

Mn 담지 미세기공 제올라이트를 이용한 악취오염물질인 아세트알데히드의 분해반응

이형원 · 이희진 · 박영권[†]

서울시립대학교 환경공학부
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Decomposition of Odor Pollutant Acetaldehyde Using Mn Loaded Microporous Zeolites

Hyung Won Lee, Heejin Lee, and Young-Kwon Park[†]

School of Environmental Engineering, University of Seoul, Seoul 02504, Korea
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Abstract

An acetaldehyde, a representative food waste odor, was decomposed using a hybrid system comprised of a non-thermal plasma and catalyst at an ambient temperature under high humidity. A five wt.% Mn was impregnated on two differently structured microporous zeolites, namely Beta and ZSM-5, with a different molar ratio of SiO₂/Al₂O₃. Under high humidity conditions, the acetaldehyde degradation was higher in zeolites with the high ratio of SiO₂/Al₂O₃. Among studied catalysts, a five wt.% Mn/Beta (SiO₂/Al₂O₃ = 300) showed the highest acetaldehyde removal activity owing to its high hydrophobicity and reducibility. During long term stability test using the same catalyst for 110 hours, the acetaldehyde removal activity was relatively well-maintained.

Keywords: Acetaldehyde, Non-thermal plasma, Mn, Beta, Ozone

1. Introduction

During collection of food wastes in container, significant amount of odors or volatile organic compounds can be generated. Among various odor compounds from food wastes, acetaldehyde is the most difficult to decompose. Therefore, suitable methods to reduce acetaldehyde vapor should be developed. Until now, many methods to reduce volatile organic compounds including acetaldehyde vapor have been suggested [1-3]. For example, adsorption can be applied to capture acetaldehyde but periodic replacement of used adsorbent may be needed. Also, catalytic combustion can be applied to decompose acetaldehyde but this process requires high temperature above 300 °C [4]. Because food wastes can be stored in a container more than two days, and collection of food wastes is collected at ambient temperature, a suitable odor removal process operated under high humidity and ambient temperature should be considered.

Recently many researchers propose a hybrid process comprised of catalyst and non-thermal plasma. The catalyst is introduced either in the discharge zone or downstream from the discharge zone (post plas-

ma-catalysis, PPC)[5-7]. The PPC system can form reactive oxygen species using O₃ emitted from the NTP system, which can enhance oxidation of VOCs. Therefore, the choice of the desirable catalyst is a crucial factor in the efficient decomposition of O₃. Among the reported catalysts, manganese loaded catalyst is one of the best catalysts for ozone oxidation of volatile organic compounds. For example, recently, Zheng *et al.* have used a vertically-oriented graphenes supported manganese catalysts to remove toluene decomposition in PPC system [8]. In addition, Wang *et al.* have compared Mn, Ag and Ce modified HZSM-5 catalysts for plasma-catalytic oxidation of adsorbed toluene and found that Ag-Mn/HZSM-5 catalyst showed better catalytic ability in both complete oxidation of the adsorbed toluene and suppression of the byproducts [9]. Zhang *et al.* reported the catalytic performance of series of 10% MnO_x/HZSM-5 catalysts with different SiO₂/Al₂O₃ ratios toward toluene decomposition [10]. These papers were performed in dry conditions, comparing the activity of the catalyst for VOCs oxidation and did not consider the effect on humidity levels. Therefore, it is needed to find a suitable catalyst which shows good activity for VOCs oxidation under high humidity.

As a catalyst support, zeolite has a wide range of applications in industry and in the laboratory with large specific surface area, long catalyst life and low cost [11-13]. Furthermore, zeolites are an important class of aluminosilicates and thus existing of wide range of SiO₂/Al₂O₃ ratios. High-silica zeolites are known to be hydrophobic, while low

[†] Corresponding Author: University of Seoul,
School of Environmental Engineering, Seoul 02504, Korea
Tel: +82-2-6490-2870 e-mail: catalica@uos.ac.kr

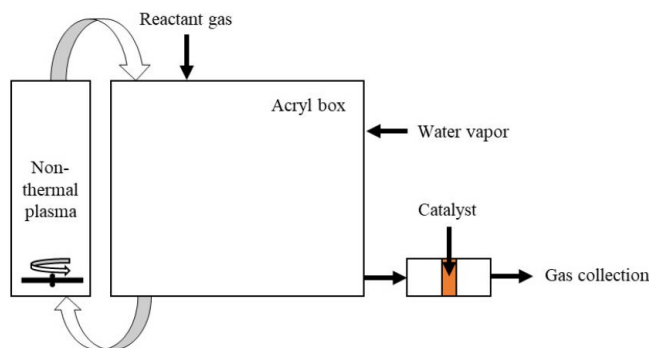


Figure 1. Schematic diagram of the experimental setup.

