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The activity and characterization of sol–gel Sn/Al_2O_3 catalyst for selective catalytic reduction of NO_x in the presence of oxygen

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Abstract

Catalytic performance of Sn/Al_2O_3 catalysts prepared by impregnation (IM) and sol–gel (SG) method for selective catalytic reduction of NO_x by propene under lean burn condition were investigated. The physical properties of catalyst were characterized by BET, XRD, XPS and TPD. The results showed that NO_2 had higher reactivity than NO to nitrogen, the maximum NO conversion was 82% on the 5% Sn/Al_2O_3 (SG) catalyst, and the maximum NO_2 conversion reached nearly 100% around 425 °C. Such a temperature of maximum NO conversion was in accordance with those of NO_x desorption accompanied with O_2 around 450 °C. The activity of NO reduction was enhanced remarkably by the presence of H_2O and SO_2 at low temperature, and the temperature window was also broadened in the presence of H_2O and SO_2, however the NO_x desorption and NO conversion decreased sharply on the 300 ppm SO_2 treated catalyst, the catalytic activity was inhibited by the presence of SO_2 due to formation of sulfate species (SO_4^{2-}) on the catalysts. The presence of oxygen played an essential role in NO reduction, and the activity of the 5% Sn/Al_2O_3 (SG) was not decreased in the presence of large oxygen.

Keywords: Selective catalytic reduction; De-NO_x; Lean burn; Sol–gel; Sn/Al_2O_3

1. Introduction

The control of NO_x emission from automobiles is a major environmental concern for both academic research and industry [1,2]. The conventional three way catalysts shows high effective for NO removal under stoichiometric conditions, but low NO reduction conversion under lean burn conditions. Selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons is believed to be a possible way to solve this problem, and has been extensively studied [3–5].

$$NO + HC + O_2 \rightarrow \text{intermediates} \rightarrow N_2 + CO_2 + H_2O \quad (1)$$

Up to date, a large number of catalyst systems have been investigated, but the ideal catalyst has not been found for SCR of NO under lean conditions. The zeolite-based catalysts are unlikely to be suitable as an automotive catalyst for a practical use due to its poor hydrothermal stability in the presence of water vapor and at a high temperature [6–8]. Noble metal-based catalyst Pt/Al_2O_3 appears to offer the good activity and stability, but the low selectivity and narrow temperature window are still a problem [9–12]. The metal oxide catalysts have attracted much attention because they show good activities at high temperature, besides they are more stable than zeolites in hydrothermal conditions [13–15].

SnO_2 was reported to be a good metal oxide catalyst for NO reduction by hydrocarbons in the presence of oxygen by Teraoka et al. in 1993 [16]. After that, Miyadera et al. [17], Maunula et al. [18] and Kung et al. [19,20] reported that tin supported on alumina prepared by impregnation method (IM) for the SCR of NO by propene, Wei et al. [21] reported that lean burn Sn/Al_2O_3 catalyst prepared by coprecipitation method (CP). The results showed that the NO conversions and the temperature windows were much difference over the Sn/Al_2O_3 prepared with IM and CP method and the catalytic activities were all inhibited in the presence of H_2O and SO_2.

Generally, the high activity and selectivity of metal-supported alumina are responsible for the loading and dispersion. For example, the activities of Ga/Al_2O_3 [22,23] and Co/Al_2O_3 [24,25] were studied most extensively. The catalysts prepared by the sol–gel method have high activity; moreover, they show better tolerance to water vapor and SO_2 than those of catalysts prepared by IM or CP method.

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Therefore, as for a metal oxide catalyst, high dispersion is associated with high activity and stability, the single step sol–gel method is a useful method to prepare catalysts with highly dispersed species, and has been recognized as interesting procedures to prepare catalysts.

In this paper, the catalytic activities of Sn/Al_2O_3 catalysts prepared by impregnation and sol–gel method with various Sn loading were studied in detail, and the physical properties of 5% Sn/Al_2O_3 (SG) catalyst were characterized by BET, XRD, XPS and TPD. The catalytic activities for NO_x reduction by propene in the absence and presence of H_2O and SO_2 were investigated; the effects of SO_2 and oxygen concentration on activity were also studied.

