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Catalytic Oxidation of Benzene Using Mesoporous α -Mn₂O₃

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The catalytic oxidation of benzene was carried out over mesoporous α -Mn₂O₃, MnO_x/KIT-6, and bulk commercial Mn oxides (Mn₂O₃, MnO₂, and MnO). The catalysts were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, Brunauer–Emmett–Teller analysis, and temperatureprogrammed reduction analysis. MnO_x/KIT-6, prepared by impregnating MnO_x on KIT-6, exhibited a low activity for the oxidation of benzene, whereas mesoporous α -Mn₂O₃, manufactured using KIT-6 as the template, showed a high activity. The order of the activities of bulk Mn oxides for benzene decomposition was shown to be Mn₂O₃ > MnO₂ > MnO. Therefore, the high activity of mesoporous α -Mn₂O₃ is attributed to the uniform distribution of highly active Mn₂O₃ in the mesoporous structure.

Keywords: Mesoporous α -Mn₂O₃, Benzene, Oxidation.

1. INTRODUCTION

Air pollutants are produced as a result of human activities, directly or indirectly causing discomfort and disease. Among other air pollutants, volatile organic compounds (VOCs) are defined as compounds of carbon excluding carbon monoxide, carbon dioxide, carbonic acid, metal carbonates, and ammonium carbonate. VOCs are emitted from various sources including mobile sources such as vehicles, petroleum chemical factories, dye works, and construction materials such as paints, adhesives, and interior materials. VOCs emitted from factories and mobile sources react photochemically with nitrogen oxides (NO_r) in the air to produce ground-level ozone and smog, whereas those emitted from construction materials cause sick building syndrome and respiratory disorders. Therefore, the control and restriction of VOC emissions has become an important issue in air-quality management.¹

Among VOCs, benzene is the most representative species. It is widely used because of its outstanding

properties as a solvent, although it is a carcinogenic substance requiring great care when used.¹

There are various techniques for the removal of VOCs, e.g., direct combustion, catalytic oxidation, and catalytic ozonation. Although all these techniques are efficient for the removal of VOCs, direct combustion requires high temperatures (600–900 °C), while catalytic oxidation can decompose VOCs at much lower temperatures (300–400 °C), thus lowering the maintenance costs.^{1–11} The catalytic ozonation of VOCs can take place at even lower temperatures. The products of catalytic ozonation, however, include hazardous species such as CO, formic acid, acetic acid, acetaldehyde, oxalic acid, and unreacted ozone, which require post-treatment equipment,¹² while H₂O and CO₂ are the main products of catalytic oxidation.

Noble metals such as Pt and Pd and transition metals including Mn and Cu are usually used for the catalytic oxidation of VOCs. In particular, transition metals are cost-effective compared to noble metals, and are therefore attracting much attention in this regard.^{1–4, 12}

In this study, the catalytic oxidation of benzene was carried out over Mn-based catalysts. Mesoporous α -Mn₂O₃

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was applied to the catalytic oxidation of benzene for the first time. For the investigation of the effect of the addition of Cu as a promoter, 15 wt% Cu was added to the mesoporous α -Mn₂O₃ (hereafter, 15 wt% Cu/Mesoporous α -Mn₂O₃), and its catalytic activities before and after the addition of Cu were compared. Another catalyst, 15 wt% MnO_x/KIT-6, was synthesized by impregnating MnO_x on the mesoporous α -Mn₂O₃. The catalytic activity of this material was compared with that of mesoporous α -Mn₂O₃. The activities of commercial manganese oxides (Mn₂O₃, MnO₂, and MnO) for VOC removal were also evaluated.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Catalysts

Mesoporous α -Mn₂O₃ was prepared using a nanoreplication method.³ KIT-6 was used as the template, with manganese (III) nitrate hexahydrate $(Mn(NO_3)_2 \cdot 6H_2O)$, Aldrich) as the precursor. The molar ratios of KIT-6, $Mn(NO_3)_2 \cdot 6H_2O$, and H_2O were 0.1136, 0.0158, and 0.1667, respectively. In a typical synthesis, the precursor was dissolved in distilled water and then impregnated on the silica template. For the spontaneous infiltration of the manganese precursor into the pores of the silica template, the sample was dried overnight at 80 °C. Subsequently, the sample was heated at 550 °C under ambient conditions for 3 h. The silica template was mostly removed using 2 M NaOH aqueous solution twice. Eventually, the mesoporous α -Mn₂O₃ material was obtained by washing the sample several times with distilled water and acetone, and then drying at 80 °C.

