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Lean NO_x Catalysis over Sn/γ-Al_2O_3 Catalysts

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Sn/γ-Al_2O_3 were effective and highly stable catalysts for NO reduction with propene under high partial pressures of oxygen and water. The activity depended on the Sn loading. For a 10 wt% Sn/Al_2O_3 at 475–500°C, 58% conversion of 1000 ppm NO to N_2 was obtained in the presence of 10% water and 15% O_2, at a space velocity of 30,000 h^{-1}, and 77% conversion at 15,000 h^{-1}. The NO conversion increased with O_2 partial pressure but was suppressed by water below 500°C. The activity was also suppressed by SO_2 but could be restored slowly after the removal of SO_2. © 1999 Academic Press

The increasingly stringent government regulations on the emission level of nitrogen oxides from transportation vehicles resulted in the recent intense research in the area of catalytic reduction of NO_x to N_2 with hydrocarbons. This is particularly so for emissions from diesel engines which cannot be treated effectively with the highly developed three-way catalysts. For such an application, a practical catalyst needs to be effective in the presence of about 10% oxygen and 10% water vapor, a condition that precludes the use of most of the metal–ion exchanged zeolite catalysts reported to date as it causes the destruction of the zeolite structure and limits the life-time of the catalysts (1, 2).

Metal oxides supported on alumina have also been investigated for NO_x reduction under these conditions. It has been found that, among different variables, the effectiveness of these catalysts for NO_x reduction depends on the state of the metal oxide on the alumina, which in turn depends on the loading of the metal oxide, the calcination temperature, and the source of alumina. This has been shown recently for Ag/Al_2O_3 (3–5), Au/Al_2O_3 (6, 7), and Co/Al_2O_3 catalysts (8). In general, the zeolite-supported catalysts are more effective at lower temperatures and lower oxygen partial pressures, whereas the corresponding alumina-supported catalysts are more effective at higher temperatures and higher oxygen partial pressures.

Previously, it has been suggested that the competitive factor can be used to compare the effectiveness of lean NO_x catalysts (9), which is defined as the ratio of the moles of NO reduced to N_2 to the moles of oxygen atoms needed theoretically to convert the reacted hydrocarbon to CO_2 and H_2O. A competitive factor of unity would mean that every molecule of hydrocarbon reacted to form CO_2 and H_2O is used to reduce NO to N_2. Generally, for a reducible metal oxide, a high dispersion is associated with a high competitiveness factor and values between 8% and 11% are typical of some of the better catalysts reported in the literature (1–10). For most catalysts, the competitiveness factor decreases with increasing temperature and increasing partial pressure of oxygen. Bulk SnO_2, albeit relatively inactive, has a competitiveness factor of around 9% in a feed with a high O_2 partial pressure (10%), 4400 ppm NO and 4400 ppm C_2H_4 (11). Based on results from other systems, it appears plausible that the performance of SnO_2 could be improved by dispersing it on a support. The improvement may arise due to higher competitive factor as a result of higher dispersion of Sn^{4+} ions, or because of increase in the surface area of SnO_2. Sn oxide, unlike many first row transition metals, does not form compounds with alumina, and the solubility of Sn^{4+} in alumina is very low because of its charge. Indeed, it has been reported that an increase in activity (as measured by the W/F) over the bulk SnO_2 was observed for a 2 wt% Sn/Al_2O_3 (12), and a recent report showed that Sn/Al_2O_3 is effective also using propene as the reductant (13). The competitiveness factors observed, however, are similar to that for bulk SnO_2, and are significantly better than for Sn/ZSM-5 catalyst (14).

Here, we report the catalytic properties of highly active Sn/γ-Al_2O_3 for lean NO_x reduction. The γ-Al_2O_3, prepared using a complexing agent, has been demonstrated to be unusual in its capacity to disperse cobalt oxide (8). The results of our study on the effect of Sn loading and the dependence of the N_2 yield on the partial pressures of oxygen, water, and SO_2 in the feed are reported.

