

# Investigation of the catalytic effect of MnO<sub>2</sub> in the combination with activated carbon fiber on the removal of NO

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## Introduction

NO<sub>x</sub> in the urban atmosphere has been markedly reduced after the imposition of selective catalytic reduction (SCR) for flue gas, three-way catalyst system for the mobile gasoline engine, and Diesel Particulate Filter (DPF) for the diesel engine to reduce the NO<sub>x</sub> in the exhaust in addition to the low NO<sub>x</sub> exhaust combustion. Nevertheless, some particular areas such as special busy cross-sections at three dimensional intersections or surrounded by tall buildings where the natural wind fails to ventilate the atmosphere are highly contaminated with NO<sub>x</sub>, causing the health problems to the habitants in the neighborhood. Large cities or their suburbs are forced to take special actions to reduce NO<sub>x</sub> in such particular areas.

Removal of NO<sub>x</sub> in the atmosphere at room temperature has been proposed by adsorption after photo catalytic oxidation on TiO<sub>2</sub>[1], biological oxidation[2], absorption in the soil[3], and adsorption on activated carbon[4]. By such ways, adsorption of oxidized NO must be saturated at a certain level or eluted out in form of HNO<sub>3</sub>. Special cares are necessary when cleaning of atmosphere is attempted.

We have examined the combination of MnO<sub>2</sub>, urea and ACF to enhance the catalytic oxidation of NO in the atmosphere into NO<sub>2</sub> which was continuously reduced by urea on ACF into N<sub>2</sub> and H<sub>2</sub>O. More NO can be trapped over ACF than MnO<sub>2</sub> alone because of very large surface area of ACF. Thus, we can expect that NO once adsorbed over ACF can be transferred to MnO<sub>2</sub> for the successive catalytic oxidation. The spillover of NO<sub>2</sub> produced over MnO<sub>2</sub> to ACF is very concerned for the successful combination of catalyst oxidation and reduction by urea on ACF. Although the liberation of NO<sub>2</sub> from MnO<sub>2</sub> surface was observed, the transfer of NO<sub>2</sub> to ACF must be enhanced through the close contact of MnO<sub>2</sub> and ACF.

In this study, we examined the MnO<sub>2</sub> supporting effect of NO oxidation in the low NO concentration system. Supported MnO<sub>2</sub> will be expected the more removal capacity of the catalytic oxidation of NO to NO<sub>2</sub> compared to non-supported ACF, and simple mixture of MnO<sub>2</sub> powder and ACF.

## Experimental

Manganese dioxide MnO<sub>2</sub> powder, quartz wool (fine grade, 2~6 μm) was prepared using Mn nitrate (Wako, Japan). PAN based carbon fiber (SY-800) and pitch-based ACF (OG-7A) were obtained from Osaka Gas Co. The ACF calcined at 600°C for 1 h in Ar atmosphere was used for this study.

The ACF was dipped into Mn acetate and Mn nitrate solutions were stirred for 24 h at room temperature, filtered without washing, and then dried at 50 torr in a vacuum oven for 1 h. Dried samples were calcined at 300°C using horizontal type tube furnace under N<sub>2</sub> atmosphere. Fig.1 shows the preparation processes of samples in this study.

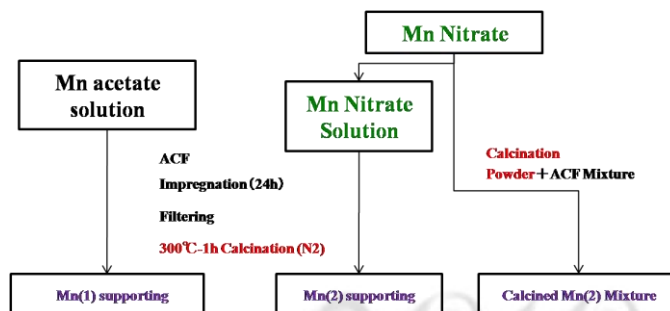


Fig. 1 Sample preparation processes in this study

Reaction of NO was carried out in a fixed bed flow reactor. The samples were closely packed into transparent quartz tube (inner diameter: 12~13 mm, outer diameter: 15 mm, length: 50 cm). The length of the packed samples was 12~24 cm. The composition and flow rate of feed NO in O<sub>2</sub>-N<sub>2</sub> mixture (21:79, vol/vol, ml) were adjusted to be 0.5~2.0 ppm and 100 ml/min, respectively. The concentration of NO at the inlet and outlet of the reactor was measured continuously by the NO<sub>x</sub> analyzer (Yanagimoto Co. Ltd., ECL-88US).