$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios is essentially hydrophilic due to the presence of hydroxyl groups on its surface. The hydrophilic zeolites can cause toxicity by occupying active sites on the surface, where the water molecules can cover the catalyst surface. The high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of zeolites provide more hydrophobicity of catalyst surface, and thus prevent adsorption of water on the catalyst. These zeolites are expected to show high activity for acetaldehyde degradation in the humid condition. In previous our study[14], we performed acetaldehyde removal using hybrid system comprised of plasma and Mn/Y catalysts. Among different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio Y supports, Mn/Y ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$) having highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio showed highest acetaldehyde removal activity. However, other representative microporous zeolites has not been applied to the removal of acetaldehyde using a hybrid system of plasma and catalysts under high humidity.

In this study, the effect of different zeolite structure (Beta and ZSM-5) and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on the removal of acetaldehyde under high humidity was investigated.

2. Experimental

2.1. Catalyst preparation

Commercial ZSM-5 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ and 280) and Beta zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ and 300) were supplied by the Zeolyst International. The detailed preparation method was described in our previous study[15].

2.2. Catalyst characterization

Brunauer-Emmett-Teller (BET) measurements were performed to determine the specific surface area of each catalyst. Temperature programmed reduction (TPR) was performed using BEL-CAT under a gas mixture (10 vol% H_2 in Ar) and the temperature of the catalysts was increased up to 600 °C at a heating rate of 10 °C min^{-1} .

2.3. Experimental setup and activity tests

Figure 1 shows a schematic diagram of catalytic non-thermal plasma system for degradation of acetaldehyde degradation. It included an acetaldehyde generator, plasma reactor, water vapor section and catalyst bed. The detailed experimental procedure was described in literature[15,16].

Table 1. BET Surface Area of the Catalysts

	$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio	Parent*	Mn-loaded
Beta	25	680 m^2/g	577 m^2/g
	300	620 m^2/g	442 m^2/g
ZSM-5	30	405 m^2/g	366 m^2/g
	280	400 m^2/g	335 m^2/g

* provided by Zeolyst.

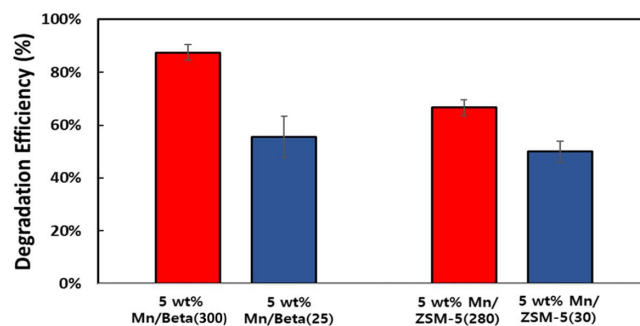


Figure 2. Acetaldehyde degradation of Mn/Beta with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ and 300) and Mn loaded ZSM-5 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ and 280), Conditions: 10 ppm acetaldehyde, under humid air.

3. Results and Discussion

3.1. Catalyst characterization

The BET surface area of parent and Mn-loaded zeolites are listed in Table 1. The order of surface area for the zeolites regardless of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios are as follows: BETA ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) > BETA ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 300$) > ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) > ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 280$). The decrease in surface area was observed in the 5 wt.% Mn-loaded zeolites. This can be related to partial blocking of some zeolite pores with manganese oxide formed on the surface of zeolite.

3.2. Catalyst activity

The effects of the acetaldehyde degradation efficiency were investigated under humid air conditions after a 30 min plasma treatment with Mn-loaded Beta zeolites and Mn-loaded ZSM-5 zeolites, which have different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios (Figure 2). Mn/Beta(300) and Mn/ZSM-5(280) removed approximately 87% and 66% of acetaldehyde at 30 min, whereas Mn/Beta(25) and Mn/ZSM-5(30) removed 55% and 50% of the acetaldehyde after the same period of time, respectively. In addition, Mn/Beta(300) and Mn/ZSM-5(280) removed the ozone completely after 30 min plasma treatment. For all zeolite, the samples exposed to more hydrophobic zeolite showed higher degradation efficiency than those exposed to lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (Figure 2). Accordingly, the acetaldehyde removal efficiency increased with increasing hydrophobicity, which is considered a major factor for the efficient decomposition of organic material under humid conditions. Also, Mn/Beta(300) showed higher acetaldehyde removal activity than

