Effect of Transition Metal Additives on Catalytic Activity of SnO$_2$ for the Selective Reduction of NO with C$_2$H$_4$

by

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The catalytic activity of SnO$_2$ for the selective reduction of NO with C$_2$H$_4$ was increased by the addition of Co, Cr and Fe, but was decreased by the addition of Cu. The optimum loading amount of the most effective Co was 0.15 wt% in metal equivalent. The promotion effect of transition metal additives in the SnO$_2$ system originated in the increasing selectivity with the suppression of undesirable oxidation of C$_2$H$_4$ by O$_2$. The promotion effect of Co was observed with catalysts calcined at 600°C in the reaction condition which had more oxidizing (higher (NO+O$_2$)/C$_2$H$_4$) and severer for the NO reduction (lower NO/O$_2$) composition.

1. Introduction

Recently, the selective reduction of nitrogen oxides with hydrocarbons in an oxidizing atmosphere (lean NOx reduction) has been receiving a great deal of attention. The pioneering works which were reported in 1990 independently by Iwamoto et al.[1] and Held et al.[2] showed that Cu ion-exchanged ZSM-5 catalysts were very active for the reaction, and they triggered the rush of studies thereafter which aimed at finding new catalyst systems or possible reaction mechanisms. The research trend in this field was summarized in review articles[3]-[7]. Lean NOx catalysts so far reported are grouped into the following three classes[4]: (*i*) microporous (zeolitic) materials (ion-exchanged zeolites and silicoaluminophosphates, metallosilicates), (*ii*) metal oxides with and without promoters (Al$_2$O$_3$, SiO$_2$-Al$_2$O$_3$, ZrO$_2$, TiO$_2$ *etc.*) and (*iii*) noble metals (Pt/Al$_2$O$_3$, Pt/SiO$_2$ *etc.*). It was reported that the addition of transition metals, especially Cu and Co, enhanced the catalytic activity of host support materials when they were present in the form of exchanged cations in zeolitic materials (category (*i*))[8],[9] or well-dispersed supported oxides on metal oxides (category (*ii*))[9]-[12].

Recently we have found that SnO$_2$ is a new catalyst for the lean NOx reduction[13], and therefore the effect of transition metal additives on the catalytic activity of SnO$_2$ for the lean NOx reduction with ethene has been examined in this study. Transition metal additives used in this study are Cr, Fe, Co and Cu which were reported to be effective in enhancing the activity of Al$_2$O$_3$[10].

2. Experimental

Hydrous SnO$_2$, the precursor of SnO$_2$, was obtained by adding ammonia to aqueous SnCl$_4$, followed by filtration, thorough washing with deionized water and drying at 110°C. Hydrous SnO$_2$ thus obtained was suspended in an aqueous solution of nitrate of Cr, Fe, Co or Cu, evaporated to dryness and then calcined in air for 5 h at 600 or 900°C. The loading amount of transition metals is expressed in terms of wt% in metal equivalent, though they are considered to be in the oxidic form. X-Ray diffraction measurements (Rigaku RINT2200) showed neither the modification of the structure of SnO$_2$ nor the presence of the metal or oxide phase of the additives probably because of the low loading of additives. The resulting cata-

lysts were pelletized, crushed and sieved, and the 250-840μm fraction was used for activity measurements. The lean NOx reduction was carried out in a fixed-bed flow reactor by feeding the He-balanced gaseous mixtures at a rate of 15cm^3 · min^{-1} over 0.25 g of a catalyst (W/F=1.0 g · s · cm^{-3}, SV =7000 h^{-1}). The gaseous components were analyzed by gas chromatography and the NO reduction activity was evaluated in terms of the conversion of NO into N$_2$. The following two reaction mixtures were used in this study.
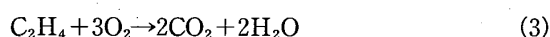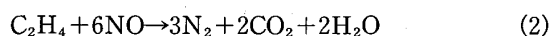
reaction gas A ; NO (2000ppm), C$_2$H$_4$ (1000ppm) and O$_2$ (10%)

reaction gas B ; NO (4400ppm), C$_2$H$_4$ (4400ppm) and O$_2$ (4.4%)

The concentration of each reactant was different between two reaction gases. In terms of the concentration ratio, the reaction gas A is more oxidizing with larger (NO+O$_2$)/C$_2$H$_4$ ratio than the reaction gas B.

