

MnO_x/TiO₂ Nanoparticle catalyst preparation by Chemical Vapor Condensation (CVC) and Removing Indoor Air Pollutants

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Abstract — This paper investigates the effect of Mn loading on the oxidation of acetaldehyde, toluene as well as formaldehyde over manganese oxides supported on titania (Mn/TiO₂) honeycomb to be compared with the absorption technique. This study examined the catalytic conversion of gaseous acetaldehyde on Mn/TiO₂ catalysts in the presence of ozone, as well as the effect of the support material (TiO₂) characteristics. Mn/TiO₂ honeycomb catalyst with high oxidation activity for acetaldehyde was synthesized by the CVC method. The performance of this ozone catalyst system was investigated by treating artificially generated acetaldehyde at a concentration level of 10 – 30 ppm in a 1-m³ bench scale chamber. It was found that the acetaldehyde concentration in the 1-m³ chamber can be decreased to the almost zero value in one hour.

Keywords — oxidation of acetaldehyde, Manganese Oxide, TiO₂, honeycomb catalyst.

I. INTRODUCTION

RECENTLY, our research group in KIST (Korea Institute of Science and Technology, Seoul, Korea) successfully synthesized MnO_x catalyst based on TiO₂ support materials by a CVC method (chemical vapor condensation); the resulting Mn₂O₃/CVC TiO₂ material showed high dispersion, large surface area, and small crystallite size. Moreover, these samples possessed a higher catalytic oxidation activity for acetaldehyde decomposition than Mn₂O₃/commercial TiO₂ particles (P25), even at room temperature (25°C). Mn-loaded TiO₂ showed improved catalytic properties because of the addition of transition metals; 5 wt% Mn/TiO₂ holds great promise for use in catalytic reactions.

Three methods, namely source control, increasing ventilation, and air cleaning, are commonly suggested to improve air quality. These methods differ from traditional pollution-control methods such as adsorption that merely transfer pollutants from the gaseous phase to the solid phase.

Among the various techniques used for effective removal of indoor air pollutants such as volatile organic compounds (VOCs), catalytic oxidation is one of the useful methods for

treating indoor air polluted with VOCs, especially at low concentration levels [1].

Catalytic oxidation by ozone is an effective method for low-temperature oxidation of VOC, with wide application range varying from the purification of indoor air to the elimination of pollutants in gaseous industrial streams. A favorable synergetic effect between the mixed transition metal oxides was attributed to the improvement in their oxidation abilities. Manganese oxides have been widely used as metal-oxide catalysts because of their high economic value, potential applications in oxidation states, and exposed Mn⁺ and O₂⁻ on the surfaces [2, 3].

II. MATERIAL AND METHODS

A. Catalyst preparation

TiO₂ nanomaterials were synthesized by a chemical vapor condensation and loaded with 5 wt% manganese by impregnation[5].(Fig. 1) The oxidation catalyst was prepared by the sol-gel coating method. The cordierite honeycomb substrates were treated for 2 h in nitric acid solution. The coating solution was prepared using the Mn/TiO₂ catalyst, a bentonite and DI water (12 : 3 : 35 wt%). The honeycomb substrates were immersed in the solution for 5 min, and then removed for drying at 100°C for 3h. This coating process can be repeated three times.

Then, the catalysts were dried overnight at 100°C and calcined at 500°C for 6 hours.

B. Catalytic oxidation reactor

A cylindrical catalytic oxidation reactor (length: 168 mm, diameter: 60 mm) with an inner volume of 475 cm³ was used (Fig. 2). Ozone producing UV lamps, emitting UV light at both rays 185 nm and 254 nm, were placed at the center of the reactor. The irradiation process was performed using a low-pressure mercury lamp with a maximum emission at 254 nm and a minimum emission (<5%) at 185 nm (G12T5VH, Hansung Co. Ltd.). The Mn/TiO₂ honeycomb cordierite catalyst is located at the end of the reactor.

