Catalytic activity of manganese oxide type raney catalyst prepared by alkali treatment of metal silicide

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Manganese oxide particles were prepared by alkaline treatment of the manganese and silicon compound. Silicon was selectively dissolved by the alkaline treatment, forming an aggregate structure of plate-like particles. Consequently, owing to the high specific surface area and surface exposure of the manganese, the catalyst exhibited excellent behavior in the oxidative decomposition of benzene.

Key-words : Raney catalyst, Manganese oxide, Benzene, Oxidative decomposition

Raney catalysts are known to exhibit an excellent performance because of their high specific surface area.¹ The most common Raney catalyst is Nickel based and can also be synthesized using manganese (Mn) and Copper (Cu). These elements are expected to have high catalytic activity for the oxidative decomposition of Volatile Organic Compounds (VOCs).²–⁴ Noble metal catalysts exhibit high catalytic activity at very low temperatures but they are not widely used in industrial processes because they are expensive, volatile, and can be sintered.⁵ Unlike noble metals, many activated transition metal oxides are known to be abundant and inexpensive.⁶ Among the active oxide catalysts for oxidative decomposition of VOCs, Manganese oxide⁷–⁸ exhibits good activity and is known to be an environmentally friendly material⁹–¹¹. In contrast, it has been reported that oxidation catalysts exhibit high catalytic activity when their specific surface area is increased by controlling the size of the structure to approximately submicrometer and nanometer.¹² However, a high specific surface area catalyst cannot be synthesized by the coprecipitation method that is used for preparation of Mn oxide catalysts.⁵

In this study, we prepared Mn oxide particles with a high specific surface area synthesizing using Raney catalyst. Furthermore, the catalytic activity of the obtained Mn oxide particles for benzene oxidation decomposition is examined.

Mn oxide particles were synthesized as follows: Mn powder (>99.9%, Kanto Chemical Co.) and silicon(Si) powder (>99.9%, <1 µm, Panasonic Environmental Systems & Engineering Co.) mixture of Mn/Si = 4/7 molar ratio, and 70%/wt, of KCl (special grade of Kanto Chemical Co.) were filled in a ceramic tube (SSA-H grade, alumina 99.6%) and calcined at 900 ⁰C for 6 h to obtain manganese silicide Mn₄Si₇ (non-treated). KCl plays the role of flux and promotes the reaction between Mn and Si at low temperatures. Alkaline treatment of the synthesized Mn₄Si₇ was conducted using NaOH solution (1–10 M). The suspension of the Mn₄Si₇ and the NaOH solution was stirred at 60 ⁰C for 2 h and filtered. The resulting solid particles were dried at 50 ⁰C.

The prepared catalyst was characterized using X-ray powder diffraction (XRD), Field Emission–Scanning Electron Microscope (FE–SEM), Transmission Electron Microscope (TEM), the nitrogen adsorption method and X-ray Photoelectron Spectroscopy (XPS).

Catalytic activity tests were carried out in a conventional fixed-bed flow reactor at atmospheric pressure using 0.1 g of a prepared sample with an average particle size of 200 µm. The total flow rate of the reaction mixture was 250 mL/min, corresponding to a weight hourly space velocity of 150 L/(gh). Benzene was chosen as a representative example of VOC and was introduced into the reaction feed made of a controlled flow of dry synthetic air (N₂/O₂ = 21:79) which passes through a saturator at 35 ⁰C. The benzene concentration in the mixed gas was 250 ppm. The effluent gases were analyzed using gas chromatography (Shimazu GC–8A) equipped with a flame-ionization detector.

Figure 1(a) shows the non-alkaline treated sample (non-treated). Sharp diffraction lines of Mn₄Si₇ were
confirmed. A small diffraction peak around 28° was attributed to unreacted Si. Figures 1(b)–1(d) show the XRD patterns of the samples treated at 1, 5, and 10 M of NaOH solutions, respectively. The peak of Mn$_4$Si$_7$ decreased as the alkali concentration increased. The 5 and 10 M samples exhibited an amorphous halo observed from 30 to 40°. The amorphous material was considered to be formed on the surface by the oxidation of Mn resulting in the selective dissolution of Si. In the sample treated at 10 M, three crystalline phases of Mn$_3$O$_4$, Mn$_4$O$_7$ and cryptomelane KMn$_8$O$_{16}$ showing peaks at 12, 38 and 60° were observed.

**Figure 2** shows the FE-SEM images. Non-alkaline treated sample is the undetermined form with a size range of 1.0 to 1.7 μm, and the surface is confirmed to be smooth [Fig. 2(a)]. In the sample treated at 5 M, an aggregate structure of plate-like sub-micrometer particles with thickness of 15 to 30 nm was confirmed [Fig. 2(b)].

The TEM image shown in **Fig. 3** is one of the plate-like nanosheets identified in Fig. 2(b), observed from a direction perpendicular to the plane. 3a indicates that the contrast is uneven. This means that the thickness is not uniform. It was confirmed that the thick portion formed a shape where the flaked edge was turned up [arrow in Fig. 3(a)]. One of the plate-like nanosheets shows a polycrystalline structure with a crystallite size of about 10 nm. The interval between the lattice stripes indicated by the white line in 3b is 3.46 Å, which corresponds to the Mn$_3$O$_4$ (104).

The hysteresis curve confirmed using the nitrogen adsorption method shows a type IV, indicating the presence of mesoporous (Fig. 4). In analyzing the pore distribution, pore sizes of majorly 2 nm were confirmed. Furthermore, as summarized in **Table 1**, the specific surface area of the sample treated at 5 M has the highest value. It was inferred that voids were present in the particles due to the removal of Si caused by the alkali treatment and that also, the formation of irregularities at the surface of the particles, contributed to the increased specific surface area.

In this study, we analyzed only Mn and Si by XPS. The XPS results show that the Non-treated Si/Mn [atomic
ratio] is 15.11, which is much higher than the composition ratio of Mn$_4$Si$_7$. As a result, it is considered that Si species spread lightly on the surface. This result seemed to be due to residual Si that was confirmed by XRD. It was confirmed from the decrease in the Si/Mn ratio that Si on the sample surface was eluted and the Mn was exposed to the surface by the treatment with NaOH solution (Table 1). Furthermore, it was also observed that Si/Mn ratio was reduced by increasing the concentration of the NaOH solution.

Catalytic oxidation of benzene was performed using a non-treated sample, samples treated at 5, 1, 2.5, 5, 7.5, and 10 M. From Fig. 5, the treated at 5 M showed the highest performance. The catalyst performance was increased by increasing the concentration of the NaOH solution, but the activity was reduced with the catalyst having the NaOH solution concentration higher than 5 M. The conversion temperatures at 50 and 90% of the treated sample of 5 M showed the highest activity which was 170.2 and 208.8 °C.

In conclusion, it was confirmed that when Mn$_4$Si$_7$ was treated with 5 M of NaOH solution, a plate-like nanoparticle integrated structure containing both crystalline and amorphous parts was formed. In the benzene oxidation test, the sample treated at 5 M showed the highest activity. This is because of the high Mn exposure rate and also the high specific surface area that was excellent.

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