

Room Temperature Catalytic Ozonation of Methyl Ethyl Ketone over Mesoporous MnO_x/Al₂O₃ Catalysts

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(Received May 12, 2021; Revised June 3, 2021; Accepted June 9, 2021)

Abstract

Catalytic ozonation of methyl ethyl ketone (MEK) has been examined over mesoporous MnO_x/Al₂O₃ (MA) catalysts developed by a solvent deficient method using two different manganese precursors including manganese chloride (C) and manganese sulfate (S) at room temperature. The maximum catalytic activities of MA with C (MEK removal efficiency and ozone decomposition of 98.4 and 93.7%, respectively) were higher than those of MA with S (MEK removal efficiency and ozone decomposition of 96 and 68%, respectively). Also the catalytic stability of MA with C was much higher than that of MA with S. The physico-chemical properties of catalysts are well correlated with the activity results, which confirmed that fine dispersion of MnO_x species with high ratios of Mn³⁺/Mn⁴⁺ and more acid sites are attributed to the higher catalyst stability for the MA-C catalyst.

Keywords: Methyl ethyl ketone, Ozone, Manganese chloride, Alumina, Room temperature

1. Introduction

Recently, volatile organic compounds (VOCs) are being considered as highly toxic air pollutants which cause to severe damages on human health including irritation of mucous membrane, headache, nausea, and weakness of central nervous system[1]. Hence, the removal of VOCs is of great interest in recent decades mainly targeted on toluene, propylene and methyl ethyl ketone (MEK)[2]. Among them, MEK is one of the VOCs, released *via* direct emissions from textile dyeing and printing, petroleum refining, electronic equipment, and synthetic resin manufacturing industries. In addition to that, MEK enters the atmosphere by the atmospheric photo oxidation of VOCs such as n-butane, 2-butanol, and 3-methyl pentane[3]. Moreover, sewage sludge is also one of the causes for the MEK releases into the air[4].

A wide range of technologies including biofiltration, adsorption, combustion, and ozonation have been applied for the removal of MEK. Hajaghazadeh *et al.* studied photocatalytic oxidation of MEK using a light emitting diode system (LED)[5]. Santos *et al.* revealed non-thermal plasma technology for VOC pollution control[6,7]. However, catalytic oxidation of MEK to CO and CO₂ under ozone at room temperature is a promising method, because it is a simple and low-cost process compared with that of combustion of MEK under oxygen at high temperature[8] over non-noble metal oxides, especially MnO_x. Mesoporous

supported catalysts have a great potential in the enhancement of the ozonation of VOCs[9]. It was also reported that mesoporous MnO_x/Al₂O₃ removed toluene effectively[10]. However, mesoporous MnO_x/Al₂O₃ catalyst developed by the solid state synthesis with various precursors for MEK removal under ozone at room temperature has not yet been studied.

This work is aimed to study the effect of manganese precursors such as manganese chloride and manganese sulfate in the final catalyst composition of MnO_x/Al₂O₃ on removal efficiencies of MEK *via* ozonation at room temperature. Catalysts properties evaluated by BET surface area, HRTEM, XPS, and NH₃ TPD analyses provided valuable information on the activity difference in the catalysts.

2. Experimental

Mesoporous MnO_x/Al₂O₃ (MA) was prepared using MnCl₂ (C) and MnSO₄ · H₂O (S), and developed by a solvent-deficient method (SDM). The necessary chemicals were purchased from Sigma-Aldrich, USA. Initially, MA-C was prepared using metal precursors containing mixture of MnCl₂ (0.42 g), Al(NO₃)₃ · 9H₂O (21.41 g) and NH₄HCO₃ (13.86 g). The mixture was manually ground with a mortar for 30 min and finally collected as a gel. The received gel was subjected to calcination at 500 °C for 4 h. Similar protocol was applied for MA-S with the calculated amount of mixture of MnSO₄ · H₂O (0.3 g), Al(NO₃)₃ · 9H₂O (21.4 g) and NH₄HCO₃ (14.3 g).

The physicochemical properties were analyzed by different analytical techniques. The BET surface area of each catalyst was conducted using liquid N₂ at -196 °C (ASAP 2020, Micromeritics, USA) after degasification under vacuum at 120 °C for 1 h. The surface chemical com-

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Table 1. Physico-chemical Properties of MA-C and MA-S Samples

| Catalyst | BET surface area (m ² /g) | Pore volume (cm ³ /g) | Average pore diameter (nm) | MnO _x particle size (nm) ^a | Mn ³⁺ /Mn ⁴⁺ ratio ^b | Number of acid sites (mmol/g) ^c | | |
|----------|--------------------------------------|----------------------------------|----------------------------|--|---|--|---------------------|------------------|
| | | | | | | Weak (< 200 °C) | Strong (200–500 °C) | Total acid sites |
| MA-C | 275 | 0.38 | 5.6 | 2.0 | 1.76 | 0.15 | 2.54 | 2.69 |
| MA-S | 270 | 0.32 | 4.8 | 5.5 | 1.62 | 0.11 | 1.41 | 1.52 |

^a TEM analysis, ^b XPS analysis and ^c NH₃-TPD.

