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Catalytic reduction of NO by propene in the presence of oxygen over mechanically mixed metal oxides and Ce-ZSM-5

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The mechanical mixing of Mn_2O_3 or CeO_2 to Ce-ZSM-5 considerably enhanced the rate of the reduction of NO by propene in the low to medium temperature region, although Mn_2O_3 or CeO_2 itself was much less active for this reaction. In contrast, Mn_2O_3 was highly active and CeO_2 was moderately active for the oxidation of NO to NO_2. On the basis of the comparison of the rates of the $C_3H_6 + O_2$, $NO + C_3H_6 + O_2$ and $NO_2 + C_3H_6 + O_2$ reactions over these catalysts, a bifunctional mechanism is proposed, in which Mn_2O_3 and CeO_2 accelerate the oxidation of NO and the subsequent reaction steps between NO_2 and propene proceed on Ce-ZSM-5.

Keywords: reduction of NO; Ce-ZSM-5; mechanical mixing; Mn_2O_3; CeO_2

1. Introduction

Catalytic reduction of NO by using hydrocarbons in excess of oxygen has attracted much attention as a practical system, since patents [1] and reports of Iwamoto et al. [2] and Held et al. [3] on Cu-zeolites were published, and many catalysts such as metal ion-exchanged zeolites (e.g., Ga-ZSM-5 [4] and Co-ZSM-5 [5]) and metal oxides-supported alumina [6] have been reported. We have previously reported that Ce ion-exchanged zeolites are active for the reduction of NO by propene and that the activity is enhanced by the addition of alkaline earths to Ce-zeolite by ion-exchange or an increase in Ce-doping [7–9]. In this work, we examine the effect of the addition of various metal oxides to Ce-ZSM-5 by mechanical mixing as well as by conventional impregnation. It was reported that a mechanical mixture of perovskites and mordenite was active for this reaction [10].

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2. Experimental

Various metal oxides were mixed in a mortar for ca. 20 min with Ce-ZSM-5 prepared from Na-ZSM-5 ($SiO_2/Al_2O_3 = 23.8$). The ion-exchange level of Ce, 15%, was defined by 100× (amount of Na ion eluted)/(amount of Al in zeolite). Hereafter, these catalysts will be denoted by M + Ce-Z (M = metal oxides). All metal oxides were obtained by the calcination of corresponding metal acetates in air at 500°C. The surface areas were Cr_2O_3 (43.9 $m^2\ g^{-1}$), α-Mn_2O_3 (4.6), CuO (1.6), and CeO_2 (101.8). The structures were confirmed by XRD. For comparison, manganese oxide was impregnated into Ce-Z with aqueous solution of manganese acetate, followed by drying and calcination in air at 500°C. These are denoted by *x*% Mn/Ce-Z (*x* wt% of manganese oxide was impregnated).

The reactions were performed with a fixed-bed flow reactor as described in a previous paper [9]. A gas mixture of 1000 ppm NO, 500 ppm propene, and 2% O_2 (in He) was ordinarily fed to 0.5 g of a catalyst at a rate of 150 $cm^3\ min^{-1}$ (space velocity $= 10^4\ h^{-1}$, $W/F = 0.2$ g s cm^{-3}). The reaction temperature was lowered stepwise from 500°C.

3. Results and discussion

Fig. 1 shows the temperature dependence of the percent conversions of NO to N_2 (a) and the percent conversions of C_3H_6 to COx (b) over Ce-Z mechanically mixed with various metal oxides. The ratio of metal oxides to Ce-Z was 1 : 1 in weight. It is noteworthy that Ce-Z containing Mn_2O_3 or CeO_2 showed much higher activities than Ce-Z alone (dashed line in fig. 1) particularly in the low to medium temperature region. The activity of Ce + Ce-Z was higher than that of Ce-Z in a wide temperature range and comparable to that of Ce-Z at high temperatures. On the other hand, the addition of CuO or Cr_2O_3 lowered the activity. In this reaction system, it is inevitable that propene is oxidized wastefully by oxygen ($C_3H_6 + O_2 \rightarrow COx$), in addition to being used for the reduction of NO ($NO + C_3H_6 + O_2 \rightarrow N_2 + COx$). These two reactions are compared in fig. 2. The addition of Mn_2O_3 or CeO_2 gave higher efficiency of propene utilization than Ce-Z alone at high conversion levels. When the selectivity is defined by the preference of the latter reaction to the former as a function of temperature [9], the selectivity at 300°C was in the order of Ce + Ce-Z > Mn + Ce-Z > Cu + Ce-Z > Cr + Ce-Z. This order is in general agreement with that of the conversion to N_2.