 $(C_2H_3O_2)_2$ Cu \cdot H₂O (Copper (II) acetate monohydrate, 98+%) was used as the Cu precursor for the addition of 15 wt% Cu to the mesoporous α -Mn₂O₃ using the impregnation method. The sample was then dried at 110 °C and calcined at 300 °C.

15 wt% $MnO_x/KIT-6$ was synthesized by impregnating Mn acetate on KIT-6.¹³ Commercial Mn_2O_3 , MnO_2 , and MnO were purchased from Sigma-Aldrich.

2.2. Characterization of Catalysts

The powder X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Rigaku D/MAX-III) using Cu-K α radiation. N₂ adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2000 instrument at -196 °C (liquid N₂). Brunauer–Emmett–Teller (BET) analysis was used to estimate the BET surface area. Temperature-programmed reduction (TPR) was carried out with 0.06 g of the calcined catalyst, from room temperature to 700 °C, at a heating rate of 10 °C min⁻¹ in a flow of 10 wt% H₂/He gas. The hydrogen consumption was monitored using a thermal conductivity detector.

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2.3. Catalytic Oxidation of Benzene

Air containing 100-ppm benzene with a flow rate of 120 mL min⁻¹ was introduced into the reactor through a mass flow controller (MFC, Brooks 5850E). The size and amount of the catalyst used in the experiment were 25-35 mesh and 0.1 g, respectively. Before each experiment, the catalysts were calcined for 30 min in an electrical furnace maintained at 300 °C under an oxygen atmosphere. The reactor was maintained at the initial reaction temperature of 50 °C for 30 min. The temperature was then increased for 10 min at a rate of 5 °C min⁻¹, and was maintained at the elevated temperature for 30 min. This procedure was repeated until the temperature reached the final temperature of 400 °C. The benzene content in the product gas was analyzed using a gas chromatography flame ionization detector (GC-FID, Young Lin, column HP-5). The CO₂ content was measured using a nondispersive infrared (NDIR) sensor (LI-COR, LI-820).

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalysts

Table I shows the BET results for the various catalysts. The specific surface area of $MnO_x/KIT-6$ is the largest, while that of 15 wt% Cu/Mesoporous $\alpha-Mn_2O_3$ is the smallest. When Cu was added to the mesoporous $\alpha-Mn_2O_3$, the specific surface area and pore volume decreased; this can be attributed to the blocking of pores by Cu. Figure 1 shows the nitrogen isotherms (a) and pore-size distributions (b) of mesoporous $\alpha-Mn_2O_3$ and 15 wt% Cu/Mesoporous $\alpha-Mn_2O_3$. Hysteresis, a characteristic of mesoporous materials, was observed for both these materials. The pore size was also observed to be 2.6 and 14.2 nm for mesoporous $\alpha-Mn_2O_3$, which are within the typical mesopore size range.

Figure 2 shows the low-angle (a) and high-angle (b) XRD patterns of the two mesoporous materials. A characteristic peak of mesoporous α -Mn₂O₃ appeared in the low-angle results (Fig. 2(a)).³ This peak did not disappear when Cu was added, although the peak size decreased, indicating that the impregnation of Cu did not destroy the mesoporous structure. A characteristic peak of mesoporous α -Mn₂O₃ was also observed in the high-angle

 Table I.
 Surface areas and total pore volumes of mesoporous material samples.

Sample	$\begin{array}{c} BET\\ surface \ area \ (m^2 \ g^{-1}) \end{array}$	Pore volume (cm ³ g ⁻¹)
15 wt% MnO _x /KIT-6	314	0.52
Mesoporous α -Mn ₂ O ₃	119	0.33
15 wt% Cu/mesoporous α-Mn ₂ O ₃	55	0.22



Fig. 1. (a) Nitrogen isotherms of mesoporous catalysts (b) pore size distributions of mesoporous catalysts.

results (Fig. 2(b)).³ Again, the impregnation of Cu reduced the peak size, while a Cu peak appeared at about $2\theta = 35^{\circ}$. In the case of 15 wt% MnO_x/KIT-6, the mesopore structure and even distribution of MnO_x within the template structure were demonstrated in a previous study.¹³

