Highly Selective Reduction of NO in Excess Oxygen through the Intermediate Addition of Reductant (IAR) between Pt- and Zn-MFI Zeolites

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Ethene has been added as reductant of NO in excess oxygen between an oxidation (Pt-MFI) and a reduction catalysts (Zn-MFI). The efficiency of ethene, namely the ratio of the amount of NO reduced to that of ethene consumed, reached about 2 and was much higher than that of conventional reduction on Cu-MFI.

The intermediate addition of reductant (IAR) has been very recently suggested as a potential method to remove NO selectively in excess oxygen.[1] This method consists of the combination of an oxidation catalyst of NO to NO_2 and a reduction catalyst of NOx to N_2, and the reductant is introduced between these two catalyst beds. The advantage of this method is that we don't need to develop the catalyst on which oxygen can oxidize NO to NO_2 but do not oxidize hydrocarbons to COx and H_2O, indicating that the wasting of hydrocarbons due to combustion with oxygen could be minimized. Namely, the efficiency of hydrocarbons (E_{HC}), which is defined here as the ratio of the amount of NO reduced to that of hydrocarbons consumed, would become better by using the IAR method.

In the present research Pt-MFI has been employed as the oxidation catalyst on the basis of previous results.[1] Several kinds of metal ion-exchanged MFI zeolites such as Na-, Mg-, Ca-, Ba-, and Zn-MFI have been examined as the reduction catalysts because these zeolites have been reported to be not so active for the usual selective catalytic reduction of NO with hydrocarbons.[2] Finally the E_{HC} values of the present system were compared with those on Cu-MFI alone.

Platinum and metal ion-exchanged MFI zeolites were prepared by a conventional ion exchange method with an aqueous tetra-ammineplatinum(II) nitrate and respective metal acetate solutions. The Si/Al molar ratio of the parent MFI zeolite was 11.7. The ion exchange levels of Pt, Na, Mg, Ca, Ba, and Zn-MFI prepared were 101, 97, 55, 84, 62, and 97%, respectively. The zeolites were pressed, crushed, and sieved to obtain particles of 250-425 μm. The catalytic reduction was carried out in a conventional flow system with twin reactors made of quartz.[1] The twin reactors were placed in a single furnace. The Pt-MFI catalyst was mounted in the first reactor and the metal ion-MFI in the second one. The mixture of NO, O_2, and He (balance) (total flow rate, 124 cm^3 min^{-1}) was introduced into the first reactor. The reductant, C_2H_4, diluted in He (26 cm^3 min^{-1}) was then added into the NO+O_2 mixture between the first and the second reactors. One can change the flow route of the NO+O_2 mixture to the bypath from the first reactor to evaluate the effect of the first catalyst bed. Before the catalytic reaction, the catalysts were pretreated *in situ* at 773 K for 3 h in a He flow. The reactants were 1000 ppm of NO, 857 ppm of C_2H_4, 2% of O_2 (helium balance). A gas chromatograph and a NOx analyzer were employed to measure the concentrations of gases. The effectiveness of Pt-MFI as the oxidation catalyst of NO has already been investigated in the previous work.[1] The maximum conversion of NO to NO_2 has been observed at 523 K and is about 95%. The decrement in the conversion at higher temperature is due to the limitation of the equilibrium. The catalytic activity is much higher than those reported previously.[3, 4]

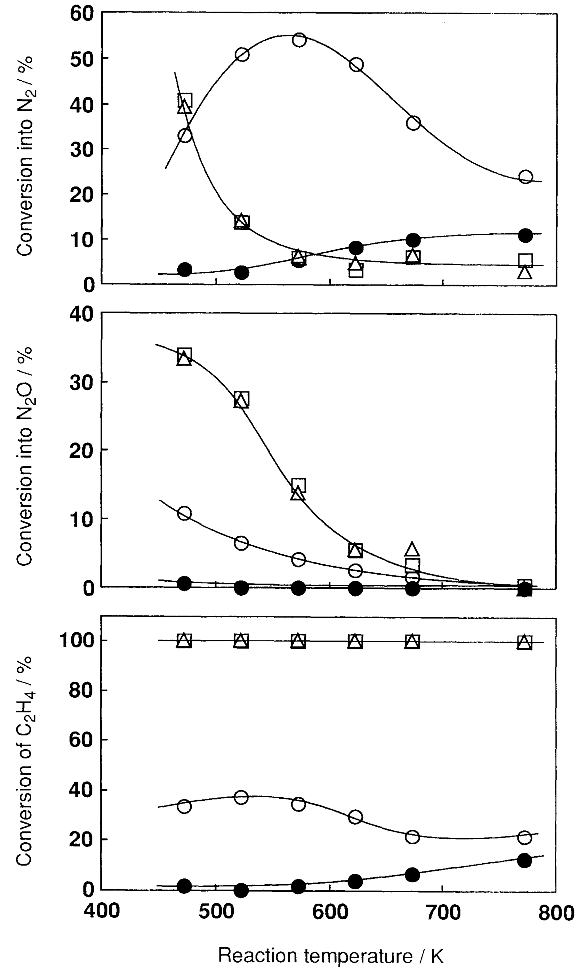

Figure 1. Catalytic reduction of NO on the IAR combination of Pt- and Zn-MFI (○), on Zn-MFI alone (●), on the physical mixture of Pt- and Zn-MFI (△), and on Pt-MFI alone (□). The experimental conditions are described in the text.

