely low dispersion between the active metal phase and supporting catalyst [34,35]. Also, it has been reported that the VOCs conversion gradually decreased after 5 h under dry air [29]. On the other hand, the removal efficiency of acetaldehyde in this experiment was up to 100% for 15 h, even under a high humidity atmosphere, as shown in Figure 7. This can be explained by the high dispersion of Mn on the NZ surface by the appropriate impregnation method while using sonication and highlights the high stability of the NTP/catalyst system applied in this research for the removal of acetaldehyde.

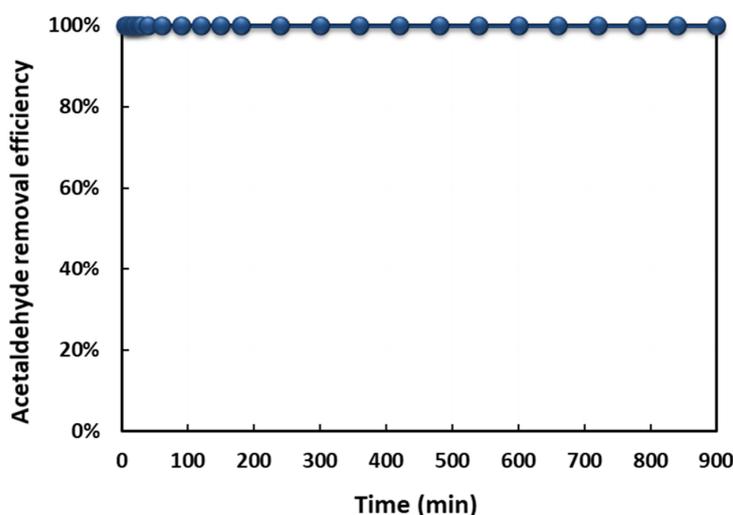


Figure 7. The long-term catalyst stability test for the acetaldehyde oxidation. Relative Humidity: 60%, The amount of catalysts: 5 g.

3. Materials and Methods

3.1. Catalyst Preparation

NZ, which consisted of SiO_2 , Al_2O_3 , CaO , Na_2O , and K_2O , was purchased (Handoo Co. Ltd., Seoul, Korea) and was used as a supporting material for Mn impregnation. The NZ was sieved to achieve a uniform particle size between 2 and 3 mm. Mn was impregnated on the NZ by the incipient wetness method. For this, manganese (II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$, 99.99%), which was purchased from Sigma-Aldrich (St. Louis, MO, USA), dissolved in distilled water and was added to a beaker containing the NZ. As the total pore volume of NZ is $0.1603 \text{ cm}^3/\text{g}$, 0.8015 mL of water was used per 5 g of NZ. After the impregnation, Mn/NZ was sonicated for 2 h. After sonication, the synthesized Mn/NZ was dried overnight at $100 \text{ }^\circ\text{C}$ and finally calcined at $350 \text{ }^\circ\text{C}$ or $550 \text{ }^\circ\text{C}$ for 2 h in air. The weight content of Mn in the Mn/NZ catalyst was controlled to 1, 3, 5, and 10 wt.% to determine the optimal metal content in the catalyst for the removal of VOCs and ozone. The specific amounts of NZ and $\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ used for the synthesis is listed on Table 2.

Table 2. Amounts of NZ and $\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ used for the synthesis.

Catalyst	NZ (g)	$\text{Mn}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$ (g)
1 wt.% Mn/NZ	5	0.228
3 wt.% Mn/NZ	5	0.691
5 wt.% Mn/NZ	5	1.173
10 wt.% Mn/NZ	5	2.480

3.2. Catalyst Characterization

All of the samples were degassed at 200 °C prior to the Brunauer–Emmett–Teller (BET) measurements. The BET surface areas (BET) were determined while using a Micromeritics ASAP 2010 (Norcross, GA, USA) nitrogen adsorption apparatus. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5000 Versa Probe (Ulvac-PHI, Kanagawa, Japan), using Al K α (1486.6 eV) radiation. The data were charge referenced to the C 1 s peak at 284.6 eV. The crystalline phase of the catalysts was obtained using an X-ray diffractometer (XRD, RINT/PMAX 2500, Rigaku, Tokyo, Japan) within the scanning angle range of 30–70 (2 theta), with CuK α radiations ($\lambda = 0.1541$ nm).

