

High Catalytic Performance of USY-Supported Manganese Oxides for VOC Control

Catalytic oxidation processes using ozone (catalytic ozonation processes) are effective for controlling volatile organic compounds in indoor air. We investigated the relationship between the local structure of active sites, manganese oxides and their catalytic activity for benzene oxidation. On the basis of EXAFS and XANES studies on the manganese oxide structures, we developed a promising catalyst, which consisted of ultrastable Y (USY) zeolite and manganese oxides. The manganese oxides were highly dispersed on USY and the manganese oxide active sites exhibited high performance for catalytic ozonation of benzene in the temperature range of 300–343 K in the presence of water vapor.

Purification of indoor air polluted with volatile organic compounds (VOCs) is an important area of research on catalysis. Catalytic oxidation with ozone (catalytic ozonation) is effective for complete oxidation of VOCs under mild conditions, particularly compared with other processes such as absorption, adsorption, and catalytic combustion. Catalytic ozonation processes have an advantage over catalytic combustion processes in that metal oxides of the first transition series (Fe, Co, Mn, and Cu) [1-5] can be used for catalytic active sites, eliminating the need for more expensive metals (e.g., Pt and Pd).

We focused on the supported manganese oxide catalysts and investigated the relationship between the structure of manganese oxides and their catalytic activity for benzene oxidation [6-11]. The structure and oxidation state of manganese oxides were investigated using EXAFS and XANES studies. The spectra were taken at the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF) on beamline BL-7C, which has a storage ring operating energy of 2.5 GeV. Catalyst samples were pressed into thin, self-supporting discs. These discs were heated in an O₂ flow for 2 h at 723 K, and then tightly sealed in polyethylene with inert gas. XAFS spectra were recorded at 296 K.

EXAFS studies revealed that the dispersion of manganese oxides can be easily controlled by selectively using the manganese precursors: highly dispersed manganese oxides were formed on the SiO₂ support when manganese acetate was used in the impregnation method. On the other hand, aggregated manganese oxides Mn₂O₃ and Mn₃O₄ were formed when manganese nitrate was used and the calcination temperature was changed. Both the highly dispersed manganese oxides

and aggregated manganese oxides exhibited benzene oxidation activity, and the product distribution (mole fraction of CO₂, CO, and formic acid) and the ratio of the amount of ozone to benzene, which characterized the efficiency of ozone utilization, were hardly affected by the dispersion of manganese oxides.

We have also investigated the effect of the catalyst support on the supported manganese oxides and have reported that the rate of benzene oxidation linearly increased with the increase in catalyst surface area. The ratio of decomposition of ozone to benzene was the lowest for SiO₂-supported manganese oxides. Therefore, SiO₂-supported manganese oxides with large surface area are promising in terms of catalytic activity and efficiency of ozone utilization.

In the case of SiO₂-supported manganese oxides, however, the amount of formic acid formed in the effluent gas stream increased when the benzene oxidation was carried out at low benzene conversion levels. Therefore, we subsequently focused on zeolite as the supporting material because of its large surface area and high capacity for formic acid adsorption. We tested various kinds of zeolite for manganese oxides and found that when zeolite Y was used as the catalyst support, the evolution of formic acid was significantly suppressed: the byproduct formic acid formed in benzene oxidation was trapped in the zeolite support and readily oxidized to CO₂. Furthermore, manganese oxide catalysts supported on ultrastable zeolite Y (Mn/USY) (Zeolyst CBV390H, SiO₂/Al₂O₃ = 180, surface area 875 m²/g) prepared by an impregnation method (Fig. 1) exhibited steady-state activity for benzene oxidation with ozone at room temperature (300 K) in the presence of water vapor.



Figure 1: Preparation process for USY-supported manganese oxide catalysts.

EXAFS studies clarified the local structure of manganese active sites on the USY support. As shown in Fig. 2, the Mn-O peak was observed at ~1.5 Å for the Mn/USY catalysts, although the Mn-Mn peaks were much lower in intensity. The quantitative analysis performed on the EXAFS spectra demonstrated that the coordination number (CN) of Mn-O was in the range of 5.1–5.2 and that of Mn-Mn was much lower (0.38–0.49). The results indicated that aggregated manganese oxides were absent and manganese oxides were highly dispersed on USY. In addition, the Mn-O and Mn-Mn coordination numbers and their bond distances were essentially unchanged when manganese oxide loading increased from 5 to 15 wt%, showing that the local structure of manganese oxides on USY was essentially independent of Mn loading.

In summary, we developed promising catalysts for reducing VOC using ozone based on XAFS studies for structural analysis of supported manganese oxides. Our next target is to design high-performance catalysts by tuning the active sites and supporting materials.

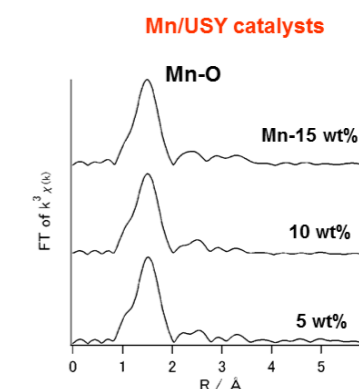


Figure 2: Mn-K edge EXAFS spectra of USY-supported manganese oxide catalysts.

REFERENCES

- [1] A. Gervasini, G.C. Vezzoli and V. Ragaini, *Catalysis Today* **29**, 449 (1996).
- [2] D. Mehandjiev, A. Naydenov and G. Ivanov, *Appl. Catal. A: General* **206**, 13 (2001).
- [3] S. Dimitrova, G. Ivanov and D. Mehandjiev, *Appl. Catal. A: General* **266**, 81 (2004).
- [4] A. Naydenov and D. Mehandjiev, *Appl. Catal. A: General* **97**, 17 (1993).
- [5] C. Reed, Y.-K. Lee and S.T. Oyama, *J. Phys. Chem. B* **110**, 4207 (2006).
- [6] H. Einaga and S. Futamura, *J. Catal.* **227**, 304 (2004).
- [7] H. Einaga and S. Futamura, *J. Catal.* **243**, 446 (2006).
- [8] H. Einaga and A. Ogata, *J. Hazard. Mater.* **164**, 1236 (2009).
- [9] H. Einaga and S. Futamura, *Catal. Commun.* **8**, 557 (2007).
- [10] H. Einaga, Y. Teraoka and A. Ogata, *Catal. Today* **164**, 571 (2011).
- [11] H. Einaga, Y. Teraoka and A. Ogata, *J. Catal.* **305**, 227 (2013).

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