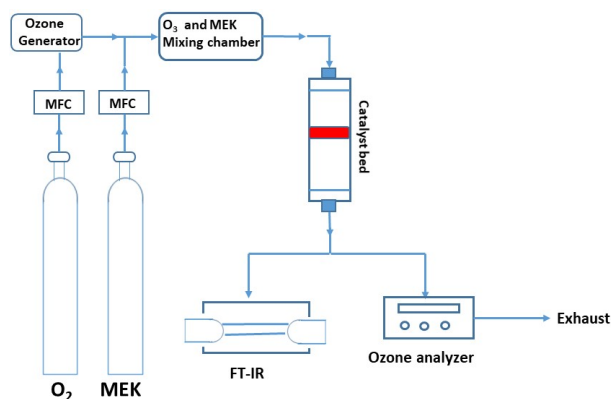


Figure 1. Schematic diagram of MEK ozonation over MA-C and MA-S catalysts.

positions were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB250, USA). The particle size distribution of MnO_x on alumina was obtained by high-resolution transmission electron microscopy (HRTEM, JEM-2100F, 200 kV, Japan). The acidity and total acid sites were calculated from temperature-programmed desorption of NH₃ (NH₃-TPD) (Autochem 2920, Micromeritics, USA).

The ozonation of MEK over MA-C and MA-S catalysts was carried by employing a stainless steel reactor (1/2 inch tube) at room temperature. A schematic diagram of the reactor setup is shown in Figure 1. Briefly, the catalyst (1.5 g) was loaded in the middle of the reactor between two quartz wool plugs. The feed of gas was introduced at the flowrate of 2 L/min with the space velocity = 80,000 mL/g/h (100 ppm MEK and 1,000 ppm O₃) with N₂ balance. The reactor outlet was directly connected to the on-line Fourier-transform infrared spectrometer (Nicolet iS10, Thermo-Fisher Scientific, USA) in order to evaluate the product gas and remaining MEK composition. Ozone consumption was measured by an ozone analyzer (Ozonetech, South Korea).

3. Results and Discussion

The physicochemical properties of the catalysts are depicted in Table 1. The BET surface areas of MA-C (275 m²/g) is higher than MA-S (270 m²/g). Similarly the pore volume and average pore diameter are higher in MA-C when compared with those of MA-S catalyst. The pore diameters of both catalysts (MA-C 5.6 and MA-S 4.8 nm) reflect generation of mesoporous in the samples. The mean particle sizes of MnO_x calculated from HR-TEM are 2 nm for MA-C and 5.5 nm for MA-S. It is obvious that MnO_x particles were more uniformly dispersed on the alumina in MA-C catalysts when compared with those

of MA-S. Further, various types of acid sites were determined by the NH₃-TPD analysis. The lower temperature desorption peak at T_{max} of 170 °C corresponds to the weak acid sites and higher temperature desorption peak at T_{max} of 270 °C ascribed to medium acid sites. The total NH₃ gas from each sample is estimated and tabulated in Table 1. Based on these results, it is clearly revealed that the catalyst prepared by the chloride precursor generates more acid sites than that prepared by the sulfate precursor even though the final composition of catalysts is same. These acid sites certainly influence the interaction between MEK molecule and alumina[11]. For the catalytic oxidation of VOCs over MnO_x-based catalysts, the strength of these surface acidic sites is strongly related to their catalytic performance[12].

Mn 2p spectra is observed in the range of 665–635 eV. The binding energies from 635–645 and 645 to 665 eV corresponds to Mn 2p_{3/2} and Mn 2p_{1/2} respectively. The abundance of Mn³⁺ and Mn⁴⁺ are calculated after deconvolution of each peak. It is important to mention that a high Mn³⁺/Mn⁴⁺ ratio is noticed for MA-C over MA-S catalysts as shown in Table 1. Whereas Al 2p spectra is noticed in the range of 80 to 60 eV with BE of 73.7, 74.1 for MA-C and MA-S, respectively which indicates the electronic structure of alumina with MnO_x. The O 1s spectra consists of lattice oxygen (529.9 eV) and chemisorbed oxygen (530.85 to 532.29 eV). The chemisorbed oxygen has great mobility compared with that of lattice oxygen and generates radicals for oxidation of MEK. It was reported that high amount of Mn³⁺ is responsible for high VOCs removal efficiency under ozone due to high ozone decomposition[13].

