

## Simultaneous Catalytic Removal of Nitrogen Oxides and Soot by Copper-Loaded MFI Zeolites

Yasutake Teraoka,\* Kazunori Kanada, Hiroshi Furukawa, Isamu Moriguchi, and Shuichi Kagawa  
Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852-8521

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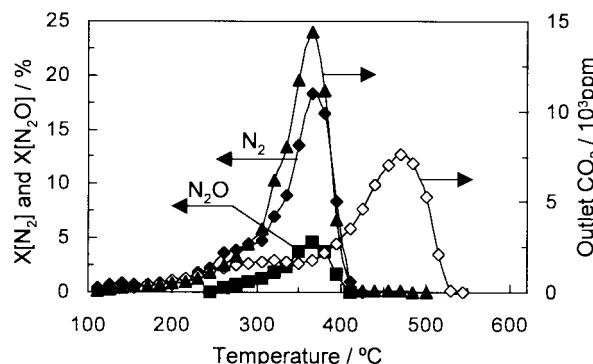
Cu-loaded MFI zeolites showed the catalytic activity for the oxidation of soot and reduction of  $\text{NO}_x$  simultaneously in the soot- $\text{NO}_x$ - $\text{O}_2$  reaction system. Ion-exchanged and impregnated catalysts showed the comparable activity, but the latter was decidedly superior to the former with respect to the selectivity to NO reduction into  $\text{N}_2$ .

Nitrogen oxides ( $\text{NO}_x$ ) and soot particulates emitted from diesel exhaust have been greatly contributing to the environmental pollution, and currently the regulation of diesel emissions becomes tightened with respect to nitrogen oxides ( $\text{NO}_x$ ) and particulate matters (PM): PM consists mainly of soot and soluble organic fraction (SOF). Apart from the catalytic after-treatments so far investigated actively, such as the selective catalytic reduction of  $\text{NO}_x$  by hydrocarbons and the oxidation of CO, gaseous hydrocarbons and SOF,<sup>1</sup> another possible option is the simultaneous catalytic removal of  $\text{NO}_x$  and PM (soot).<sup>2</sup> We have been studying the simultaneous  $\text{NO}_x$ -soot removal reaction with respect to catalyst development<sup>3-8</sup> and reaction mechanism<sup>7,9,10</sup> and revealed that mixed metal oxides with perovskite-related<sup>3,4,7,8</sup> and spinel<sup>5-7</sup> structures are promising catalysts for this reaction. This paper reports the catalytic property of Cu-loaded MFI for the simultaneous  $\text{NO}_x$ -soot removal reaction. It has turned out that Cu-loaded MFI catalysts prepared by an impregnation method are good candidates showing high activity and selectivity to  $\text{N}_2$  formation.

Na-MFI ( $\text{SiO}_2/\text{Al}_2\text{O}_3=23.3$ , MFI2) and  $\text{NH}_4$ -MFI (39.5, MFI4) were kindly supplied by Tosoh Corporation. Cu ion-exchanged MFI (Cu-MFI) was prepared as follows. The parent zeolite was treated with 0.1 M aq  $\text{NaNO}_3$  at 60 °C for 1 day, followed by a conventional ion-exchange procedure using aq Cu(II) acetate at 60 °C for 1 day. In the preparation of Cu-impregnated catalyst (Cu/Na-MFI2), Na-MFI2 powder was put in an aq solution of Cu(II) acetate, and immediately the suspension was evaporated to dryness.<sup>11</sup> Both Cu-MFI and Cu/Na-MFI2 were finally air-calcined at 550 °C for 1 h. The Cu loading was expressed by wt% of Cu: 1 wt% Cu loading corresponds to 27% and 42% ion-exchange levels for MFI2 and MFI4, respectively.

The catalytic activity for the simultaneous  $\text{NO}_x$ -soot removal was evaluated by a technique of the temperature programmed reaction (TPR).<sup>3-10</sup> A catalyst and activated carbon<sup>12</sup> (ca. 5 wt%) was well mixed by mortar and pestle. The tight mixture (0.33 g) thus obtained was packed in a reactor and heated at a rate of 1 °C min<sup>-1</sup> under flowing  $\text{NO}(0.5\%)$ - $\text{O}_2(5\%)$ -He(balance) at 20 cm<sup>3</sup> min<sup>-1</sup> and the outlet gas was analyzed with intervals of about 15 min by a TCD gas chromatograph (Shimadzu GC-8A).