2. Experimental

2.1. Catalyst preparation

The SnO_2/Al_2O_3 catalysts were prepared by two different methods [abbreviated as SnO_2/Al_2O_3 (IM) and SnO_2/Al_2O_3 (SG)]. The SnO_2/Al_2O_3 (IM) catalyst was prepared by conventionally impregnating method on the commercial Al_2O_3 with an amount of solution of $SnCl_4$. The SnO_2/Al_2O_3 (SG) catalyst was prepared by single step sol–gel method, aluminum tri-isopropoxide (AIP) was hydrolyzed at 85 °C on the evaporator with a small amount of nitric acid, and then the necessary amount of $SnCl_4{\cdot}5H_2O$ dissolved in ethylene glycol was added to the sol solution, the solvents were eliminated by heating under reduced pressure. All the catalyst precursors were dried at 110 °C over 24 h and calcined at 600 °C for 5 h. The catalysts denoted as *x* wt.% Sn/Al_2O_3, where *x* refer to metal tin loading which changed from 1 to 10 wt.%.

2.2. Catalytic activity measurement

The catalytic reduction activity was carried out in a quartz reactor with an internal diameter of 8 mm. The feed gas mixture consisted of 1000 ppm NO (or 1000 ppm NO_2), 1000 ppm C_3H_6, 8% O_2, and 100 ppm SO_2 (when used), 10% H_2O was introduced into the feed stream by a peristaltic tube pump, and the water was removed in a condenser before the gas composition analysis. A total gas flow rate of 300 ml min^{-1} was maintained using helium as the carrier gas. Before the catalytic activity evaluation, the catalysts were pretreated in the reaction feed at 550 °C for 2 h.

NO and NO_2 concentrations were continuously determined by chemiluminescent NO_x analyzer (Thermo Environmental, Model 42H), and the gas chromatograph (Shimadzu GC 17A) is equipped with a switch dual columns system and with two series columns, one is Parapak Q, for the separation of CO_2, N_2O and C_3H_6, the other is molecular sieve 13×, for O_2, N_2, and CO. At each temperature, steady state was achieved before the effluent gas was analyzed.

The activities were evaluated in terms of NO_x conversion and that of propene to CO_x, defined as $(C_{in} - C_{out})/C_{in} \times 100\%$, C_{in} and C_{out} being NO_x or propene concentration corresponding to the inlet and outlet, respectively. N_2O formation was not observed in the experiment.

2.3. Catalyst characterization

BET-surface areas were measured by N_2 adsorption using a NOVA4000 automated gas sorption system. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/MAX-RB X-ray Diffract meter with Cu Ka radiation. Photoelectron spectra (XPS) were acquires with a PHI15300/ESCA system. Al Ka radiation (1484.6 eV) was used as the source and the C 1s peak was used as a reference. A least-square routine of peak fitting was used for the analysis of XPS spectra. TEM analysis was made with a H800 transmission electron microscope.

Temperature programmed desorption (TPD) experiments were conducted by using 200 mg of a sample in a quartz reactor with an internal diameter of 6 mm. The sample was pretreated in a flow of He at 600 °C for 1 h and then cooled to room temperature under the same gas flow. The adsorption was performed by passing a gas mixture containing 1000 ppm NO, with or without 10% O_2 diluted in He through the sample bed at the room temperature for 2 h. After the adsorption gas was purged with He until no NO was detected in the effluent. TPD measurements were carried out up to 600 °C with a heating rate of 10 °C min^{-1} in the flowing He. The gas flow rate was fixed at 50 ml min^{-1}. Four masses characteristic of He ($m/e = 4$), NO ($m/e = 30$), O_2 ($m/e = 32$), and NO_2 ($m/e = 46$) were monitored continuously by a quadruple mass spectrometer (QuadStar 422) as a function of temperature.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Physical properties of the catalysts

The surface areas of the Sn/Al_2O_3 (SG) with various Sn loadings are summarized in Table 1. With the increase of Sn loadings from 1 to 10 wt.%, the surface areas of the Sn/Al_2O_3 decreased monotonously. It is proposed that the active species of SnO_2 dispersed on the surface of alumina lead to the decreases of the surface area from 263 to 215 m^2 g^{-1}.