Figure 2(a) displays the catalytic ozonation of MEK over MA-C with the maximum removal efficiency of 98% for 30 min but it gradually dropped with increasing time, which indicates the role of active MnO_x species (Mn³⁺) in the catalysts. At an early time of reaction, these species are more but slowly turned in to be less active species (Mn⁴⁺), demonstrating the oxidation of MnO_x under ozone[12]. On the other hand, the decreasing trend for MEK oxidation from 98 to 77% and ozone decomposition from 94 to 64% is well associated with the effective ozone decomposition over Mn³⁺ active sites. In the case of MA-S, the initial MEK removal efficiency (98%) and ozone decomposition (68%) rate are good, however they finally reached to 68 and 58%, respectively as shown in Figure 2(b), due to pore blockage with organic residues such as acetic acid and formic acid which formed by the reaction.

Figure 3(a) and (b) represents the CO and CO₂ amount produced from MEK ozonation over MA-C and MA-S catalysts. The results explain the higher amount of CO₂ than CO, which could be attributed to the high oxidation ability of MA catalysts. Both catalysts effectively

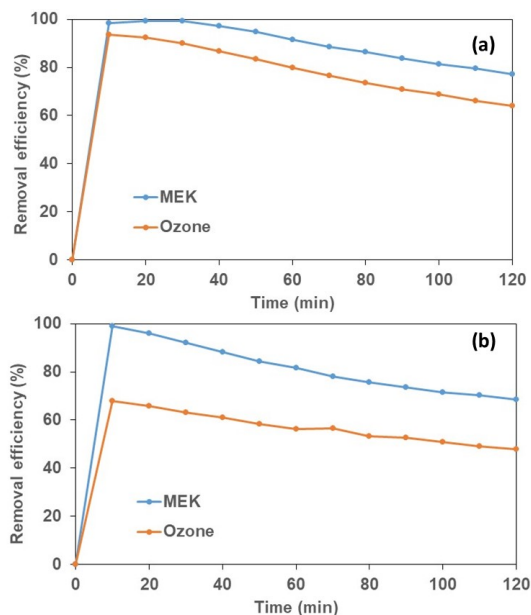


Figure 2. Removal efficiency of MEK under ozone *via* catalytic ozonation over (a) MA-C and (b) MA-S samples.

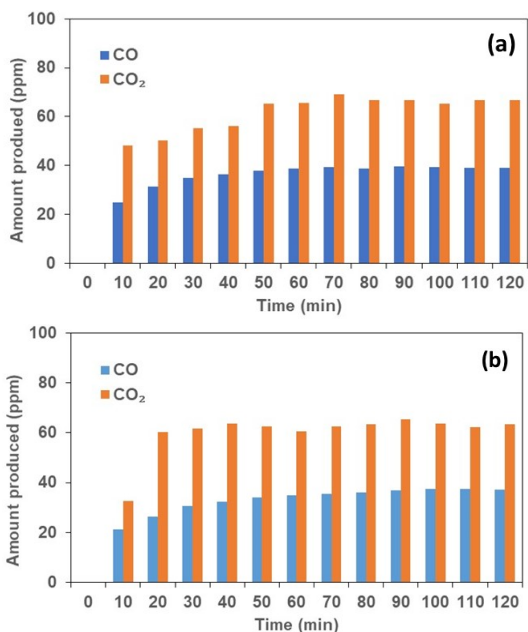


Figure 3. Production of CO and CO₂ from catalytic ozonation of MEK over (a) MA-C and (b) MA-S catalysts.

convert the MEK to CO and CO₂ gases at room temperature. However, it is obvious that the MA-C catalyst exhibited more CO and CO₂ content than the MA-S catalyst. Therefore, the catalytic ozonation of MEK is associated with the precursor of manganese that can give birth to more active MnO_x species[13].

According to the physicochemical properties of MA-C and MA-S catalysts as shown in Table 1, it is evident that the high surface area, originated from mesopores, enables high dispersion of MnO_x on alumina, which leads to a decrease in the size of MnO_x[12], but the size

of MnO_x nanoparticles are significantly different as 2 and 5.5 nm for MA-C and MA-S, respectively. These 2 nm particles can be easily converted to Mn³⁺ compared to bigger 5 nm sized MnO_x[12]. It is clearly observed from the XPS analysis where the MA-C catalyst has exhibited higher ratios of Mn³⁺/Mn⁴⁺. It is also worth noting that ozone decomposition is more efficient over Mn³⁺ than Mn⁴⁺ as reported by Jia *et al.*[13]. Moreover, the high amount of acid sites (2.7 mmol/g) in the MA-C catalyst is responsible for high adsorption of MEK on the surface during the course of the reaction that ultimately improve the MEK removal efficiency.

4. Conclusion

MEK ozonation was carried out over mesoporous MnO_x/Al₂O₃ catalysts prepared by the SDM using two different precursors, manganese chloride and manganese sulfate. The catalytic activity of MA-C was superior to MA-S. The smaller particle size of MnO_x (2 nm), high acid sites and more number of Mn³⁺ sites were attributed to the best MEK oxidation *via* ozone decomposition on MA-C. Therefore, ozonation of MEK over MnO_x/Al₂O₃ have a great potential for the catalytic oxidation of VOCs with ozone at room temperature.

Acknowledgement

This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT (2017M1A2A2086839).

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