

CATALYTIC DECOMPOSITION OF DIOXINS OVER MANGANESE OXIDE

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Introduction

It is known that dioxins in the flue gas emitted from municipal waste incinerators can be reduced to below the strict emission limits by utilizing the TiO₂-based V₂O₅-WO₃ catalyst.^{1,2} This catalyst decomposes dioxins effectively at around 220°C. However, the temperature of the flue gas is around 160°C due to the usage of a bag-filter, which is used to remove the dust. At 160°C, acidic ammonium sulfate, NH₄HSO₄, which is a product of NH₃ and SO_x in the flue gas, deposits onto the catalyst and decreases the catalytic activity.³ Therefore, the flue gas needs to be re-heated to around 220°C at which temperature NH₄HSO₄ can not deposit on the catalyst. On the other hand, this re-heating operation is reported to increase the dioxins concentration.⁴ To avoid this problem, proper catalyst which does not lose its activity at around 160°C should be studied.

Manganese oxide, MnOx, has been proposed as one of the candidate.^{5,6} The advantages of manganese oxide are, 1) this catalyst has a high oxidation activity at a low temperature range and 2) the ammonium sulfate problem does not occur on this catalyst because of its high NH₃ decomposing ability.⁵ Therefore, strong dioxins decomposing activity is expected by the usage of manganese oxide. The form of the catalyst is important from a practical point of view. Honeycomb form is required to avoid the dust trouble.

In this report, several types of the manganese oxide were examined in the pellet form and the effect of the additives such as Fe was investigated in honeycomb form to find the maximum ability of the catalyst.

Method and Materials

Preparation of Catalysts. Figure 1 shows an example of the procedure scheme for the catalyst preparation. Composite oxides of Fe and Mn (Fe/MnOx) were prepared by coprecipitation and oxidation from a mixed aqueous solution of FeSO₄ and MnSO₄. The pellet type catalysts were molded by being mixed with Al₂O₃ sol, extruded into the size of 1/8 inch diameter, and dried at 100°C for 2h in air. Honeycomb catalysts were molded by being mixed with inorganic additives for molding such as TiO₂ and an organic binder, extruded into a honeycomb form, dried at 100°C for 2h, and calcined at 400°C for 4h in air. The honeycomb section is 150mm square and there are 35 cells. Ruthenium (Ru) compounds were added to a few catalysts. Addition of Ru compounds was carried out by spraying of Ru compounds aqueous solution for pellet, and by impregnation for honeycomb.

Apparatus and Procedures. Ortho-dichlorobenzene (DCB) was used as the model compound of dioxins to survey a suitable catalyst in the first step. It is said that the oxidized scheme of DCB is similar to that of dioxins, and that DCB is hardly decomposed more than dioxins.⁷ Catalytic reactions were carried out in a flow reactor (21mm internal diameter and 1.2m length) equipped

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with DCB supplying unit. O_2 (10vol%), H_2O (10vol%), DCB(10ppm), and N_2 were introduced to the reactor. DCB conversions were examined by measuring the concentration of DCB before and after the catalyst using a gas chromatograph.

In the next step, dioxins decomposition activities were examined in the laboratory for the manganese oxides chosen in the DCB test. Catalytic reactions were carried out in a flow reactor (square 29mm and 1.2m length) in the same way as the DCB Test. The supplying of dioxins to the catalysts were carried out as follows. Supplied dioxins had three congeners of 2,3,7,8-T4CDD, 1,2,3,6,7,8-H6CDD, and O8CDD. Each dioxin was dissolved with nonane ($n-C_9H_{20}$), then the solution was introduced to the gas. These dissolved dioxins were evaporated in the gas by heating, and supplied to the catalysts. The concentration of supplied dioxins was almost controlled at $10ng/Nm^3$. Dioxins concentrations before and after the catalysts were measured by the Japanese Welfare Ministry standard method.

In the final step, dioxins removal activities of the catalysts were examined with the exhaust stream emitted from an actually operating fluidized-bed incinerator with a bag-filter. The reactors and the measurement methods used for this actual gas were the same as the case of dioxins test in the laboratory.