In Figure 1, the activities of four kinds of catalytic systems in the combination of Pt and Zn have been depicted; the series combination of the Pt-MFI catalyst (0.4 g) and the Zn-MFI catalyst (0.4 g), the Zn-MFI catalyst alone (0.4 g) without the Pt-MFI catalyst, the physically mixed catalysts of Pt-MFI (0.4 g) and Zn-MFI (0.4 g), and the Pt-MFI catalyst alone (0.4 g). The respective reaction systems are abbreviated as Pt|Zn, Zn, Pt+Zn, and Pt. Figure 1 clearly shows the great difference between the results of the Pt|Zn and the Zn systems. With Pt-MFI as the oxidation catalyst the catalytic activity of Zn-MFI for the NO reduction was greatly enhanced at 473-773 K. At the same time the conversion levels of C_2H_4 were also increased. It is evident that the increments of NO and C_2H_4 conversions are attributable to the formation of NO_2 on Pt-MFI. Figure 1 also indicates that there is the formation of N_2O at 473-623 K. This might suggest the easy formation of N_2O in the presence of NO_2, though the reaction mechanism is not clear yet.

The results of the Pt|Zn system can be compared with those of the Pt+Zn system. The degree of conversion of NO to N_2 of the latter was much lower than that of the former as shown in Figure 1 and almost the same as that of the Pt-MFI alone. Therefore it follows that only Pt-MFI in the physical mixture of Pt-MFI and Zn-MFI is an active phase and Zn-MFI is little used in the reaction.

Another interesting phenomenon should be noted in Figure 1. The conversion levels of ethene on the Pt|Zn system were 20-40% in the temperature range 473-773 K. In contrast, those on the Pt+Zn and the Pt alone systems were always 100%. This indicates that the IAR method is effective for little wasting of reductant due to the combustion with oxygen, or for utilization of hydrocarbon in the selective catalytic reduction of NO in excess oxygen. The change in the E_{HC} value with the reaction temperature is summarized in Figure 2. One can see the volcano-shaped dependence of the efficiency on the reaction temperature and the maximum value of approximately 2 at 623 K. The E_{HC} value of 2 suggests the following reactions on the IAR system.

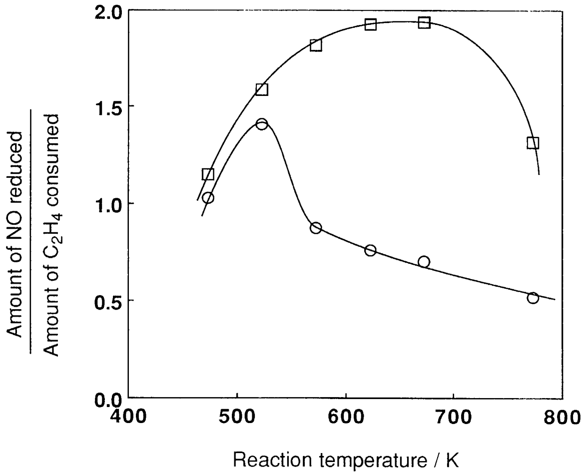

Figure 2. Efficiency of ethene for reduction of NO to N_2 on the combination catalyst of Pt-MFI-101 and Zn-MFI-97 (□) and on Cu-MFI-112 (○). The experimental conditions are the same as those in Figure 1.

$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO_2 + C_2H_4 + O_2 \rightarrow N_2 + 2CO_2 + 2H_2O$$

The efficiency of ethene on Cu-MFI alone under the usual flow system, where the mixture of $NO+O_2+C_2H_4$ was introduced on the catalyst, has been depicted in Figure 2 for comparison. At the low temperature region the E_{HC} values of the IAR system with Pt- and Zn-MFI catalysts were almost the same as those on Cu-MFI, whereas the values at higher temperatures were much greater. It follows that the IAR method is very useful in the wide temperature range and the waste of hydrocarbons can be prevented even at high temperatures.

The conversions to N_2 on the physical mixture of Pt-MFI and metal ion-exchanged MFI zeolites were almost the same as that on Pt-MFI alone, as evidently shown in Figure 1 and the previous report.[1] The conversion to N_2 and E_{HC} on the Pt|metal ion systems, therefore, are compared with those on the metal ion-exchanged MFI alone in Table 1. The reaction temperatures listed were those at which the maximum conversions to N_2 were observed. Table 1 shows the great increment in the conversions to N_2 by emplyoing the IAR metohd on all of these catalysts. The E_{HC} values were also increased except the Ba system. The order of the catalytic activity of metal ion-exchanged MFI combined with Pt-MFI is Zn > Mg > Ba > Ca > Na, though the reason is not clear yet.

Table 1. Conversion of NO to N_2 and efficiency of ethene for selective reduction of NO (E_{HC})

Metal Ion	Metal ion-MFI alone			Pt|Metal ion IAR system		
	T / K^a	Conv. to N_2 / %	E_{HC}	T / K^a	Conv. to N_2 / %	E_{HC}
Na	673	3.6	0.23	473	16.6	0.87
Mg	773	7.3	1.15	573	37.9	1.20
Ca	773	14.4	0.32	573	32.4	1.09
Ba	673	8.3	1.48	523	36.6	1.16
Zn	773	11.2	1.05	573	54.1	1.81

[a] At the temperature maximum conversion of NO to N_2 was observed.

The present findings conclude the great effectiveness of the IAR method to reduce NO with hydrocarbons in the presence of excess oxygen. The effect of water addition to the system should be clarified in the future. There are many possibilities of the combination of the oxidation and the reduction catalysts, depending on the conditions of exhausts and the kinds of reductants.

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