Figure 3 shows the TPR analysis results for mesoporous α -Mn₂O₃ and Cu/Mesoporous α -Mn₂O₃. The addition of Cu resulted in a single peak appearing at 300 °C, indicating that the reduction took place at a lower temperature than before the addition of Cu. This result implies that Cu/Mesoporous α -Mn₂O₃ has a higher reducing power (i.e., higher oxygen mobility) than mesoporous α -Mn₂O₃. It was previously reported that MnO_x/KIT-6 is composed of well-distributed MnO_x such as Mn₂O₃ and MnO₂.¹³

3.2. Results of Catalytic Oxidation of Benzene

Figure 4 compares the results for the catalytic oxidation of benzene over different catalysts: mesoporous α -Mn₂O₃, 15 wt% Cu/Mesoporous α -Mn₂O₃, bulk Mn oxides (Mn₂O₃, MnO₂, and MnO), and 15 wt% MnO_x/KIT-6. Generally, carbon balance was achieved between the benzene conversion and CO₂ production at 300 °C indicating that most of the benzene was converted to CO₂ through the oxidation reaction. At lower temperatures, on the other hand, carbon balance was not achieved because a considerable amount of benzene was not decomposed, but adsorbed on the surface of the catalysts. When commercial bulk Mn catalysts were used for the oxidation of benzene, the order of catalytic activity was Mn₂O₃ > MnO₂ > MnO at 300 °C,



Fig. 2. XRD patterns of mesoporous catalysts (a) at low angle (b) at high angle.

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Fig. 3. TPR analysis results of mesoporous catalysts.

that is, the Mn₂O₃ phase showed the highest activity for benzene oxidation. The higher activity of mesoporous α -Mn₂O₃ compared with bulk Mn₂O₃ can be attributed to the even distribution of Mn₂O₃ in the mesoporous structure. In particular, the benzene conversion of mesoporous α -Mn₂O₃ was more than double that of bulk Mn₂O₃ at 300 °C. This result demonstrates that mesoporous α -Mn₂O₃ is an excellent catalyst for benzene oxidation. The benzene conversion and CO₂ yield were slightly increased when 15 wt% Cu/Mesoporous α -Mn₂O₃ was used, which is consistent with its higher reducibility compared with mesoporous α -Mn₂O₃ (Fig. 3). However, further study would be required to evaluate the catalytic activity of Cu/Mesoporous α -Mn₂O₃ more quantitatively.

The activity of 15 wt% $MnO_x/KIT-6$ was generally low. This result is contrary to that reported in a previous study for the catalytic ozonation of benzene, in which $MnO_x/KIT-6$ showed a higher activity than mesoporous α -Mn₂O₃.^{3, 13} Ozone molecules can be decomposed easily over the well-distributed MnO_x surface of MnO_x/KIT-6 into oxygen radicals via the following reaction:¹³

$$0_3 + * \rightarrow 0_2 + 0^*$$

The oxygen radicals can then oxidize the benzene adsorbed on the catalyst surface. Because 15 wt% $MnO_x/KIT-6$ has a larger specific surface area than mesoporous α -Mn₂O₃, the amount of benzene adsorbed on the catalyst surface is larger for $MnO_x/KIT-6$, which leads to a higher reaction activity. In the catalytic oxidation, on the other hand, it is not ozone but oxygen molecules that participate in the reaction. Therefore, the characteristic of





Fig. 4. Benzene conversion and CO_2 yield obtained using different catalysts.

the manganese oxide is a more important factor than the specific surface area in determining the catalytic activity. Unlike 15 wt% $MnO_x/KIT-6$, in which various manganese oxides with different oxidation states, e.g., Mn_2O_3 and MnO_2 , co-exist,¹³ mesoporous α -Mn₂O₃ contains only well-distributed Mn_2O_3 , which has the highest activity among the manganese oxides, resulting in its higher catalytic activity.

4. CONCLUSIONS

Mesoporous α -Mn₂O₃, which contains well-distributed Mn₂O₃, the most active manganese oxide for benzene oxidation, showed a very high catalytic activity for the decomposition of benzene. On the other hand, 15 wt% MnO_x/KIT-6, which contains various manganese oxides with different oxidation states, exhibited a relatively low catalytic activity for the decomposition of benzene, in spite of its large specific surface area.

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