The overall reaction of the lean NO reduction by C$_2$H$_4$ can be written as :

$$6x\text{NO}+(x+y)\text{C}_2\text{H}_4+3y\text{O}_2$$
$$\rightarrow 3x\text{N}_2+2(x+y)\text{CO}_2+2(x+y)\text{H}_2\text{O} \qquad (1)$$
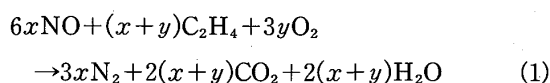
This reaction can be considered to be the sum of two competing reactions of the oxidation of C$_2$H$_4$ by NO (reaction 2) or O$_2$ (reaction 3).

$$\text{C}_2\text{H}_4+6\text{NO}\rightarrow 3\text{N}_2+2\text{CO}_2+2\text{H}_2\text{O} \qquad (2)$$
$$\text{C}_2\text{H}_4+3\text{O}_2\rightarrow 2\text{CO}_2+2\text{H}_2\text{O} \qquad (3)$$

In this respect, the reaction gas A with smaller NO/ O$_2$ ratio can be said also to be severer condition than the reaction gas B for the reduction of NO to take place.

3. Results and Discussion

3. 1 Temperature dependence of lean NOx reduction

Figure 1 and 2 show the temperature dependence of lean NOx reduction over SnO$_2$ in reaction gases A and B, respectively. In both cases, the production of CO$_2$ due to the oxidation of C$_2$H$_4$ by O$_2$ and NO started at around 300°C, and at the same time the formation of N$_2$ was observed. This confirms the occurrence of the lean NOx reduction. The

conversion of C$_2$H$_4$ came to the completion at 400°C in the reaction gas A while at 500°C in the reaction gas B. This reflects the difference in the gaseous composition ; the reaction gas A is more oxidizing than the reaction B. The lower maximum conversion of NO into N$_2$ in the reaction gas A, as compared with that in the reaction gas B, can be attributed to the lower NO/O$_2$ ratio.

3. 2 Effect of transition metal additives

Figure 3 shows the NO reduction activity in the reaction gas A of SnO$_2$ with and without 0.15 wt% transition metal additives calcined at 600°C. The conversion of C$_2$H$_4$ reached completion above 400 °C over all the catalysts. The addition of Cr, Fe, Co and Cu caused a significant change in activity
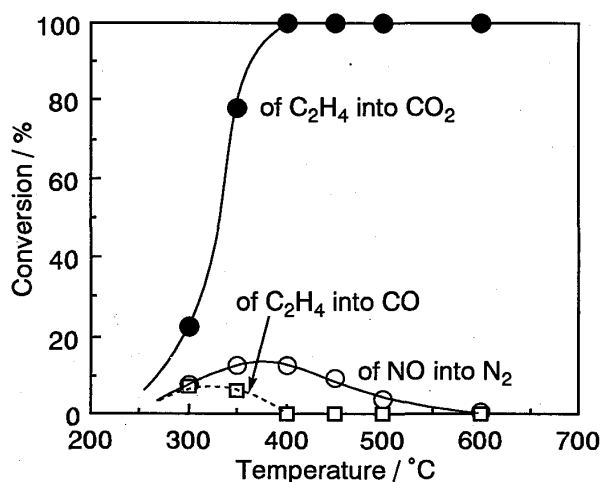

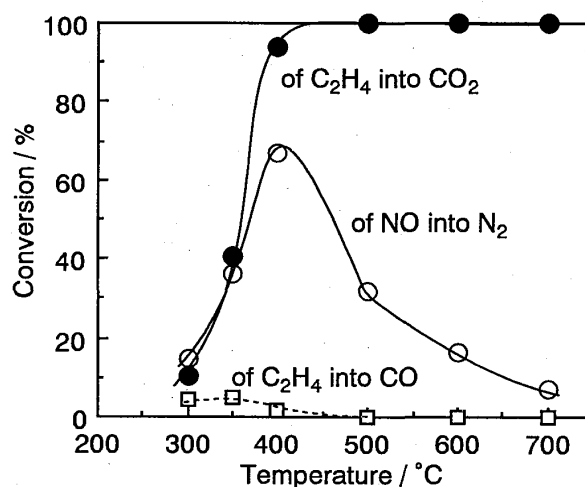Fig. 1 Selective reduction of NO with C$_2$H$_4$ in reaction gas A over SnO$_2$ calcined at 600°C.