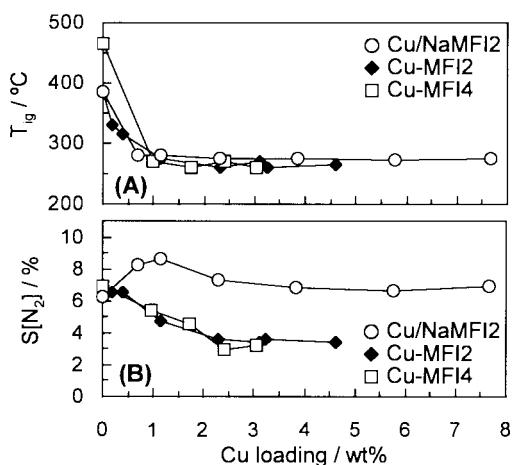
TPR result over 3.1 wt% Cu-MFI2 in the  $\text{NO}-\text{O}_2$ -He atmosphere is shown in Figure 1. The formation of  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  at the same temperature range evidenced the occur-



**Figure 1.** Temperature programmed reaction of simultaneous  $\text{NO}_x$ -soot removal over 3.1 wt% Cu-MFI2 (closed symbols) and Na-MFI2 (open symbol). Only the  $\text{CO}_2$  formation curve is shown for Na-MFI2.  $X[\text{N}_2]$  and  $X[\text{N}_2\text{O}]$  are conversions of NO into  $\text{N}_2$  and  $\text{N}_2\text{O}$ , respectively.

rence of the simultaneous  $\text{NO}_x$ -soot removal reaction: the soot pre-mixed with the catalyst was oxidized by either  $\text{NO}_x$  or  $\text{O}_2$  to produce  $\text{CO}_2$ , and  $\text{NO}_x$  was reduced by the soot into  $\text{N}_2$  and  $\text{N}_2\text{O}$ . The  $\text{CO}_2$  formation over Na-MFI2 took place at higher temperature region than that over 3.1 wt% Cu-MFI2 (Figure 1). In addition, the soot was completely oxidized into  $\text{CO}_2$  over all the Cu-loaded catalysts, while CO amounting about 18% of  $\text{CO}_2$  was formed over Na-MFI (not shown in Figure 1). These results indicate that Cu introduced in MFI zeolites effectively works as a catalyst for the simultaneous  $\text{NO}_x$ -soot removal reaction. From the TPR result, ignition temperature ( $T_{ig}$ ), which was used as a measure of activity, was obtained by extrapolating the steeply ascending portion of the  $\text{CO}_2$  formation curve to zero  $\text{CO}_2$  concentration (estimation error;  $\pm 5$  °C), and total amounts of  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{N}_2\text{O}$  formed throughout the TPR run,  $V[\text{CO}_2]$ ,  $V[\text{N}_2]$  and  $V[\text{N}_2\text{O}]$ , were obtained by integrating the respective curves. The selectivity to  $\text{N}_2$  formation ( $S[\text{N}_2]$ ) was defined by  $V[\text{N}_2]/V[\text{CO}_2]$ , which corresponds to a fraction of soot used for the reduction of NO into  $\text{N}_2$ .

In Figure 2,  $T_{ig}$  value (A) and the selectivity to  $\text{N}_2$  formation (B) are plotted as a function of the Cu loading. For all the catalyst systems, the  $T_{ig}$  values decreased, or the soot ignition activity increased, with increasing the Cu loading and reached the constant activity above ca. 1 wt%. These results indicate that the soot ignition activity of Cu-loaded MFI in the simultaneous  $\text{NO}_x$ -soot removal reaction is almost exclusively determined by the Cu loading (wt%) irrespective of the Si/Al ratio of MFI, preparation methods and existing state of Cu. As for the selectivity to  $\text{N}_2$  formation, both the ion-exchanged catalysts, Cu-MFI2 and Cu-MFI4, showed nearly the same tendency that the  $S[\text{N}_2]$  gradually decreased with increasing the Cu loading and reached the steady value above ca. 2.3 wt%. On the other hand, impregnated Cu/Na-MFI2 showed higher  $S[\text{N}_2]$  values



**Figure 2.** (A) Soot ignition temperature,  $T_{ig}$ , and (B) selectivity to  $N_2$  formation,  $S[N_2]$ , of Cu-loaded MFI catalysts as a function of Cu loading.

than the ion-exchanged catalysts in the whole Cu-loading range examined, with a moderate maximum at 1.2 wt% loading. Furthermore, Cu/Na-MFI2 were superior to Cu-MFI2 with respect to less amount of  $N_2O$  formation. The selectivity to  $N_2O$ ,  $V[N_2O]/(V[N_2]+V[N_2O])$ , over catalysts with  $>1$  wt% Cu loadings were 7.1–12.2% and 14.9–23.9% for Cu/Na-MFI2 and Cu-MFI2, respectively. As a result, impregnated Cu/Na-MFI2 with the Cu loadings higher than ca. 1 wt% are good catalysts showing both high activity and selectivity to  $N_2$  formation.

