BL-12C/2018G063

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

Kyoko NAKAMURA, Nobuyuki ICHIKUNI*, Takayoshi HARA and Shogo SHIMAZU
Graduate School of Science and Engineering, Chiba University,
1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan

1 Introduction

Manganese catalysts attract considerable attentions from both academia and industry due to the low cost in contrast to the precious metal catalysts. Furthermore, manganese oxide was 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 nanocluster, 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 nanocluster on SiO_2 (Aerosil, #200) and Al_2O_3 (Aerosil, Alumina C) support was prepared by a colloidal method. Colloidal Mn particles were prepared by reducing $Mn(OAc)_2$ with $NaBH_4$ 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 k^3-weighted Mn *K*-edge EXAFS. The peak intensity of colloid derived catalysts (d and e) are smaller than that of reference compounds (a-c), which indicated the nanosized manganese oxide formation in the catalysts.

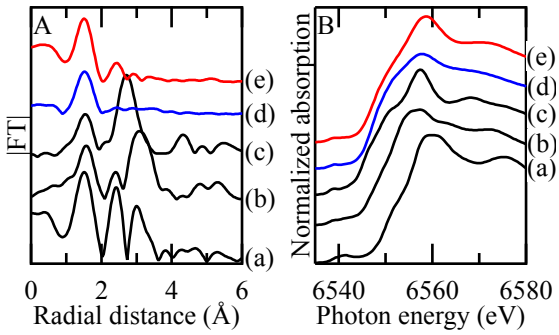


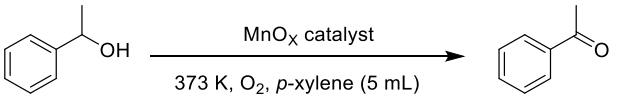
Fig. 1. (A) FT of Mn *K*-edge EXAFS spectra and (B) Mn *K*-edge XANES spectra for (a) MnO_2, (b) Mn_2O_3, (c) Mn_3O_4, (d) Mn/SiO_2, (e) Mn/Al_2O_3.

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 $MnOx/Al_2O_3$, the ratio of MnO_2 was increased compared to $MnOx/SiO_2$.

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 $MnOx/Al_2O_3$. Our previous studies have shown that good redox property of MnO_2 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 MnO_2 on alumina support lead to good activity for this reaction.

Table 1 Acetophenone yield[a] and pattern fitting results[b] of prepared catalysts



Catalyst	Yield[c] (%)	Composition (%)			
		MnO_2	Mn_2O_3	Mn_3O_4	MnO
Mn/SiO_2	13	8	51	31	10
Mn/Al_2O_3	43	38	23	39	0

[a]1-Phenylethanol (1 mmol), MnOx catalyst (0.10 g, S/C = 18), solvent: *p*-xylene (5 mL), atmosphere: O_2 (1 atm), reaction temperature: 373 K, reaction time: 6 h. [b]Determined by XANES pattern fitting analysis. [c]Determined by gas chromatography using an internal standard technique.

Acknowledgement

This study was supported by JSPS KAKENHI Grant Number 17K06912.

Reference

[1] K. Nakamura, N. Ichikuni *et al.*, *Catal. Today* **352**, 250 (2020).

* ichikuni@faculty.chiba-u.jp