Fig. 2 Selective reduction of NO with C$_2$H$_4$ in reaction gas B over SnO$_2$ calcined at 600°C.

which depended largely on the kind of additives. The NO conversion into N_2 below 400°C increased markedly by the addition of Co and Cr, and moderately by the addition of Fe, while it decreased by the addition of Cu. Accordingly the order of the additive effect in the present SnO_2 system was Co $\geq$ Cr > Fe > none > Cu ; the Cr loaded catalyst was comparable at 350°C but inferior at 300°C to the Co loaded catalyst. In the lean NOx reduction by C_2H_4 over transition metal loaded ZSM-5 zeolites[8),9)], Al_2O_3[9),10)] and SiO_2-Al_2O_3[9),11)], Cu has been reported to be one of most effective additives especially with lowering the active temperature range. In the present SnO_2 system, however, the addition of Cu caused the decrease in activity at lower temperatures though the conversion into N_2 above 450°C increased by the addition of Cu.

3. 3 Effect of loading amount of Co

The effect of the loading amount of Co in the catalysts calcined at 600°C is shown in Fig. 4 for the lean NOx reduction at 350°C in the reaction gas A. With an increase in the Co loading, the conversion of C_2H_4 tended to decrease while the conversion of NO into N_2 attained the highest at 0.15 wt% of Co, indicating that 0.15% loading is the optimum in the reaction gas A over the catalysts calcined at 600°C.

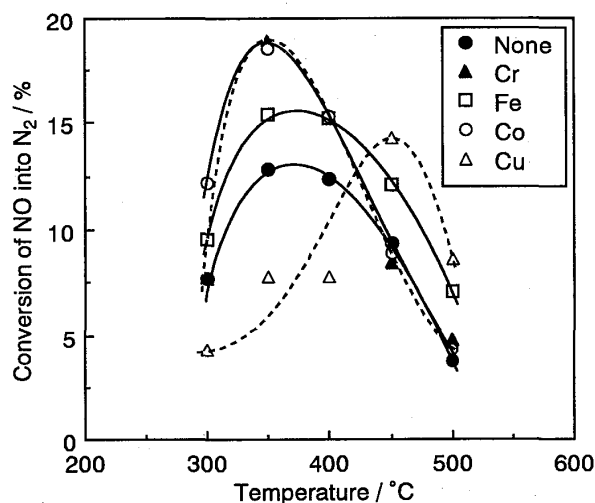It was revealed that the promotion effect of Co

was dependent on the composition of the reaction gas and the calcination temperature of the catalyst. As shown in Fig. 5, the promotion effect of Co was not observed in the reaction gas B ; the conversion of NO into N_2 decreased slightly and monotonically with an increase in the Co loading. As compared with the reaction in the gaseous mixture A, the
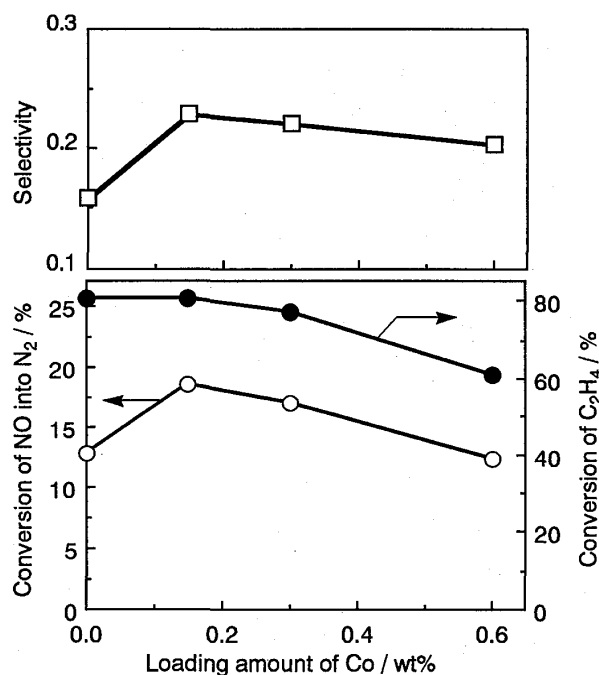

Fig. 4 Effect of the loading amount of Co on NO reduction activity of Co loaded SnO_2 prepared at 600°C. The reaction was carried out in reaction gas A at 350°C. The selectivity is the ratio of the conversion of NO into N_2 to the conversion of C_2H_4.