Table 1
The surface area of Sn/Al_2O_3 catalysts (SG) with various Sn loading

Catalysts	Sn loading (wt.%)	Surface area (m^2 g^{-1})
Sn/Al_2O_3 (fresh)	1	263
	2	251
	5	238
	10	215

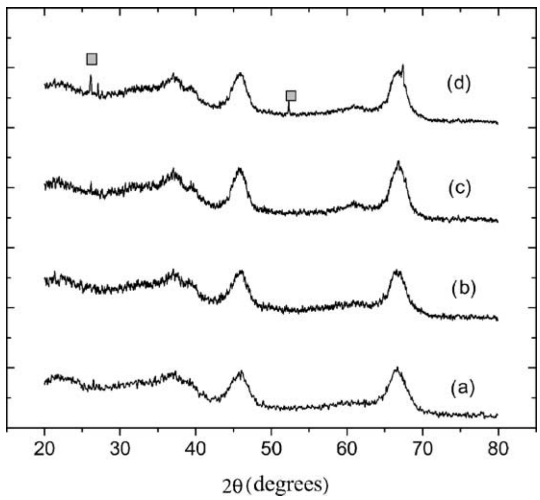

Fig. 1. XRD patterns for SnO_2/Al_2O_3 with various Sn loadings. (■) SnO_2, (a) 1 wt.% Sn, (b) 2 wt.% Sn, (c) 5 wt.% Sn, (d) 10 wt.% Sn.

Fig. 1 shows the XRD pattern of Sn/Al_2O_3 (SG) with various Sn loadings, the major feature of the XRD pattern belonged to Al_2O_3. The 10% Sn/Al_2O_3 showed two major peaks of SnO_2, for the Sn/Al_2O_3 with the Sn loading below 5%, the active sites of SnO_2 were not detected because the crystallite size were too small or disordered to be detected by XRD. TEM data (not shown here) for 5% Sn/Al_2O_3 catalyst (SG) showed that consist of agglomerated primary particles with typical sizes in the range of 5–15 nm. Since Sn^{4+} and Sn^{2+} oxides have the similar XPS Sn $3d_{5/2}$ binding energies, it is difficult to confirm the oxidation state of tin by XPS spectra of 5% Sn/Al_2O_3.

In order to acquire the information of sulfur on the 5% Sn/Al_2O_3 catalyst (SG), the catalyst was pretreated in 300 ppm SO_2 for 12 h (treated catalyst), the S 2p spectra of the treated 5% Sn/Al_2O_3 catalyst (SG) is shown in Fig. 2. The results showed that the sulfur in the surface mainly exists as sulfate; this is in according with the results of other metal oxide alumina-based catalysts [26].

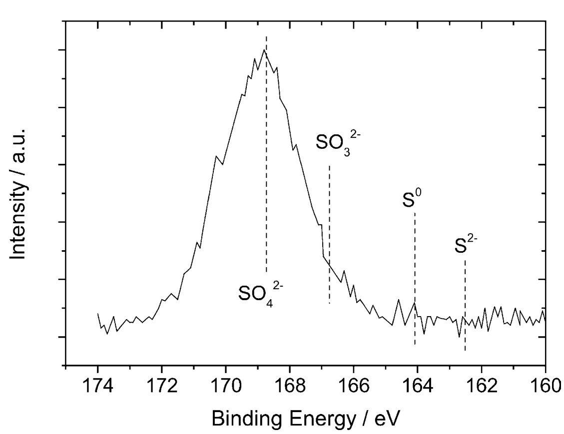

Fig. 2. S 2p XPS spectra of the spent Sn/Al_2O_3 catalyst.

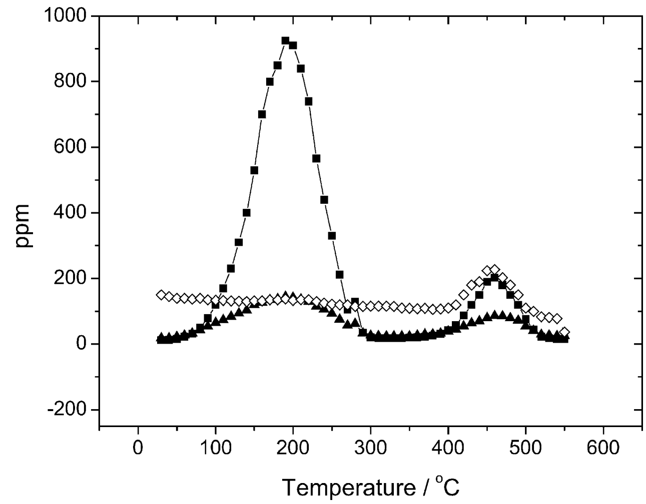

Fig. 3. TPD profiles after adsorption of NO on 5% Sn/Al_2O_3 catalysts. (■) TPD of NO, (▲) TPD of NO_2; (◇) TPD of O_2.