Fig. 3 shows the effect of mixing ratio of Mn_2O_3 to Ce-Z. The presence of Mn_2O_3 accelerated the oxidation of propene in all cases, but Mn_2O_3 itself was not active at all for the reduction of NO. Therefore Ce-Z is indispensable for this reaction. With the increase in the amount of Mn_2O_3 added to Ce-Z, the activity in the low temperature region increased in general, but the selectivities decreased, result-

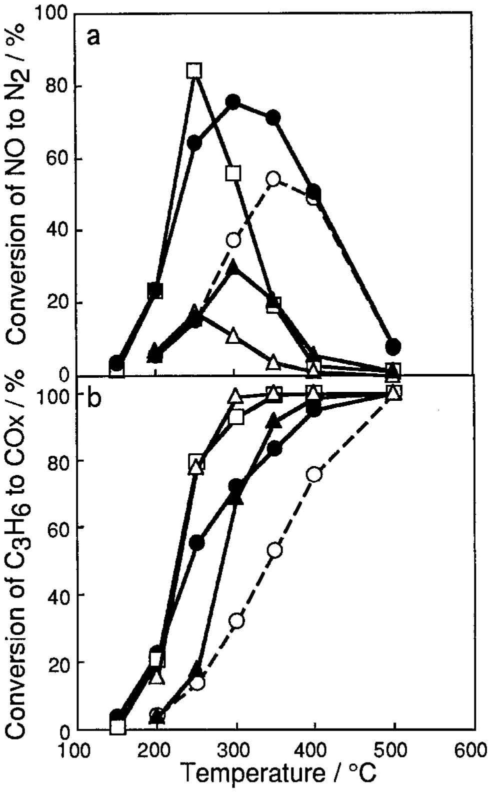

Fig. 1. Temperature dependence of the conversion of NO to N_2 (a) and the conversion of C_3H_6 to COx (b) over Ce-ZSM-5 mixed with various metal oxides for the reduction of NO by propene. (□) Mn + Ce-Z, (●) Ce + Ce-Z, (▲) Cu + Ce-Z, (△) Cr + Ce-Z, (○) Ce(15%)-Z alone. NO: 1000 ppm; C_3H_6: 500 ppm; O_2: 2%; total flow-rate: 150 cm^3 min^{-1}; catalyst weight: Ce-Z alone: 0.5 g, others: metal oxides (0.25 g) + Ce-Z (0.25 g).

ing in lower activities at high temperatures. Hence, there was an optimum content of Mn_2O_3 for the reduction of NO.

Mn-impregnated Ce-Z showed considerably lower activities than the mechanical mixtures for the reduction of NO. The maximum conversions of NO to N_2 decreased, while the temperature region for the appearance of activity was lowered with the increase in the amount of Mn added. Furthermore, a mechanical mixture of 50% Mn/Ce-Z and Ce-Z (4 : 6, total amount of Mn in the mixture was 20% as Mn_2O_3) exhibited a higher activity than 20% Mn/Ce-Z. These results show that mechanical mixing is more effective than impregnation.

Next, this promoting effect was examined in more detail. We have reported that the initial step of the reduction of NO is the oxidation of NO to NO_2; in the case of Ce-Z this step is catalyzed by the Ce ion [11]. The same initial step has been reported with regard to H- [12], Ga- [13], and Cu-zeolites [14]. Hence, the oxidation of NO to NO_2 was carried out over these metal oxides; the results are shown