γ-Al_2O_3 was prepared from the hydrolysis of Al isopropoxide in 2-methylpentane-2,4-diol following the procedure of Maeda *et al.* (15). The Sn/Al_2O_3 catalysts were prepared by incipient wetness impregnating with an amount of ethanol solution of $SnCl_2$ (Aldrich, 99.99+%) equal to the pore volume (1.4 cm^3 g^{-1}). The concentrations of $SnCl_2$ in the solution were adjusted so as to yield the desired Sn loadings in the final catalysts. The samples were then dried

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TABLE 1

Sample	Sn content (wt%)	Surface area ($m^2 g^{-1}$)	Competitiveness factor (temp. °C)
Al_2O_3	0	242	
Sn1	1.3	232	8.6 (525)
Sn5	4.6	224	10.1 (475)
Sn10	8.1	213	8.2 (500)
Sn15	14	184	9.4 (475)

in an air oven at 100°C overnight, and then calcined at 500°C for 4 h and then at 800°C for 2 h. The BET surface areas of the samples and their Sn contents are shown in Table 1.

X-ray diffraction of the samples showed diffraction peaks of only γ-Al_2O_3 for sample Sn1, and additional peaks due to SnO_2 also for samples Sn5, Sn10, and Sn15. The same diffraction pattern was obtained for sample Sn10 after reaction, except that the SnO_2 peaks were slightly broader. From the areas of the SnO_2 peaks, it was estimated that about $40 \pm 10\%$ of the Sn in Sn5, and $100 \pm 15\%$ of the Sn in Sn10 and Sn15 samples were in the crystalline form. Interestingly, the peak widths for the Sn5 and Sn10 samples were narrow, close to the instrument line width, but that for Sn15 was considerably wider. This suggests the there is a significantly higher degree of disorder in the SnO_2 crystallites in Sn15. This will be described in detail in a later publication (16).

NO reduction was carried out in a flow of 5 to 15% O_2, 0 to 10% H_2O, 0.1% NO, and 0.1% propene, with the balance being He. Unless noted, the total flow rate was 200 ml/min, and 0.2 g of catalyst was used, which corresponded to a space velocity of 30,000 h^{-1}. The catalysts were pretreated in the reaction feed at 600°C for 2 h before the data were collected. The reaction products were analyzed by gas chromatography as described earlier (8). NO conversions was determined by the N_2 produced. No N_2O was detected. Thus, the N_2 yield equaled the NO conversion.

Figure 1 shows the NO and propene conversions using 15% O_2 and 10% H_2O as a function of temperature for a Sn10 catalyst at two space velocities (15,000 and 30,000 h^{-1}). As expected, conversions of NO to N_2 at the lower space velocity were higher at lower temperatures. Significant conversions could be detected above 350°C, even in the presence of 15% O_2 and 10% H_2O. The N_2 yield versus temperature profile was volcano-shaped, similar to the behavior of other lean NO_x catalysts. At a space velocity of 30,000 h^{-1}, a maximum N_2 yield of about 58% was obtained at 500°C, which corresponded to an integral reaction rate of 2.9×10^{-2} mol NO/min-mol Sn. The maximum yield for 15,000 h^{-1} space velocity was 77% for an integral rate of 1.9×10^{-2} mol NO/min-mol Sn. In order to illustrate the effect of different variables more clearly, a space velocity of 30,000 h^{-1} was chosen as the standard test condition.

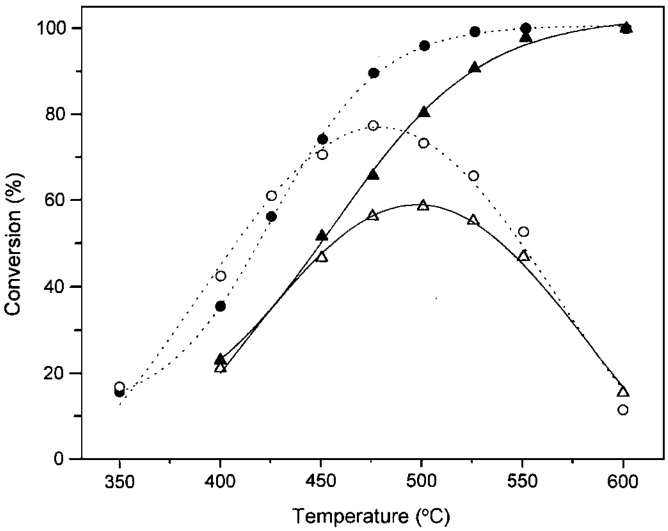

FIG. 1. The effect of space velocity on the NO reduction activity over Sn10 catalyst (0.1% NO, 0.1% C_3H_6, 15% O_2, 10% H_2O). Total flow 100 cc/min (○: N_2 yield, ●: C_3H_6 conversion) or 200 cc/min (△: N_2 yield, ▲: C_3H_6 conversion).