3.1.2. NO TPD studies

Figs. 3 and 4 illustrates the TPD profiles of NO_x and O_2 on the 5% Sn/Al_2O_3 catalysts (SG) after adsorption mixture of NO or $NO + O_2$, respectively. Obviously, they show two desorption peaks both for NO and for NO_2, one is at low temperature, the other is at high temperature, meanwhile, accompanied with the desorption of O_2 at the higher temperature. The influence of SO_2 on the NO_x–TPD profiles is shown in Fig. 5. When the 5% Sn/Al_2O_3 (SG) was treated by the 300 ppm SO_2 for 12 h, a drastic change of NO_x desorption peak were observed. Compared with the NO_x–TPD profiles of fresh catalyst (Fig. 4), the desorption peaks of NO and NO_2 disappeared at the low temperature, and the desorption peak at the high temperature decreased sharply and the peak temperature shifted to lower temperature by 50 °C. The detailed quantitative results are given in Table 2.

As for TPD after adsorption of NO, the temperature of desorption peaks were at 190 °C and at 450 °C, and the

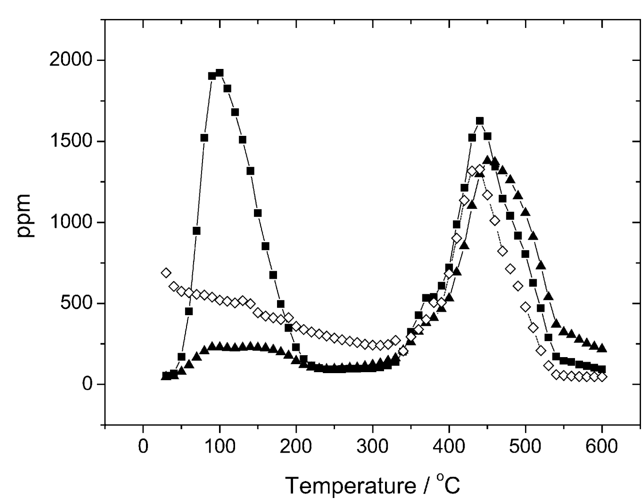

Fig. 4. TPD profiles after adsorption of $NO + O_2$ on 5% Sn/Al_2O_3 catalysts. (■) TPD of NO, (▲) TPD of NO_2; (◇) TPD of O_2.

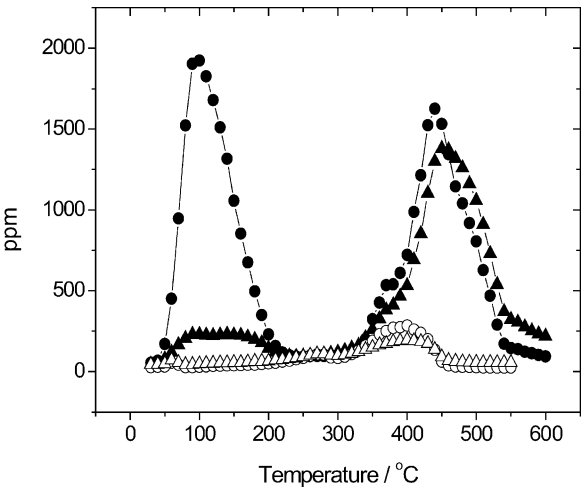

Fig. 5. TPD profiles of NO and NO_2 on fresh or SO_2-treated Sn/Al_2O_3 catalysts. (○, ●) TPD of NO, (△, ▲) TPD of NO_2; (●, ▲) fresh sample, (○, △) SO_2-treated sample.

desorption species was mainly NO. At low temperature, the total amount of NO_x ($NO + NO_2$) desorption was 132.6 μmol g^{-1}, at the high temperature the total amount of NO_x was 29.6 μmol g^{-1}, meanwhile accompanied with 26.3 μmol g^{-1} desorption oxygen. When the adsorption mixture were $NO + O_2$, the temperature of desorption peaks were at 140 and at 450 °C. The total amount of NO_x desorption was 243.3 μmol g^{-1} at low temperature, while the total amount of NO_x desorption was 410 μmol g^{-1} and accompanied with 148 μmol g^{-1} desorption oxygen at the high temperature. As for the SO_2 treated catalyst, the amount of NO and NO_2 desorption were 32.6 and 28.6 μmol g^{-1}, respectively, and the total amount of NO_x desorption was only about one-seventh that of the fresh catalyst.