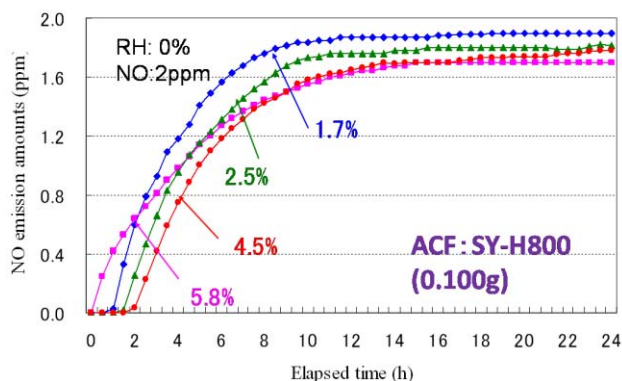
## Results

Fig. 2 shows the oxidation of 2 ppm of NO in air over various amounts of MnO<sub>2</sub> supported ACF. Over MnO<sub>2</sub> supported ACF, NO was oxidized into NO<sub>2</sub>. No nitric product was found for a certain time of period of which length was strongly dependent upon the concentration of NO. NO of 2 ppm was removed completely for 2 hs over 4.5 wt% MnO<sub>2</sub> supported ACF.

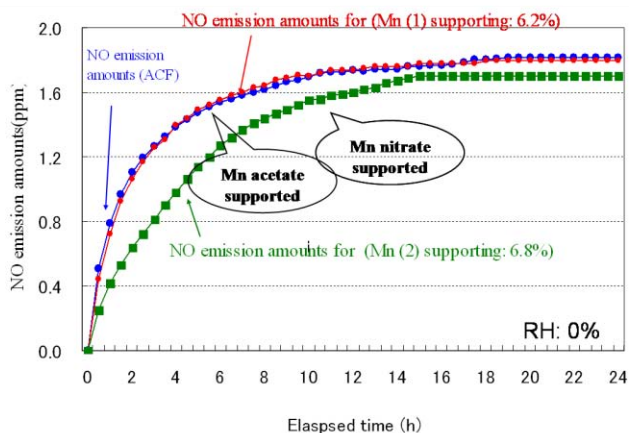
Fig. 3 shows the effect of the supporting method of MnO<sub>2</sub> on ACF. MnO<sub>2</sub> supported ACF using the precursor of Mn nitrate showed more oxidation amounts of NO than that from the precursor of Mn acetate. The careful examination of the reason for this difference is under progress now.

Fig. 4 shows the effect of the mixture and supported MnO<sub>2</sub> with/on ACFs on NO oxidation into NO<sub>2</sub>. ACF alone showed very low oxidation activity of NO. Compared to simple mixture of MnO<sub>2</sub> with ACF, MnO<sub>2</sub> supported ACFs showed higher oxidation activities. Among MnO<sub>2</sub> supported ACFs, MnO<sub>2</sub> supported on pitch based ACF showed the highest oxidation activity of NO. Especially, MnO<sub>2</sub> supported

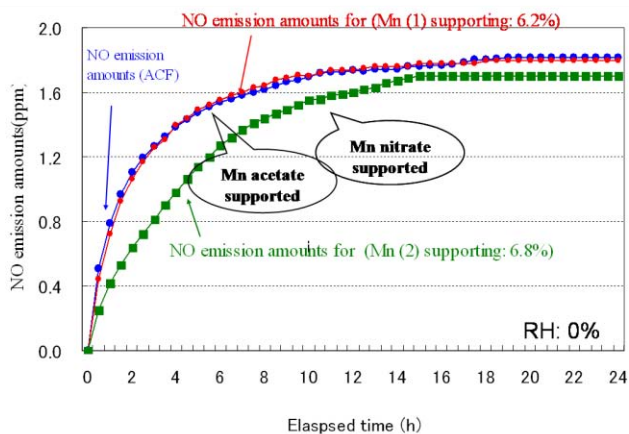
ACF carried out higher NO oxidation activities even if the smaller amounts of MnO<sub>2</sub> was used compared to the simple mixture of MnO<sub>2</sub> and ACF.



**Fig.2** NO oxidation activities of MnO<sub>2</sub> supported ACFs according to the supporting amount of MnO<sub>2</sub>



**Fig. 3** NO oxidation activities of MnO<sub>2</sub> supported ACFs according to the different precursors of MnO<sub>2</sub>



**Fig. 4** The effect of the mixture and supported MnO<sub>2</sub> with/on ACFs on NO oxidation into NO<sub>2</sub>

## Conclusion

The combination of MnO<sub>2</sub> over ACF provides NO oxidation at room temperature. Compared to simple mixture of MnO<sub>2</sub> with ACF, MnO<sub>2</sub> supported ACFs showed higher oxidation activities. Among MnO<sub>2</sub> supported ACFs, MnO<sub>2</sub> supported on pitch based ACF showed the highest oxidation activity of NO. Especially, MnO<sub>2</sub> supported ACF carried out higher NO oxidation activities even if the smaller amounts of MnO<sub>2</sub> was used compared to the simple mixture of MnO<sub>2</sub> and ACF.

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