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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. and Held et al. 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. Lean NOx catalysts so far reported are grouped into the following three classes: (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)) or well-dispersed supported oxides on metal oxides (category (ii)).

Recently we have found that SnO$_2$ is a new catalyst for the lean NOx reduction, 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$_3$.

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-

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lyst were pelleted, 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 15cm³•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 N₂. The following two reaction mixtures were used in this study.

reaction gas A; NO (2000ppm), C₂H₄ (1000ppm)
and O₂ (10%)

reaction gas B; NO (4400ppm), C₂H₄ (4400ppm)
and O₂ (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+O₂)/C₂H₄ ratio than the reaction gas B.

The overall reaction of the lean NO reduction by C₂H₄ can be written as:

\[6x\text{NO} + (x+y)\text{C}_2\text{H}_4 + 3y\text{O}_2 \rightarrow 3x\text{N}_2 + 2(x+y)\text{CO}_2 + 2(x+y)\text{H}_2\text{O}\]  

This reaction can be considered to be the sum of two competing reactions of the oxidation of C₂H₄ by NO (reaction 2) or O₂ (reaction 3).

\[
\text{C}_2\text{H}_4 + 6\text{NO} \rightarrow 3\text{N}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (3)
\]

In this respect, the reaction gas A with smaller NO/O₂ 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 SnO₂ in reaction gases A and B, respectively. In both cases, the production of CO₂ due to the oxidation of C₂H₄ by O₂ and NO started at around 300°C, and at the same time the formation of N₂ was observed. This confirms the occurrence of the lean NOx reduction. The conversion of C₂H₄ 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 N₂ in the reaction gas A, as compared with that in the reaction gas B, can be attributed to the lower NO/O₂ ratio.

#### 3.2 Effect of transition metal additives

Figure 3 shows the NO reduction activity in the reaction gas A of SnO₂ with and without 0.15 wt% transition metal additives calcined at 600°C. The conversion of C₂H₄ reached completion above 400°C over all the catalysts. The addition of Cr, Fe, Co and Cu caused a significant change in activity.
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which depended largely on the kind of additives. The NO conversion into N₂ 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 SnO₂ system was Co > 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 C₂H₄ over transition metal loaded ZSM-5 zeolites⁹,¹⁰, Al₂O₃⁹,¹⁰ and SiO₂-Al₂O₃⁹,¹¹, Cu has been reported to be one of most effective additives especially with lowering the active temperature range. In the present SnO₂ system, however, the addition of Cu caused the decrease in activity at lower temperatures though the conversion into N₂ 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 C₂H₄ tended to decrease while the conversion of NO into N₂ 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 N₂ decreased slightly and monotonically with an increase in the Co loading. As compared with the reaction in the gaseous mixture A, the

![Fig. 3 NO reduction activity in reaction gas A over SnO₂ (●) and 0.15 wt% Cr (▲), Fe (□), Co (○) and Cu (△) loaded SnO₂. Catalysts were prepared at 600°C.](image)

![Fig. 4 Effect of the loading amount of Co on NO reduction activity of Co loaded SnO₂ prepared at 600°C. The reaction was carried out in reaction gas A at 350°C.](image)

![Fig. 5 Effect of the loading amount of Co on NO reduction activity of Co loaded SnO₂ prepared at 600°C. The reaction was carried out in reaction gas B at 400°C.](image)
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$_2$H$_4$ 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 CoO, 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$_2$H$_4$ 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$^2$g$^{-1}$ 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$_2$O$_3$ and SiO$_2$-Al$_2$O$_3$ systems$^{9-11}$ 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$_2$H$_4$ still remained in the effluent gas; the ratio of the conversion of NO into N$_2$ to that of C$_2$H$_4$ is used as a measure of the selectivity. At both temperatures,

![Fig. 6](image)

**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](image)

**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.
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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$_2$H$_4$ 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$_2$O$_3$ and SiO$_2$–Al$_2$O$_3$ 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$_2$.$^{19}$ 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$_2$O$_3$, SiO$_2$–Al$_2$O$_3$) 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”.

References
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