Results and Discussion

DCB and Dioxins Decomposition Activity of Pellet Catalyst. In the first step of the survey for suitable manganese oxides, pellet type catalysts were used. Figures 2 and 3 show the conversions of DCB and dioxins over the pellet catalysts, respectively. The order of the conversions of DCB corresponded to those of dioxins. The DCB removal activities of Fe/MnOx and MnOx were higher than that of TiO_2 -based $V_2O_5-WO_3$. Furthermore, the addition of the Ru compound was found to be effective in improving the removal activity of manganese oxide at a low temperature. However, DCB removal activities were not observed with Ru compound supported on Al_2O_3 . With regard to the state of Ru examined by the XPS analysis, only Ru(IV) was observed in the case of Ru supported on Al_2O_3 . As for the manganese oxide, a major state of Ru was Ru(IV) similarly to the case of Al_2O_3 , but Ru(VI) was a little observed.

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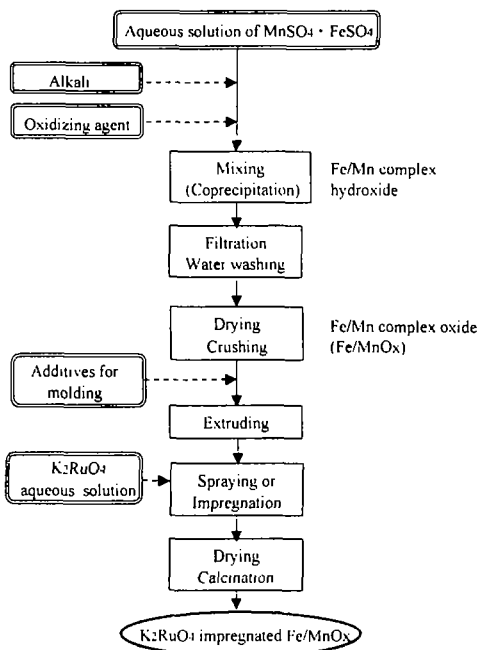


Figure 1. Preparation procedure of catalyst

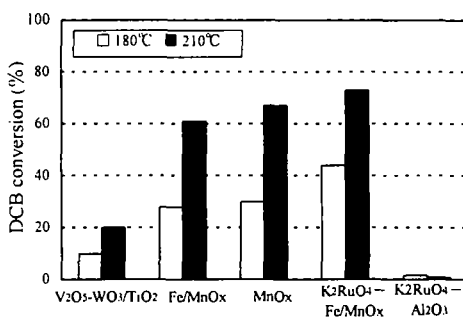


Figure 2. DCB conversion of the pellet catalysts, at $SV\ 9000h^{-1}$, and DCB conc. 10ppm

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It is known that K_2RuO_4 can exist stably only in a strong alkali aqueous solution. Therefore, Ru in $K_2Ru(VI)O_4$ must be hydrolyzed at the spraying stage which is necessary to dilute the K_2RuO_4 . In the case of Ru supported on Al_2O_3 , this hydrolysis caused the reduction and the deactivation of the Ru. As for the manganese oxide, the reduction of Ru must occur at spraying as in the case of Al_2O_3 , but Ru is possibly reoxidized to Ru(VI) by the manganese oxide which have strong oxidizing ability. The high DCB removal activities of the Ru on manganese oxide can be attributed to the high oxidation state of Ru.

However, since the Ru compound has the possibility of evaporation at elevated temperatures, more examination about the durability is necessary.

DCB Decomposition Activity of Honeycomb Catalyst. Honeycomb is a more complex shape than pellet, and requires a more advanced molding technique to get high strength and dimension accuracy. Therefore, additives such as an inorganic compound to get high strength, and an organic binder for shape maintenance after extruding, are necessary.

The activity of TiO_2 -based Fe/MnOx honeycomb that changed the ratio of Fe and Mn is shown in Figure 4. FeOx that doesn't contain Mn didn't exhibit activity, and the activities rose in accordance with the increase of the Mn containing rate. In the case of an organic binder used, when Mn/(Fe+Mn) rates were larger than 0.7, the conversion declined again, and the conversion wasn't observed in the case of MnOx which doesn't contain Fe. On the other hand, in the case without an organic binder, MnOx exhibited a high activity.

Figure 5 shows the relationship between the Mn/(Fe+Mn) ratios and the oxidation numbers of Mn in honeycomb. In the case without an organic binder, the oxidation-number was an almost constant value regardless of the Fe content. On the other hand, when an organic binder was used and the Mn/(Fe+Mn) ratio was larger than 0.7, the number declined to 3.0.