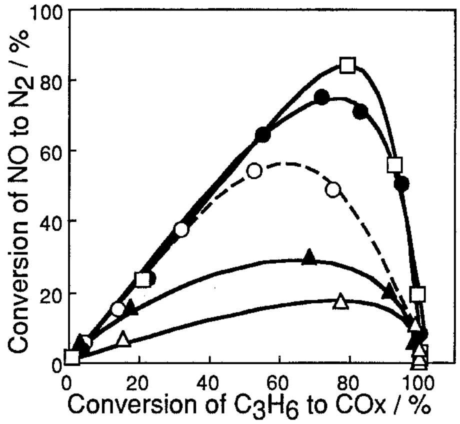

Fig. 2. Correlation between the conversion of C_3H_6 to COx (fig. 1b) and the conversion of NO to N_2 (fig. 1a) over Ce-ZSM-5 mixed with various metal oxides. (□) Mn + Ce-Z, (●) Ce + Ce-Z, (▲) Cu + Ce-Z, (△) Cr + Ce-Z, (○) Ce(15%)-Z alone.

in fig. 4. Table 1 compares the results of the $C_3H_6 + O_2$, $NO + C_3H_6 + O_2$ and $NO_2 + C_3H_6 + O_2$ reactions over these catalysts. Mn_2O_3 showed much higher activity for the oxidation of NO than Ce-Z alone (fig. 4). However, as shown in table 1, Mn_2O_3 itself was inactive for the reduction of NO or NO_2 to N_2 by propene (exp. nos. 2 and 3), indicating that Ce-Z is necessary for the formation of N_2. Table 1 also shows that the extent of propene oxidation was greater for Ce-Z (exp. no. 11) than for Mn_2O_3 (exp. no. 10) in the case of the $NO_2 + C_3H_6 + O_2$ reaction. This fact demonstrates that the reaction between NO_2 and propene (the step subsequent to the oxidation of NO) is faster over Ce-Z than over Mn_2O_3. All these

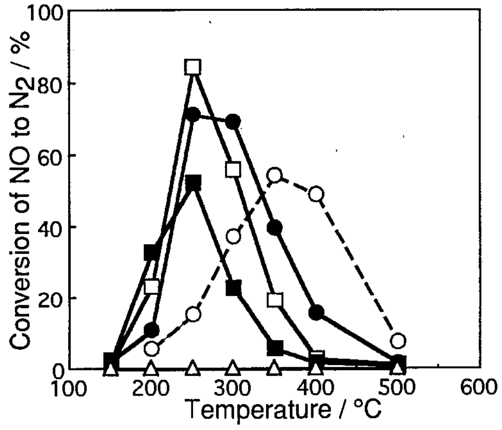

Fig. 3. Effect of mixing ratio of Mn_2O_3 to Ce-ZSM-5. (○) Ce-Z, (●) 20% Mn + Ce-Z, (□) 50% Mn + Ce-Z, (■) 80% Mn + Ce-Z, (△) Mn_2O_3. NO: 1000 ppm; C_3H_6: 500 ppm; O_2: 2%; total flow-rate: 150 cm^3 min^{-1}; catalyst weight: 0.5 g.

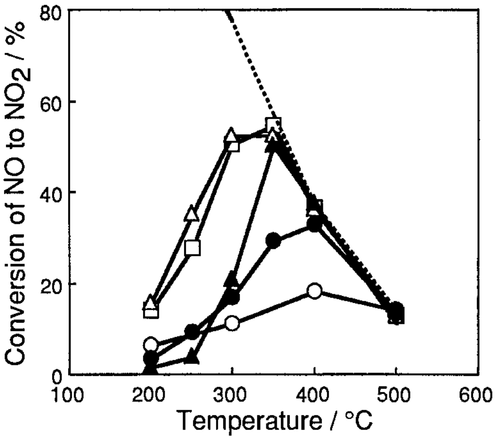

Fig. 4. Oxidation of NO to NO_2 over various metal oxides. (□) Mn_2O_3, (●) CeO_2, (▲) CuO, (△) Cr_2O_3, (○) Ce(15%)-Z, (- - -) %conversion at equilibrium. NO: 1000 ppm; O_2: 2%; total flow-rate: 150 $cm^3\ min^{-1}$; catalyst weight: 0.5 g.