Fig. 3 NO reduction activity in reaction gas A over SnO_2 (●) and 0.15 wt% Cr (▲), Fe (□), Co (○) and Cu (△) loaded SnO_2. Catalysts were prepared at 600°C.
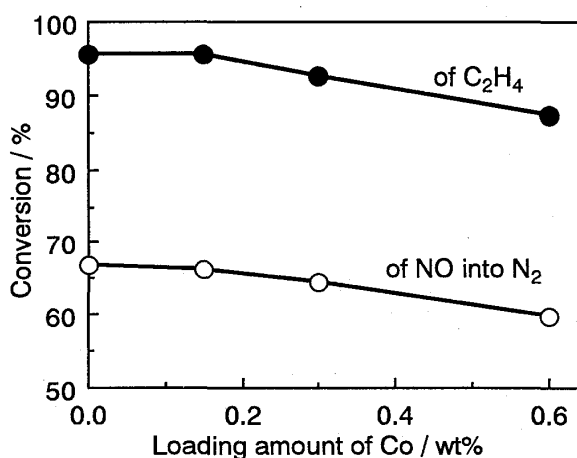

Fig. 5 Effect of the loading amount of Co on NO reduction activity of Co loaded SnO_2 prepared at 600°C. The reaction was carried out in reaction gas B at 400°C.

conversion of NO into N_2 is quite high in the reaction gas B. As stated below, the addition of Co does not enhance the activity (reaction rate). It can thus be speculated that the promotion effect of Co, even if operative, is not observable in the reaction gas B in which the NO reduction proceeds at higher rate even on the Co-free (pure) SnO_2.

Over the catalysts calcined at 900°C (Fig. 6), the dependence on the Co loading of the activity in the reaction gas A was complicated. On increasing the Co loading, the conversion of C_2H_4 monotonically decreased below 0.5 wt% and suddenly increased above 0.5 wt% Co. On the other hand, the reduction of NO into N_2 decreased slightly with an increase in the Co loading and eventually disappeared above 0.5 wt% loading. These results strongly suggest that the active species is different below and above 0.5 wt% loading of Co. It is well known that cobalt oxides are very active for the complete oxidation of hydrocarbons. Accordingly, particles of the cobalt oxide, probably Co_3O_4, may be formed on the surface of the SnO_2 support above 0.5 wt% loading, and they may catalyze preferentially the oxidation of C_2H_4 with O_2. The fact that promotion effect was not observed on the catalysts calcined at 900°C (Fig. 6) would be explained as follows. The specific surface area of SnO_2 was 18.6 and 5.4 m^2g^{-1} after calcination at 600 and 900°C, respectively. If the optimum loading of

Co is assumed to be proportional to the specific surface area, the promotion effect in the catalysts calcined at 900°C might be observed at around 0.04 wt% loading. The another possible explanation is that the calcination at elevated temperatures like 900°C might cause the formation of solid solution of Co into SnO_2 which alters the catalytic property of SnO_2.