These results suggest that Mn in MnOx was reduced and deactivated by the organic binder at

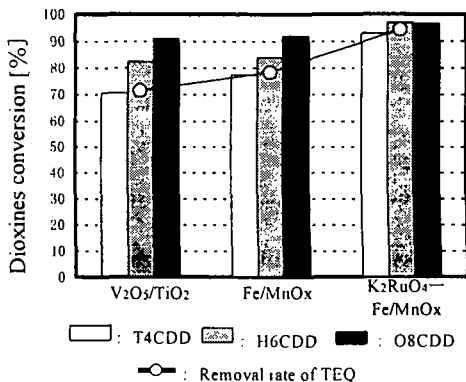


Figure 3. Dioxins conversions with the pellet catalysts, at $SV\ 30000h^{-1}$, and Each dioxin conc : $10ng/Nm^3$.

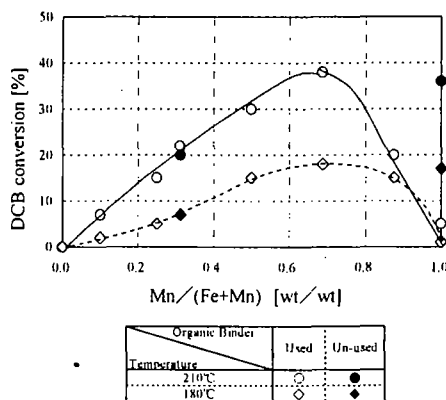


Figure 4. Relationship between Mn/(Mn+Fe) ratios and DCB conversions, at $SV\ 9000h^{-1}$, and DCB Conc. : 10ppm.

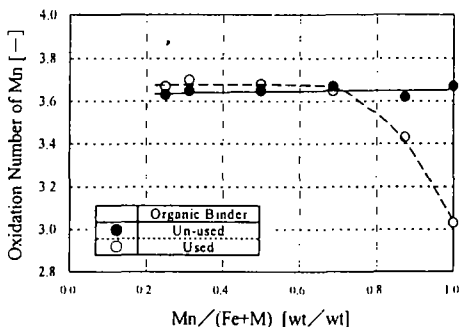


Figure 5. Relationship between Mn/(Mn+Fe) ratios and oxidation numbers of Mn.

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the calcination step. In the case of Fe/MnOx, as is shown in Figure 6, Fe³⁺ in Fe/MnOx can be considered to be reduced into Fe²⁺ by the organic binder, this reduced Fe²⁺ can be oxidized by O₂ in air quickly, and then this O₂ is reduced to O₂⁻ or O₂²⁻ which have a strong oxidation ability simultaneously. This active oxygen species can reoxidize the reduced Mn. As described above, Fe in Fe/MnOx can prevent from the reduction of Mn in calcination, and it enables the use of the organic binder that is preferable to use at the extruding step. Figure 5 suggests that the most suitable Mn/(Mn+Fe) ratio which brings such an effect is approximately 0.7.

Consequently, though the activity of Fe/MnOx pellet is inferior to that of MnOx, Fe/MnOx was considered as more suitable for honeycomb molding.

Dioxins Decomposition Activity of Honeycomb Catalyst. Table 1 shows the dioxins conversions with honeycomb catalysts, which were applied to the flue gas from a municipal solid waste incinerator. It was confirmed that TiO₂-based Fe/MnOx honeycomb catalyst has higher dioxins decomposition activity than conventional TiO₂-based V₂O₅-WO₃ catalyst in the case of the actual gas, as well.

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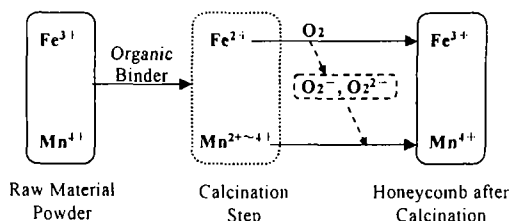


Figure 6. The effect of the Fe in the manganese oxide honeycomb

Table 1. The dioxins conversion over TiO₂ based Fe/MnOx and TiO₂ based V₂O₅-WO₃

	TiO ₂ based Fe/MnOx	TiO ₂ based V ₂ O ₅ -WO ₃
Dioxins concentration		
Inlet [ng-TEQ/Nm ³]	0.13	
Outlet [ng-TEQ/Nm ³]	0.010	0.022
Conversion [%]	92	83

Temperature 170°C, SV 5000h⁻¹