results show that the added Mn_2O_3 accelerates the oxidation of NO and the reaction between NO_2 and propene proceeds over Ce-Z. In other words, Mn_2O_3 and Ce-Z accelerate the reaction bifunctionally. Furthermore, the addition of NO or NO_2 to $C_3H_6 + O_2$ did not affect the oxidation of propene in the case of Mn_2O_3 alone, namely, $NO_2 + C_3H_6 + O_2 \approx NO + C_3H_6 + O_2 \approx C_3H_6 + O_2$ (exp. nos. 1,

Table 1
Comparison of the percent conversions of C_3H_6 to COx and NOx to N_2 among several reactions

Exp. no.	Catalyst	Reaction	Conv. to COx (to N_2, in parentheses) (%)		
			200°C	250°C	300°C
1	Mn_2O_3 [a]	$C_3H_6 + O_2$	15.8	60.6	91.0
2		$NO + C_3H_6 + O_2$	15.9 (0)	60.0 (0)	89.6 (0)
3		$NO_2 + C_3H_6 + O_2$	20.0 (0)	63.5 (0)	94.4 (0)
4	Cr_2O_3 [a]	$C_3H_6 + O_2$	21.6	95.9	100
5	Mn + Ce-Z [a]	$C_3H_6 + O_2$	14.5	41.1	75.3
6		$NO + C_3H_6 + O_2$	20.8 (23.4)	79.5 (84.3)	93.0 (55.9)
7		$NO_2 + C_3H_6 + O_2$	53.0 (62.1)	82.2 (88.6)	99.0 (62.9)
8	Cr + Ce-Z [a]	$C_3H_6 + O_2$	20.3	79.8	96.7
9		$NO + C_3H_6 + O_2$	15.6 (6.8)	77.7 (17.4)	99.1 (10.7)
10	Mn_2O_3 [b]	$NO_2 + C_3H_6 + O_2$	3.3 (0)	19.5 (0)	33.0 (0)
11	Ce-Z [b]	$NO_2 + C_3H_6 + O_2$	11.1 (5.8)	42.1 (23.8)	43.2 (27.1)
12	Na-Z [b]	$NO_2 + C_3H_6 + O_2$	11.2 (7.7)	44.7 (18.2)	43.4 (16.9)

[a] NO or NO_2: 1000 ppm; C_3H_6: 500 ppm; O_2: 2%; W/F: 0.2 $g\ s\ cm^{-3}$.
[b] W/F: 0.02 $g\ s\ cm^{-3}$.

2, and 3), while the order was $NO_2 + C_3H_6 + O_2 > NO + C_3H_6 + O_2 > C_3H_6 + O_2$ over Mn + Ce-Z (exp. nos. 5, 6, and 7), in accordance with the fact that the reaction between NO_2 and propene is rapid on Ce-Z [11]. The bifunctional nature is further supported by the result that Na-Z, which was almost inactive for the reduction of *NO* but active for the reduction of *NO_2* [11], exhibited a high activity even for the reduction of *NO* when it was mixed with Mn_2O_3.

According to the above bifunctional mechanism, there evolves a problem that Cr + Ce-Z was much less active for the reduction of NO (fig. 1), although Cr_2O_3 had a high activity for the NO oxidation (fig. 4). This is explained as follows. The oxidation of propene by oxygen was much faster on Cr_2O_3 than it was on Mn_2O_3 (exp. no. 1 and 4, table 1), although the oxidation of NO proceeded at comparable rates (fig. 4). Therefore, in the case of Cr + Ce-Z most of propene is oxidized by oxygen wastefully on Cr_2O_3 particles before reaching the Ce-Z particles and reacting with NO_2 there. In agreement with this idea, the extent of propene oxidation for the $NO + C_3H_6 + O_2$ reaction was close to that observed for the $C_3H_6 + O_2$ reaction in the case of Cr + Ce-Z (exp. nos. 8 and 9, table 1); the similarity of the two rates means that the interaction of $C_3H_6 + O_2$ with NOx is very small in this case. The variation with the content of Mn_2O_3 in the mixed catalysts as shown in fig. 3 is consistent with this explanation, i.e., with the increase in the Mn_2O_3 content, the wasteful combustion of propene becomes dominant, although the low temperature activity increases. The reason why CeO_2 was effective in a wide temperature range as an additive is therefore its moderate oxidation activity which is sufficient for the NO oxidation, but not too high to cause extensive wasteful oxidation of propene.

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