In comparison with the results of adsorption mixture of NO and $NO + O_2$, the amount of desorption for any species after adsorption of $NO + O_2$ is much larger than that of adsorption of NO. It is of interesting that the ratio of NO_2 to NO is similar at low temperature, but the ratio of NO_2 to NO after adsorption of $NO + O_2$ is about two times than that of adsorption of NO_x at high temperature. It is indicated that oxygen did not participate the desorption of NO and NO_2 at low temperature, so we presumed that the desorption peak at low temperature due to the physical adsorption on the internal surface of catalysts. At the higher temperature, the ratio of NO_2 to NO increased as compared with that at low temperature, at the time the desorption of NO and NO_2 accompanied with O_2, therefore, it is suggested that the desorption of NO_x and O_2 at high temperature due to the chemical desorption, and the desorption of NO_x and O_2 was attributed to the decomposition of nitrate (NO_3^{1-}) formed on the catalyst surface. But for the SO_2 treated catalyst, the NO_x adsorption/desorption was inhibited by the SO_4^{2-} species covered on the surface of the catalyst, and then caused a decrease of the capacity for the formation of nitrate species (ad-NO_3^{1-}), which have been proposed as key intermediates in the NO reduction reaction [27,28].

3.2. *Catalytic activities*

3.2.1. *Effect of Sn loading*

Fig. 6 shows the effect of Sn loadings on catalytic activities of Sn/Al_2O_3 catalyst prepared by different methods for NO conversion by propene in the temperature range of 250–550 °C. Both for catalysts prepared by IM and for catalysts prepared by SG method, with the increase of Sn loading from 1 to 5 wt.%, the maximum NO conversion increased, however, when Sn loading reached 10 wt.%, no further improvement of the maximum NO conversion was observed, so the optimal Sn loading were about 5 wt.%. However, the catalytic activities of Sn/Al_2O_3 (SG) are much higher than Sn/Al_2O_3 (IM) for the same Sn loading in the range of 1–10%. For the 1% Sn/Al_2O_3 (IM) catalyst, the peak NO conversion of 41% was obtained at 550 °C. But for the 1% Sn/Al_2O_3 (SG) catalyst, the peak NO conversion of 76% was obtained at 500 °C instead. As the Sn loading fixed at 5%, the maximum NO conversion was 82% over Sn/Al_2O_3 (SG) while that was 58% on the Sn/Al_2O_3 (IM) at 450 °C. With the increase of Sn loading, the temperature of the maximum NO conversion shifted to a lower temperature region, and the propene conversion increased due to the increase of Sn loading (not shown here), it is indicated that the SnO_2 active species is not only the SnO_2/Al_2O_3 reduction site but also an oxidation site over the Sn/Al_2O_3 catalyst. Based on the results of catalytic activities of catalysts with various Sn loadings, we focused on 5% Sn/Al_2O_3 catalyst prepared by sol–gel method in the following study.

Table 2
Peak temperatures and quantities of species desorbed after adsorption of NO or $NO + O_2$ over fresh or treated 5% Sn/Al_2O_3 (SG) catalysts

	Sorption mixture		NO		NO_2		NO_2/NO		O_2
Fresh catalyst	NO	T_{Peak} (°C)	190	450	190	450	190	460	460
		Amount of adsorpted (μmol g^{-1})	107	18.2	25.6	11.4	0.239	0.626	26.3
	$NO + O_2$	T_{Peak} (°C)	100	440	140	450	∼140	∼450	450
		Amount of adsorpted (μmol g^{-1})	198	202	45.3	208	0.228	1.03	148
Treated catalyst	$NO + O_2$	T_{Peak} (°C)		400		400		400	
		Amount of adsorpted (μmol g^{-1})		32.6		28.6		0.87	