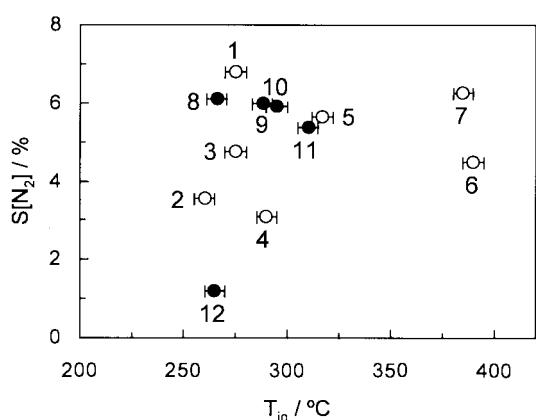
Figure 3 shows the relation between  $T_{ig}$  and  $S[N_2]$  in order to compare the catalytic performance for the simultaneous  $NO_x$ -soot removal. Among ion-exchanged MFI catalysts

investigated, the most active catalyst was the Cu-exchanged catalyst, 3.5 wt% Cu-MFI2. The impregnated 3.8 wt% Cu/Na-MFI2 was more selective to the  $N_2$  formation than Cu/Al<sub>2</sub>O<sub>3</sub>, CuO and any of the metal exchanged catalysts. As compared with mixed metal oxide catalysts so far reported, 3.8 wt% Cu/Na-MFI2 is medium in activity but the most selective to the  $N_2$  formation: the highest selectivity was about 6% attained by La<sub>0.9</sub>K<sub>0.1</sub>Cu<sub>0.7</sub>V<sub>0.3</sub>O<sub>x</sub><sup>3</sup> La<sub>1.9</sub>K<sub>0.1</sub>Cu<sub>0.95</sub>V<sub>0.05</sub>O<sub>4</sub><sup>4</sup> and Cu<sub>0.95</sub>K<sub>0.05</sub>Fe<sub>2</sub>O<sub>4</sub><sup>6</sup> (see Figure 3). Moreover, the Cu-loaded MFI catalysts have an advantage over the other  $NO_x$ -soot removal catalysts that they catalyze the HC-SCR reaction: it was experimentally confirmed that when the mixture of soot and 4.6 wt% Cu-MFI2 was heated in an O<sub>2</sub>-NO-C<sub>2</sub>H<sub>4</sub> stream, C<sub>2</sub>H<sub>4</sub>-SCR reaction proceeded in addition to the  $NO_x$ -soot removal.

In conclusion, it has turned out that Cu/Na-MFI2 prepared by impregnation method is a promising  $NO_x$ -soot removal catalyst showing medium soot ignition activity and high selectivity to  $N_2$  formation. This letter reports only the evaluation of the catalytic performance. There remain many subjects to be investigated in future studies such as reasons why impregnation method or CuO on the outer surface of MFI affords high selectivity to  $N_2$  formation and why Cu ions exchanged in zeolite pores catalyze the reaction involving soot, which is present on the outer surface.

#### References and Notes

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11. During the evaporation-to-dryness process, a small portion of Cu ions might be ion-exchanged. However, a majority of them were deposited on the outer surface of MFI and were present as CuO after calcination, which was confirmed by H<sub>2</sub>-TPR as well as color of the catalysts.
12. Activated carbon (Nakalai Chemicals) was used as a substitute for the diesel soot, because under the present experimental condition its reactivity was almost the same as that of the dry soot obtained by the incomplete combustion of diesel oil and so far used in our laboratory.<sup>3–10</sup>



**Figure 3.** Relation between soot ignition temperature,  $T_{ig}$ , and selectivity to  $N_2$  formation,  $S[N_2]$ .

1. 3.8 wt% Cu/Na-MFI2
2. 3.5 wt% Cu-MFI2
3. 1.2 wt% Cu-MFI2
4. 12 wt% Pt-MFI2
5. 2.8 wt% Co-MFI2
6. 3.3 wt% Pd-MFI2
7. Na-MFI2
8. Cu<sub>0.95</sub>K<sub>0.05</sub>Fe<sub>2</sub>O<sub>4</sub>
9. La<sub>0.9</sub>K<sub>0.1</sub>Cu<sub>0.7</sub>V<sub>0.3</sub>O<sub>x</sub>
10. La<sub>1.9</sub>K<sub>0.1</sub>Cu<sub>0.95</sub>V<sub>0.05</sub>O<sub>4</sub>
11. 3.5 wt% Cu/Al<sub>2</sub>O<sub>3</sub>
12. CuO