3.3. NTP/Catalyst System

Figure 8 presents a schematic diagram of the NTP/catalyst hybrid system that was used for the degradation of VOCs. The NTP/catalyst hybrid system consisted of a VOCs generator, a plasma reactor, and a catalyst bed. The Mn/NZ was loaded onto the catalyst bed (height = 24.5 cm, i.d. = 1.27 cm) located at the downstream of the plasma reactor. The concentration of reactant gas, acetaldehyde in a mixture of nitrogen, and air gas, was controlled by adjusting the flow rates of the standard gas (100 ppm of acetaldehyde in nitrogen gas) and air (dilution gas). The gas stream was injected to the reactor through an acrylic box (inner volume: 100 L). After a sufficient stabilization time (120 min), the concentration of reactant was controlled to 10 ppm at the exit line of the acrylic box by fine tuning the flow rates of acetaldehyde standard and dilution gas. The gas hourly space velocity (GHSV) of the reactant gas in the plasma zone, and the catalyst bed were set to 120/h and 222/h at ambient temperature and pressure, respectively. A dc corona reactor was used to produce plasma. The length and gap space of the discharge tube were 15 mm and 5 mm, respectively. Plasma power of 10 W was driven while using a high voltage AC power supply (12 kV, SIE = 120 J/L, 60 Hz, sine wave). During the oxidation reaction, the concentrations of acetaldehyde were measured using detection tubes (GASTEC, 92L, Measurement Range: 1–20 ppm) and ozone concentration was carried out using an ozone analyzer (Aeroqual 200) after gas sampling at the outlet. The effects of humidity in the system on the removal of acetaldehyde was also evaluated by controlling the relative humidity of the reactor to 20%, 60%, and 80%. The experiment was conducted by adjusting the initial humidity and maintaining the humidity continuously. About 25 ppm ozone was produced from NTP reactor.

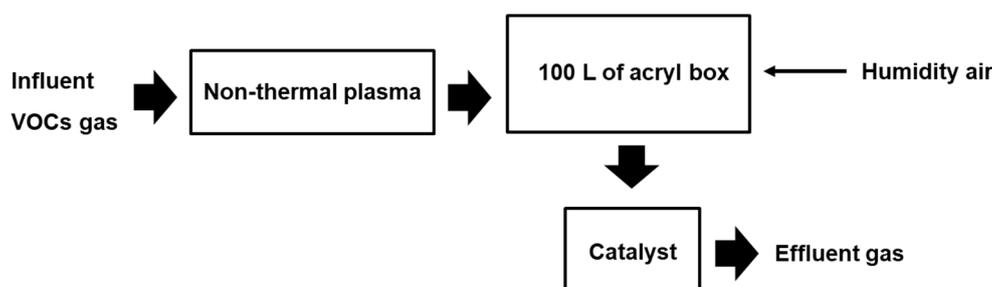


Figure 8. A schematic illustration of a non-thermal plasma (NTP)/catalyst hybrid reactor system for the VOCs decomposition from food waste.

4. Conclusions

In this study, the post-NTP/catalyst hybrid system was developed for the removal of VOCs that are emitted from food waste. The Mn-impregnated natural zeolite (Mn/NZ) was prepared, and the removal efficiencies of ozone and acetaldehyde were evaluated under a humidified atmosphere. In the presence of plasma, the Mn/NZ enhanced the removal efficiencies of ozone and acetaldehyde. The best efficiency of acetaldehyde removal was achieved when the 10 wt.% Mn/NZ was treated with sonication and calcined at 350 °C for 2 h. As a result, ozone and acetaldehyde were completely removed on 5 g of the 10 wt.% Mn/NZ catalyst with the post plasma treatment. In particular, the removal efficiencies of ozone and acetaldehyde were high, even in the presence of humid air (RH = 80%). Furthermore,

the Mn/NZ catalyst was stabilized for 15 h in the humid atmosphere. The strategy presented in this study is expected to be economical under indoor air conditions containing low VOC concentrations to remove a wide range of VOCs.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/9/389/s1>, Figure S1: XRD of the treated Mn/NZ and untreated Mn/NZ of sonication, Figure S2: The effect of humidity on the catalytic activity of the 10 wt.% Mn/NZ for the acetaldehyde oxidation and the ozone decomposition.

Author Contributions: Conceptualization, Y.-K.P.; Catalyst preparation, H.W.R. and M.Y.S.; Removal experimental, H.W.R. and M.Y.S.; Data analysis, M.Y.S., H.W.R, S.-C.J., J.S., B.-J.K. and Y.-K.P.; Writing—original draft, M.Y.S. and H.W.R.; Writing—review & editing, S.-C.J., B.-J.K., J.S. and Y.-K.P.

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Conflicts of Interest: The authors declare no conflict of interest.

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