The effect of the Mn oxidation state on the activity of supported MnOx nanocluster catalysts in the 1-phenylethanol oxidation reaction

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1 Introduction
Manganese catalysts attract considerable attention from both academia and industry due to the low cost in contrast to the precious metal catalysts. Furthermore, manganese oxides were chosen as the catalyst because it has an oxidation ability. Our previous work also showed the good activity for aerobic alcohol oxidation with supported MnOx nanoclusters, however, the effect of oxidation state on the catalytic activity has not been clarified [1].

In this work, we prepared supported MnOx catalysts with different supporting materials and investigated the local structure by utilizing XAFS. As a result, we found that adjusting the oxidation state of Mn could be a useful approach to prepare a highly efficient supported MnOx nanocluster catalyst.

2 Experiment
MnOx nanoclusters on SiO2 (Aerosil, #200) and Al2O3 (Aerosil, Alumina C) support was prepared by a colloidal method. Colloidal Mn particles were prepared by reducing Mn(OAc)2 with NaBH4 in the presence of poly(N-vinylpyrrolidone) (PVP). Subsequently, the catalyst was obtained by fixing colloidal particles on supporting materials. Mn loading amount was regulated to 3 wt%. Mn K-edge X-ray absorption fine structure (XAFS) data were collected at BL-12C of IMSS-KEK PF (Proposal No. 2018G063) with a Si(111) double crystal monochromator in transmission mode.

3 Results and Discussion
Fig. 1A shows FT spectra of k1-weighted Mn K-edge EXAFS. The peak intensity of colloidal derived catalysts (d and e) are smaller than that of reference compounds (a-c), which indicated the nanosized manganese oxide formation in the catalysts.

![FT spectra of Mn K-edge EXAFS](image)

Fig. 1. (A) FT of Mn K-edge EXAFS spectra and (B) Mn K-edge XANES spectra for (a) MnO2, (b) Mn2O3, (c) Mn3O4, (d) Mn/SiO2, (e) Mn/Al2O3.

Mn K-edge XANES spectra of catalysts are not completely same as that of any bulk MnOx, suggesting that the Mn species on catalyst exists with various oxidation states as shown in Fig. 1B. Pattern fitting of XANES was carried out in order to estimate the ratio of each component and the results are shown in Table 1. In MnOx/Al2O3, the ratio of MnO2 was increased compared to MnOx/SiO2.

Oxidation reaction of 1-phenylethanol was carried out and the results are shown in Table 1. Prepared catalysts were active for the oxidation of 1-phenylethanol using molecular oxygen without any additives such as base reagents. We have already evaluated the cluster size effect for the aerobic oxidation [1]. Therefore, high activity of the prepared catalysts might come from the decrease of cluster size.

In addition, the high yield was obtained on MnOx/Al2O3. Our previous studies have shown that a good redox property of MnO2 is beneficial for the catalytic performance of 1-phenylethanol oxidation [1]. Therefore, through the results of characterization and catalytic reaction, we concluded that the formation of MnO2 on alumina support lead to good activity for this reaction.

Table 1 Acetophenone yield* and pattern fitting results* of prepared catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn/SiO2</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>Mn2O3</td>
<td>38</td>
<td>23</td>
</tr>
<tr>
<td>Mn3O4</td>
<td>31</td>
<td>10</td>
</tr>
<tr>
<td>Mn/Al2O3</td>
<td>43</td>
<td>39</td>
</tr>
</tbody>
</table>

*1-Phenylethanol (1 mmol), MnOx catalyst (0.10 g, S/C = 18), solvent: p-xylene (5 mL), atmosphere: O2 (1 atm), reaction temperature: 373 K, reaction time: 6 h.
* Determined by XANES pattern fitting analysis.
* Determined by gas chromatography using an internal standard technique.

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Reference
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