The effect of Sn loading is illustrated in Fig. 2. The addition of Sn to γ-Al_2O_3 enhanced the NO reduction activity significantly at temperatures below 525°C (Fig. 2a). The N_2 yield increased sharply from 1 wt% to 5 wt% Sn loading, but beyond that no further improvement was observed. In fact, when the Sn loading reached 15 wt%, a slight decline in NO conversion was observed. The integral reaction rates at the point of maximum NO conversion for the various catalysts are shown in Table 2. The apparently high activity of sample Sn1, however, is misleading because these rates have not been corrected for the SnO_x dispersion. A similar trend in propene oxidation activity with Sn loading existed (Fig. 2b). Thus, the competitiveness factors at point of maximum NO conversion were not very different for catalysts with different Sn loadings, being around 9% (Table 1).

The dependence of NO conversion on the partial pressure of O_2 is shown in Fig. 3. Below 475°C, both the N_2 yield (Fig. 3a) and the hydrocarbon conversion (Fig. 3b) increased slightly with increasing O_2 partial pressure. This

TABLE 2

Integral NO Conversion Rates and the Corresponding Temperatures

Sample	Maximum NO conv. %	Temp. °C	Integral rate, 10^{-2} mol NO/min-mol Sn
Sn1	57	530	28
Sn5	59	480	5.8
Sn10	58	500	2.9
Sn15	47	475	1.5

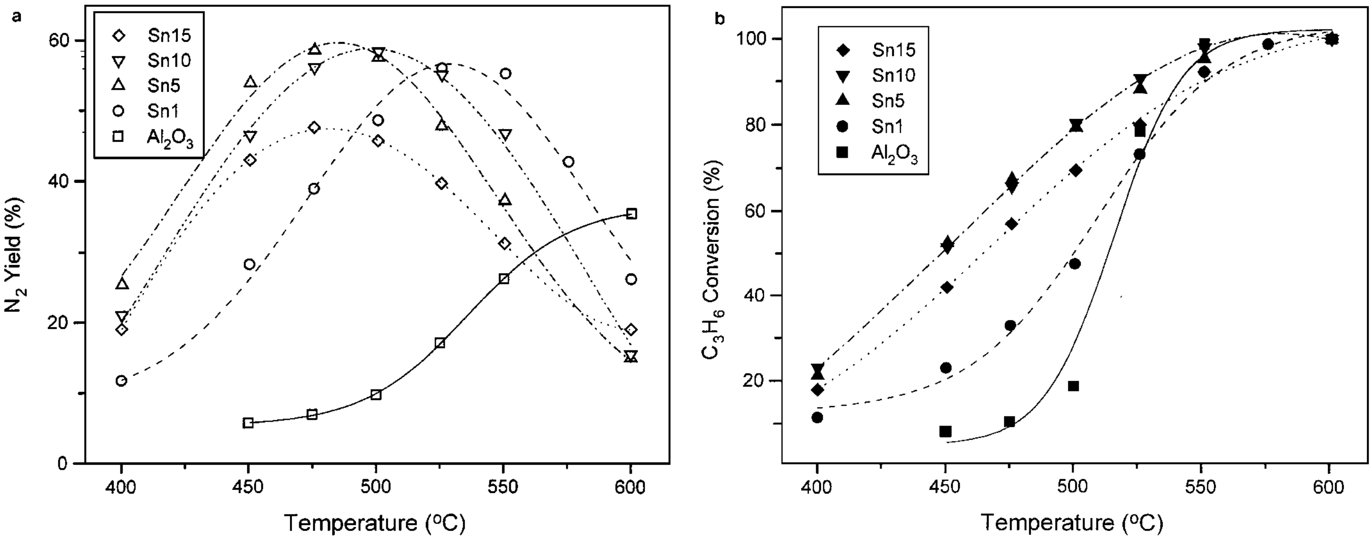

FIG. 2. The effect of Sn loading on the NO reduction activity over Sn/Al_2O_3 Catalysts (0.1% NO, 0.1% C_3H_6, 15% O_2, 10% H_2O, total flow 200 cc/min): (a) N_2 yield; (b) C_3H_6 conversion.

observation differed somewhat from those of Ref. (12), where it was reported that the NO conversion, but not the alkene conversion, decreased slowly beyond the optimal partial pressure of 4% O_2. The high N_2 yield at a high O_2 partial pressure is unusual among lean NO_x reduction catalysts, where the active component is a reducible metal cation.