3.4 Origin of the promotion effect

As seen from Fig. 3, the effective additives to SnO_2 caused the conversion of NO to increase but the active temperature range to leave intact. This is quite different from the promotion effect in ZSM-5, Al_2O_3 and SiO_2-Al_2O_3 systems[8]-[11] that effective additives enhance the "activity" with lowering the active temperature range as well as increasing the conversion of NO. In the present SnO_2 system, the promotion effect was found to originate not from the increasing "activity" but from the increasing "selectivity". In Fig. 7, the conversion of NO into N_2 over SnO_2 with and without 0.15 wt% additives is plotted against the selectivity at 300°C and 350°C where the substantial amount of C_2H_4 still remained in the effluent gas; the ratio of the conversion of NO into N_2 to that of C_2H_4 is used as a measure of the selectivity. At both temperatures,
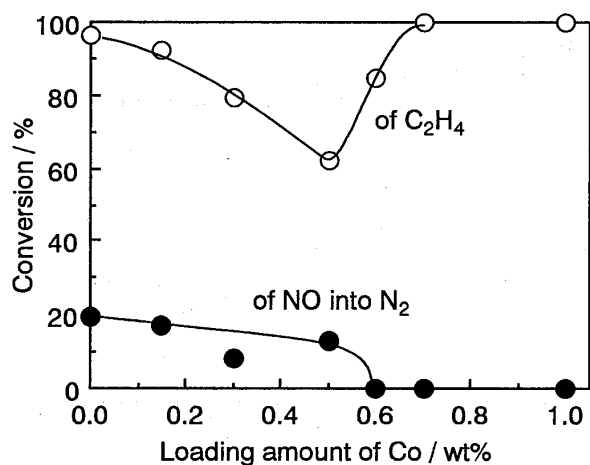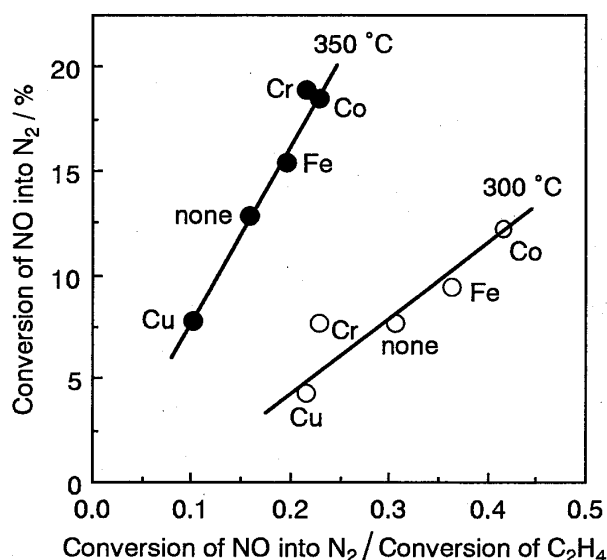
Fig. 6 Effect of the loading amount of Co on NO reduction activity of Co loaded SnO_2 prepared at 900°C. The reaction was carried out in reaction gas A at 400°C.

Fig. 7 Relation between the NO reduction activity and the selectivity of transition metal loaded SnO_2 at 300°C and 350°C. Selectivity as Fig. 4.

the NO reduction activity increases with an increase in the selectivity. This clearly indicates that the promotion effect in the SnO_2 system is due to the increasing selectivity with the suppression of undesirable oxidation of C_2H_4 by O_2. The parallel variation of the conversion of NO and the selectivity against the Co loading (Fig. 4) also shows that the change in the NO reduction activity is associated with the change in the selectivity.

It has been reported that the lean NOx reduction activity of transition metal free H-ZSM-5, Al_2O_3 and SiO_2-Al_2O_3 stems from the acidic property[14),15)] while that of the transition metal containing catalysts does from the redox property of the added transition metals[9)]. The addition of transition metals to acidic supports results in the creation of new redox-type active sites which enable the oxidation (activation) of hydrocarbons to occur at lower temperatures and therefore the change of the reaction mechanism. This is considered to be the origin of the "activity" promotion effect of transition metals in acidic supports. We reported previously that the NO reduction activity of pure SnO_2 exhibited a volcano-shape dependence on the concentration of O_2[13)]. Since this behavior is typical to the transition metal containing catalysts like Cu-ZSM-5[9)], the pure SnO_2 is reasonably classified into the redox-type lean NOx catalyst. It is speculated at present that the difference in the inherent catalytic property between the redox-type SnO_2 and acid-type supports (H-ZSM-5, Al_2O_3, SiO_2-Al_2O_3) might be the cause of different promotion effect of transition metal additives. The added transition metals might modify the redox-type active sites of SnO_2 so as to increase the selectivity. Further studies should be necessary to clarify the active center of SnO_2 and to reveal the reason why the addition of active transition metals to SnO_2 results in the increasing "selectivity" rather than in the increasing "activity".

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