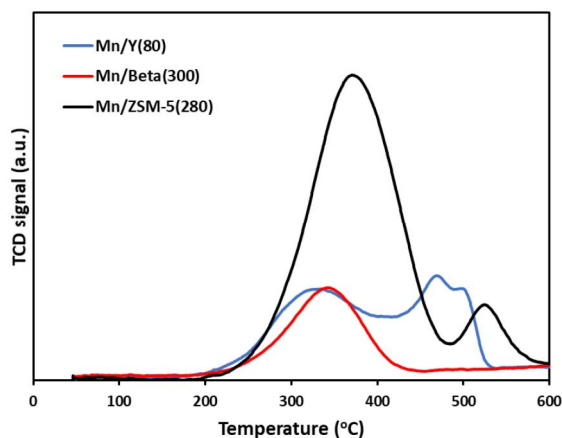


Figure 3. TPR profiles of Mn/Y(80), Mn/Beta(300) and Mn/ZSM-5(280).

Mn/Y(80) which showed good acetaldehyde removal activity in our previous study[14].

The catalytic properties according to the type of support can be explained based on the reduction characteristics analyzed by H₂-TPR. Figure 3 shows the reduction behaviors of Mn/Y(80), Mn/Beta(300), and Mn/ZSM-5(280) catalyst. Mn/Y(80) showed broad reduction peaks centered at 335.1 °C and 498.4 °C. Because of the strong interaction of Y with the large pores and MnOx, they could not be reduced easily and broad peaks were formed in the high temperature region[14]. Mn/Beta(300) showed a single reduction peak at 342.7 °C. Two reduction peaks were observed at 370.3 °C and 523.6 °C in Mn/ZSM-5(280). A low-temperature peak below 400 °C was attributed to the reduction of MnO₂ and Mn₂O₃ to Mn₃O₄[17]. These low-temperature hydrogen consumption peaks revealed highly dispersed and easily reducible MnOx species[18]. On the other hand, the peak at approximately 500 °C in Mn/Y(80) and Mn/ZSM-5 catalysts indicates that Mn₃O₄ was reduced to MnO. Kim *et al.* examined the removal of VOCs over manganese oxide catalysts and reported that the catalytic activity was related to the oxygen mobility. The reduction temperature shifting to a higher temperature reduces the lattice oxygen mobility on the catalyst. A higher oxygen mobility means higher catalyst activity[19]. This suggests that Mn/Beta(300), which had a single reduction peak at low temperatures compared to Mn/Y(80) and Mn/ZSM-5(280), showed high activity in the removal of acetaldehyde.

A long term stability test was carried out with 5 wt.% Mn/Beta (SiO₂/Al₂O₃ = 300), which showed high activity for the acetaldehyde removal efficiency (Figure 4). The plasma system was repeatedly turned on for 20 min and turned off for 10 min during the reaction. This is because the amount of ozone generated increased as the plasma apparatus was operated. Figure 8 shows the removal efficiency of acetaldehyde and ozone for 110 h. The acetaldehyde removal efficiency was 100% and 67% at the highest and lowest, respectively, showing an average efficiency of 83% for 110 h. The acetaldehyde degradation efficiency was not constant because acetaldehyde removal was affected by the ozone generated in the plasma. The average concentration of ozone was 60 ppm in the plasma system in on mode and 35 ppm in

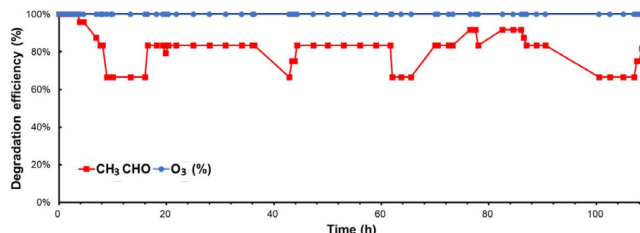


Figure 4. Long term stability test of Mn/Beta(300). Conditions, 10 ppm acetaldehyde, 12,000 mL g⁻¹ h⁻¹ WHSV, under humid air.

the system in off mode. The ozone generated was removed completely by the catalytic reaction.

4. Conclusion

The acetaldehyde removal by the hybrid plasma-catalyst system was performed. The catalysts were 5 wt.% Mn loaded zeolites (Beta and ZSM-5) with different SiO₂/Al₂O₃ ratios. The acetaldehyde degradation efficiency was higher with higher SiO₂/Al₂O₃ ratio under high humidity conditions owing to higher hydrophobicity of the zeolite surface. When the relative humidity was 60%, the acetaldehyde removal efficiency was the highest at 87% in the reaction over the 5 wt.% Mn/Beta (SiO₂/Al₂O₃ = 300). This may be due to its highest hydrophobicity and reducibility. Also, a long term stability test showed that removal activity of 5 wt.% Mn/Beta (SiO₂/Al₂O₃ = 300) was relatively maintained well.

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