The effect of water partial pressure is shown in Fig. 4. H_2O suppressed NO conversion below 500°C, and the inhibitory effect was more severe at lower temperatures (Fig. 4a). Nonetheless, at 450°C, a N_2 yield of 46% was still obtained with 10% water. Propene conversion was similarly suppressed (Fig. 4b), and it appears that there is no preferential inhibition of the combustion sites as the competitiveness factors did not change significantly with the water partial pressure. This result differs from the work of Miyadera *et al.* (13), where they reported an increase in the competitiveness factor in the presence of water.

Finally, the effect of SO_2 was examined and the results are shown in Fig. 5. Addition of 30 ppm SO_2 in the feed did not suppress the NO reduction activity at 475°C until after about 4 h on stream. The NO conversion declined slowly for 10 to 15 h from 58% to 40%, when the activity appeared to be stabilized. The conversion recovered slowly upon

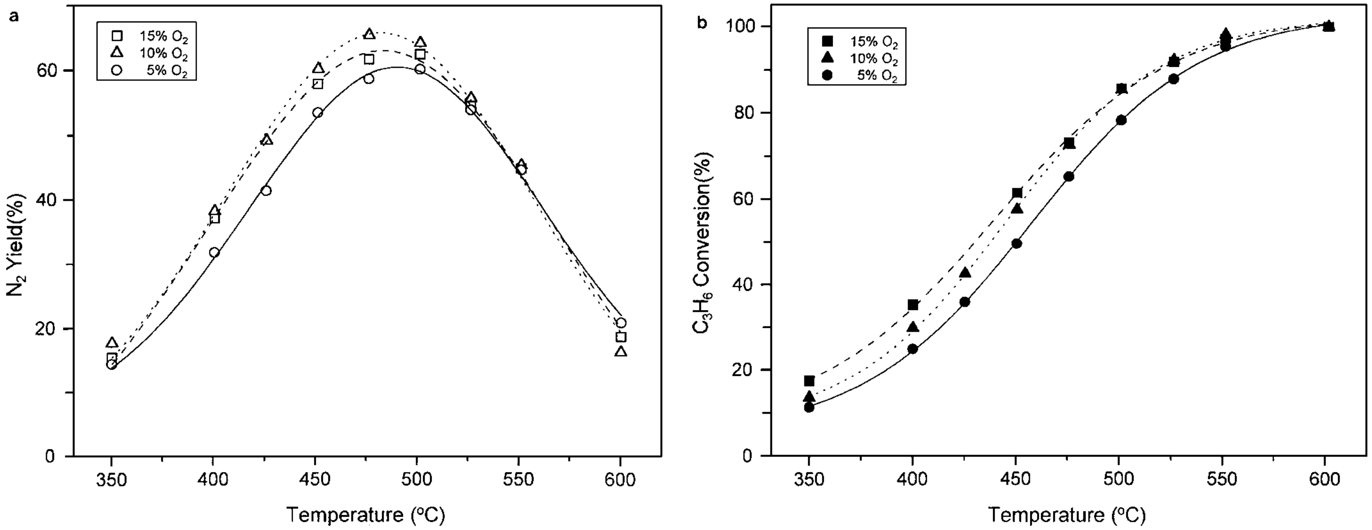

FIG. 3. The effect of O_2 partial pressure on the NO reduction activity over Sn10 sample (0.1% NO, 0.1% C_3H_6, 5–15% O_2, 4% H_2O, total flow 200 cc/min): (a) N_2 yield; (b) C_3H_6 conversion.