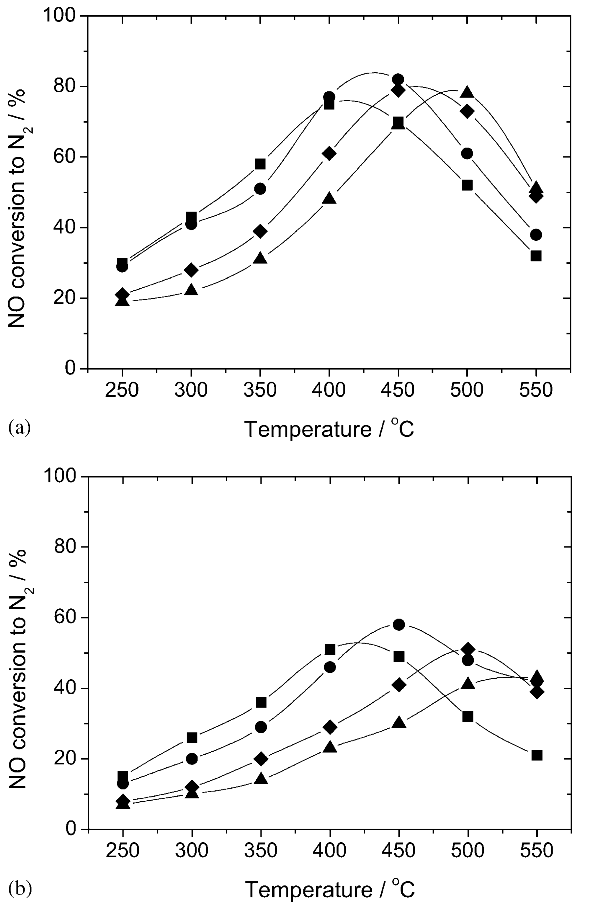

Fig. 6. NO conversion over Sn-Al_2O_3 catalysts prepared by different methods in the absence of H_2O and SO_2. (a) sol–gel, (b) impregnation. -▲- 1% Sn; -◆- 2% Sn; -●- 5% Sn; -■- 10% Sn. Reaction gas: 1000 ppm NO, 1000 ppm C_3H_6, 8% O_2, He as the balance. $W/F = 0.1\,\mathrm{g\,s\,cm^{-3}}$.

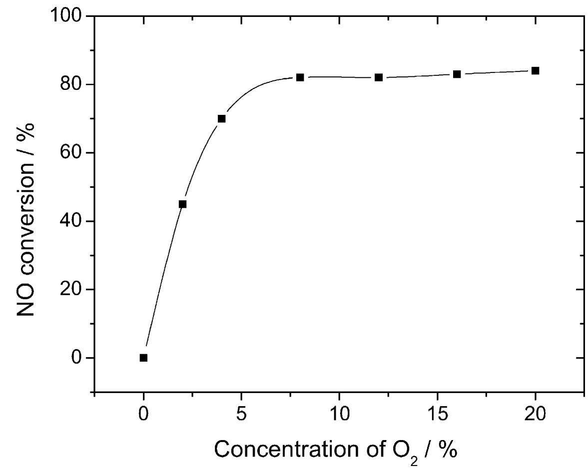

Fig. 7. Effect of O_2 concentration on NO reduction over 5% Sn/Al_2O_3 (SG) catalyst. Reaction temperature: 450 °C. Reaction gas: 1000 ppm NO, 1000 ppm C_3H_6, 0–20% O_2, He as the balance. $W/F = 0.1\,\mathrm{g\,s\,cm^{-3}}$.

3.2.2. Effect of O_2 concentration

The most active 5% Sn/Al_2O_3 (SG) was further tested to evaluated the effect of oxygen content on the NO conversion at the temperature of 450 °C. The dependence of catalytic activity on oxygen concentration for NO conversion at 450 °C is shown in Fig. 7. Little NO conversion to N_2 was observed in the absence of oxygen, but NO conversion increased sharply with the oxygen concentration up to 4%. Further increase the oxygen concentration, the NO conversion almost maintained unchanged when the oxygen increased from 8 to 20%. The results indicated that the oxygen played a key role in the selective catalytic reduction of NO by propene, because oxygen would contribute to several reaction steps such as hydrocarbon oxidation to partially oxidized ones and NO oxidation to NO_2, which were probably the active intermediate species in the NO reduction process. From the results of TPD measurement, the oxygen was also essential for the amounts of desorption and the ratio of NO_2 to NO desorption species (Table 2).