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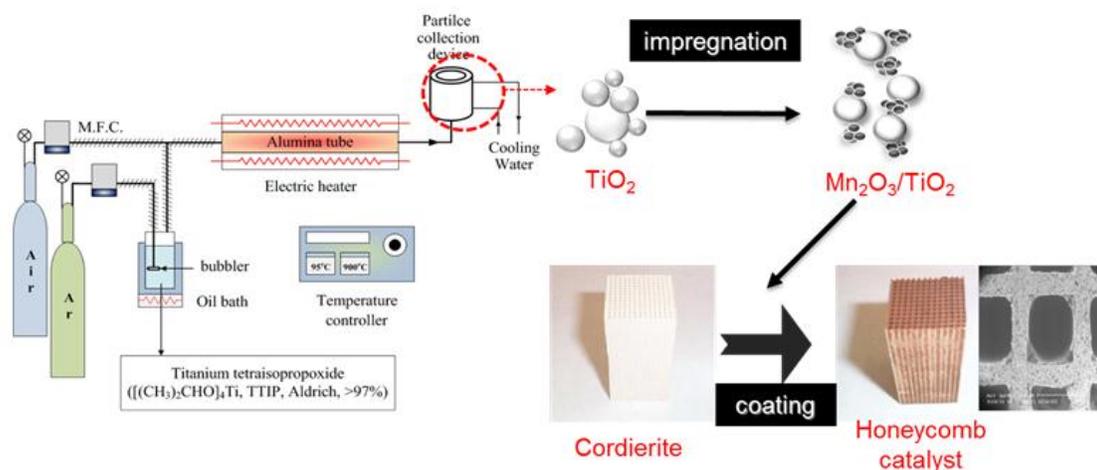


Fig. 1 Schematic of honeycomb catalyst preparation with CVC-synthesized TiO_2 particles

C. Bench scale chamber system

The chamber setup used in this study is described in Fig. 2. Acetaldehyde was introduced at a constant rate to the 1-m³ bench scale chamber. The chamber was built entirely of polycarbonate panels to minimize surface losses of the analytes including acetaldehyde. The mixture is shaken until adsorption equilibrium is reached. The catalytic reaction into the reactor was performed for 12 hours. This means that a steady state can be reached regarding the partition of acetaldehyde in the gas phase and in the adsorbed phase.

During the experiments, the organic compounds were measured only in the gas phase and a fraction of acetaldehyde is present on the honeycomb catalyst surface at the beginning of the reaction.

The catalytic oxidation reactor was installed on an external ductwork loop and operated in the recirculation mode, by re-introducing the cleaned air, processed by the catalytic oxidation reactor, into the chamber. The acetaldehyde concentration was adjusted by mixing the standard form of acetaldehyde (500 ppm) with clean air. Ozone was generated from a UV lamp inside the reactor.

The chamber temperature was set to 25°C (room temperature). This arrangement produces 10 and 30 ppm of acetaldehyde concentrations. For comparison, commercial catalysts (P25, Degussa) loaded with Mn were also prepared by the same method.

Finally, a gas sample from the chamber was analyzed using a Fourier-transform infrared spectrophotometer (1400-F, MIDAC, California, USA) equipped with a cell having optical length of 10.0 m and a volume of 4.0 L.

III. RESULTS AND DISCUSSION

A. Catalytic oxidation of acetaldehyde

Ozone is transported to the catalyst and that the ozone molecule produces two active atomic oxygen and one oxygen radical, both capable of oxidizing of acetaldehyde to carbon

monoxide (CO). Moreover, manganese oxides are often employed as catalysts for low temperature oxidation of carbon monoxide with ozone [6].

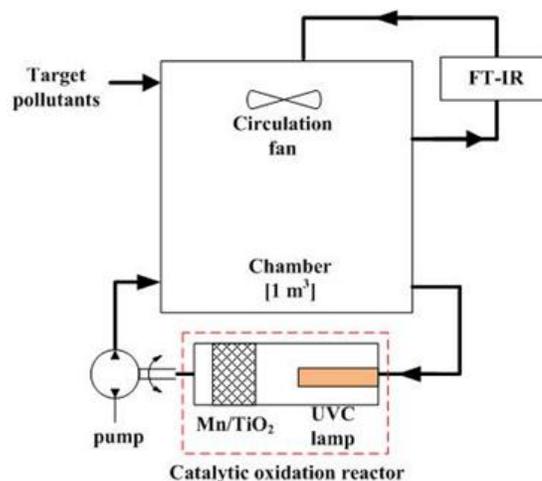


Fig. 2 Schematic of 1m³ polycarbonate with external catalytic oxidation reactor recirculation loop