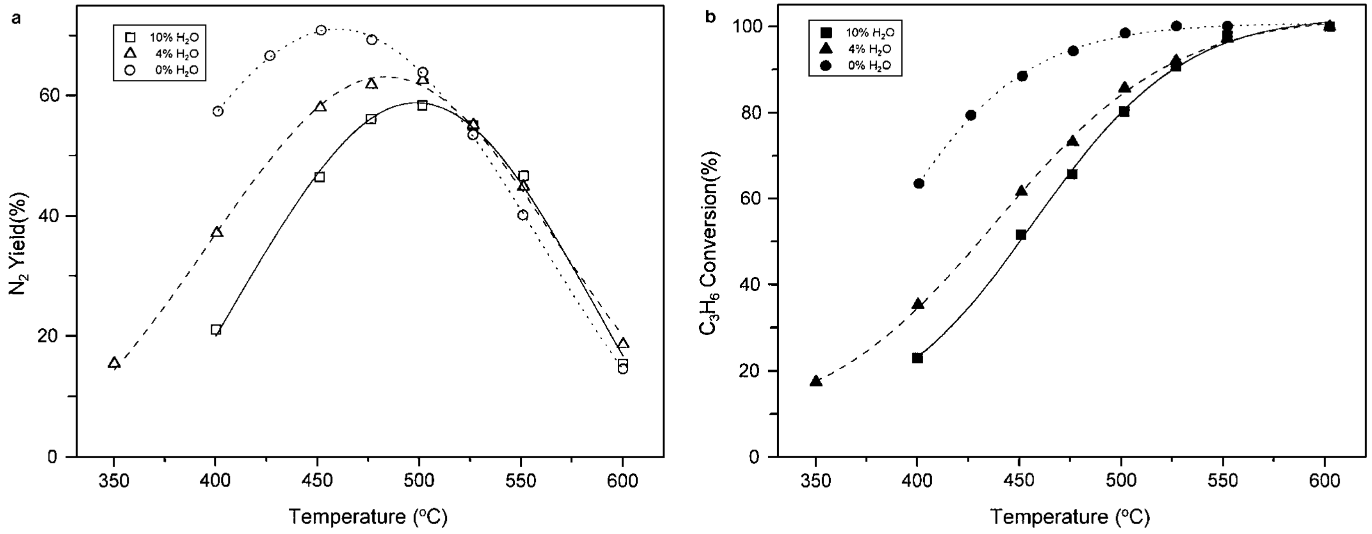

FIG. 4. The effect of H_2O partial pressure on the NO reduction activity over Sn10 catalyst (0.1% NO, 0.1% C_3H_6, 15% O_2, 0–10% H_2O, total flow 200 cc/min): (a) N_2 yield; (b) C_3H_6 conversion.

removal of SO_2 from the feed to 52%. In another experiment in which the activity of the catalyst between 450 and 550°C was examined, the conversion at 475°C recovered to over 60%. In addition, when SO_2 was reintroduced, the conversion returned to 40%. Thus, SO_2 is not a permanent poison for the Sn active sites. Instead, it is adsorbed quite strongly on Al_2O_3, which has a rather high sorption capacity, and the slow recovery of the activity was due to slow desorption of SO_2 from it. Without SO_2, the activity of the catalyst did not decrease after six days of experiments in the presence of 10% H_2O, and it might even increase slightly.

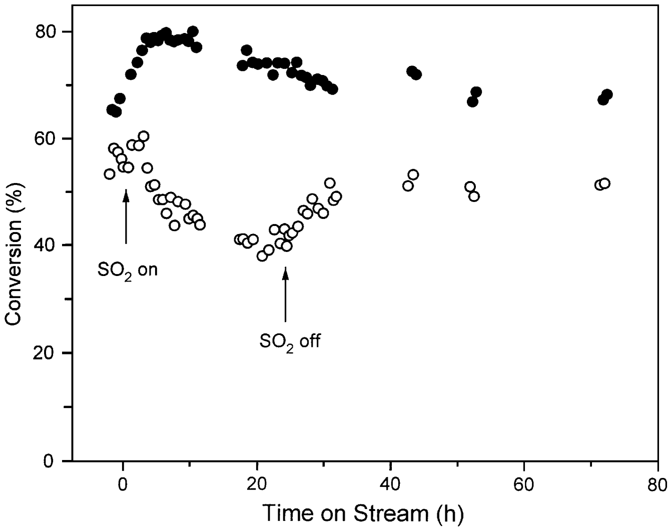

FIG. 5. The effect of SO_2 on the NO reduction activity over Sn10 catalysts: O, N_2 yield; ●, C_3H_6 conversion (0.1% NO, 0.1% C_3H_6, 15% O_2, 10% H_2O, 30 ppm SO_2, total flow 200 cc/min).

In summary, the data presented show that Sn/Al_2O_3 are effective NO_x reduction catalysts. Although the nature of the active sites is not yet known at present, these catalysts showed stable, high activities above 400°C, even at high partial pressures of O_2 and H_2O. This temperature range would be suitable for treatment of exhaust from heavy duty diesel engines. Although the activity was suppressed by SO_2, the effect was reversible. Together with other Al_2O_3-supported catalysts that have demonstrated high NO_x conversion ability, it appears probable that effective NO_x reduction catalysts can be prepared on alumina and perhaps other supports, in addition to zeolites, especially for high stability under harsh conditions of high temperatures and water partial pressures.

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