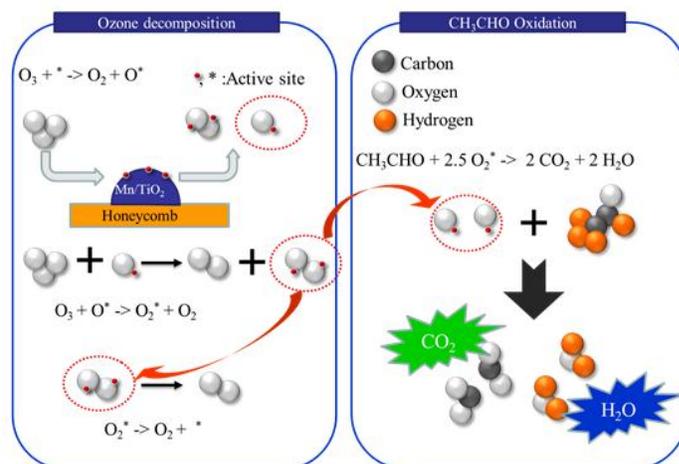


Fig. 3 Schematic of Ozone decomposition on the surface of Mn/TiO_2 particles and Acetaldehyde (CH_3CHO) oxidation process

Fig. 4 shows the higher acetaldehyde removal efficiency of Mn/TiO₂ (CVC) honeycomb catalyst by catalytic oxidation, than Mn/TiO₂ (P25) honeycomb catalyst. Such behaviors can be accounted for by high SSA of Mn/TiO₂ (CVC) catalyst particle, which is one of the important factors for VOC oxidation [7]. The supported manganese oxide catalysts with high surface area are effective for catalytic oxidation of acetaldehyde from the standpoint of catalytic activity and efficiency for ozone utilization

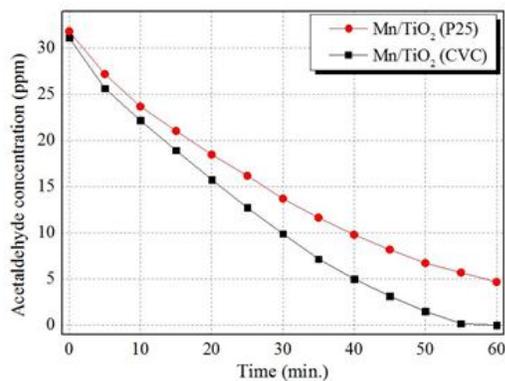


Fig. 4 Catalytic oxidation of acetaldehyde of Mn/TiO₂ (CVC) and Mn/TiO₂ (P25)

Fig. 5 shows the variation of acetaldehyde concentration in air with the reaction time for three different initial concentrations ranging from 10 to 30 ppm. The initial slope increased with increasing initial concentration of acetaldehyde, which shows that higher concentration leads to higher catalyst oxidation. The graphical determination of the half reaction time ($T_{1/2}$) for each reaction (Fig. 3) indicates that this parameter does not depend on initial concentration of acetaldehyde in the investigated concentration range. The value of $T_{1/2}$ is around 20 min, during acetaldehyde removal. Thus, the acetaldehyde concentration can be decreased to almost zero in one(1) hour.

Although the irradiation is provided by the 254-nm lamp, ozone acts not only as an electron acceptor to produce O₃, but also as a source to generate hydroxyl radicals, which have strong ability to oxidize acetaldehyde. Therefore, the combination UV lamp with ozone can enhance the conversion of acetaldehyde.

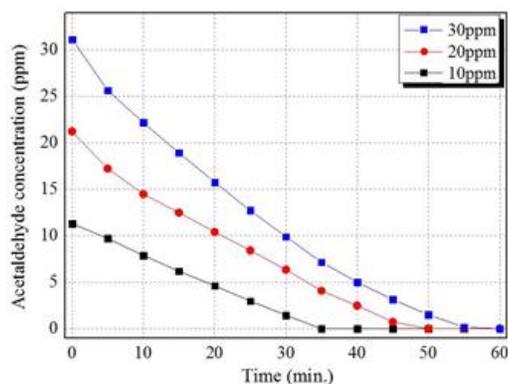


Fig. 5 Catalytic oxidation of acetaldehyde at various initial concentration using Mn/TiO₂(CVC)

IV. CONCLUSIONS

This study examined the catalytic conversion of gaseous acetaldehyde on Mn/TiO₂ catalysts in the presence of ozone, as well as the effect of the support material (TiO₂) characteristics. Mn/TiO₂ honeycomb catalyst with high oxidation activity for acetaldehyde was synthesized by the CVC method.

The performance of this system was investigated by treating artificially generated acetaldehyde at a concentration level of 10 – 30 ppm in a 1-m³ bench scale chamber.

It was found that the acetaldehyde concentration can be decreased to the almost zero value in 1 hour.

Thus, it can be concluded that it is very important to promote synergetic capability, transfer/diffusion and reaction activity for the catalysts used in the catalytic oxidation of acetaldehyde.

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