3.2.3. Comparison of reactivity between NO and NO_2

A few researchers have reported that the NO oxidation to NO_2 is a slow step in the NO reduction reaction by hydrocarbons [29–31]. In order to confirm the role of NO_2 in the SCR of NO over Sn/Al_2O_3 catalyst by propene, the catalytic activity of 5% Sn/Al_2O_3 (SG) for the reaction system of NO–C_3H_6–O_2 and NO_2–C_3H_6–O_2 were measured. Fig. 8 shows the results of NO_x conversion over 5% Sn/Al_2O_3 (SG) catalyst between NO and NO_2 in the absence of H_2O and SO_2. It is evident that the reactivity of NO_2 is much higher than that of NO at the entire temperature range; meantime the propene conversion is enhanced considerably by using NO_2 instead of NO. More than 60% NO_2 conversion was observed at a wider temperature range of 300–500 °C, and the maximum NO_2 conversion reached nearly 100% at the temperature range of 400–450 °C.

Based on the above results, it is indicated that the participation of NO_2 in NO reduction by propene, and the NO oxidation into NO_2 might be a limiting factor in NO reduction; NO oxidation to NO_2 must be still a slow step. At least, NO_2 is likely to react more quickly with propene on the surface of the catalyst to form ad-$NO_3{}^{1-}$ species that have been proposed as key intermediates in the reaction [4,27,28].

3.2.4. Effect of H_2O and SO_2

Considering that the actual exhaust contains significant amounts of water vapor and SO_2, the effects of water vapor and SO_2 on NO reduction over the single step sol–gel 5% Sn/Al_2O_3 (SG) catalyst for selective catalytic reduction of NO by propene were investigated. Fig. 9 shows the effect of water vapor and SO_2 on 5% Sn/Al_2O_3 (SG) catalyst for selective catalytic reduction of NO by propene. It can be seen that Sn/Al_2O_3 shows high activity around 450 °C in the absence of water vapor and SO_2, such a temperature of maximum NO conversion was in accordance with that of NO_x and O_2 desorption peak around 450 °C (Fig. 4).

When added 10% water vapor into the reaction gas, the catalytic activity was not depressed but enhanced slightly, although the maximum NO conversion decreased. The reasons of H_2O promotional effect are the selective inhibition

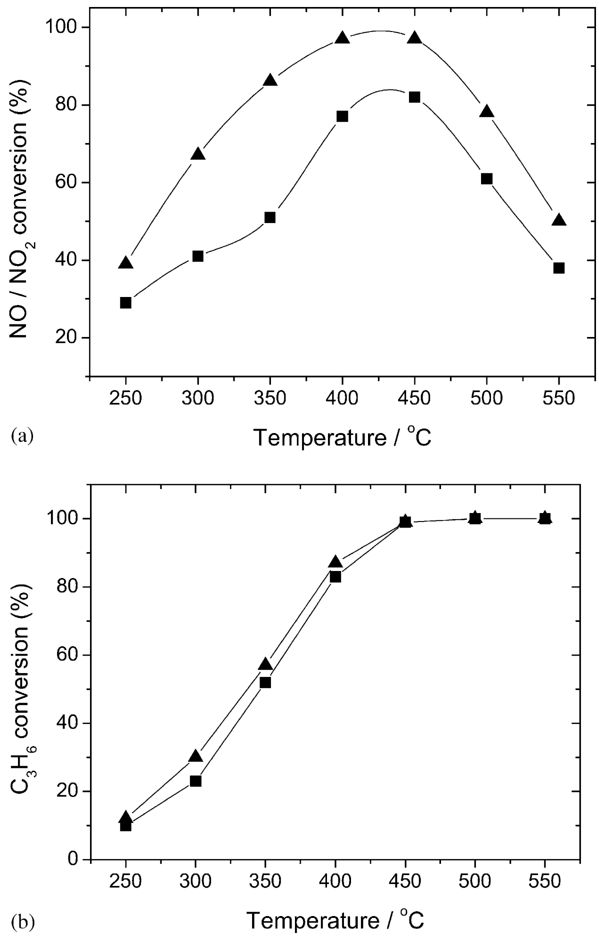

Fig. 8. Comparison of reactivity and propene conversion between NO and NO_2 over 5% Sn/Al_2O_3 (SG) catalysts in the absence of H_2O and SO_2. (■) $NO + C_3H_6 + O_2$; (▲) $NO_2 + C_3H_6 + O_2$. Reaction gas: 1000 ppm NO (or 1000 ppm NO_2), 1000 ppm C_3H_6, 8% O_2, He as the balance. $W/F = 0.1\,g\,s\,cm^{-3}$.

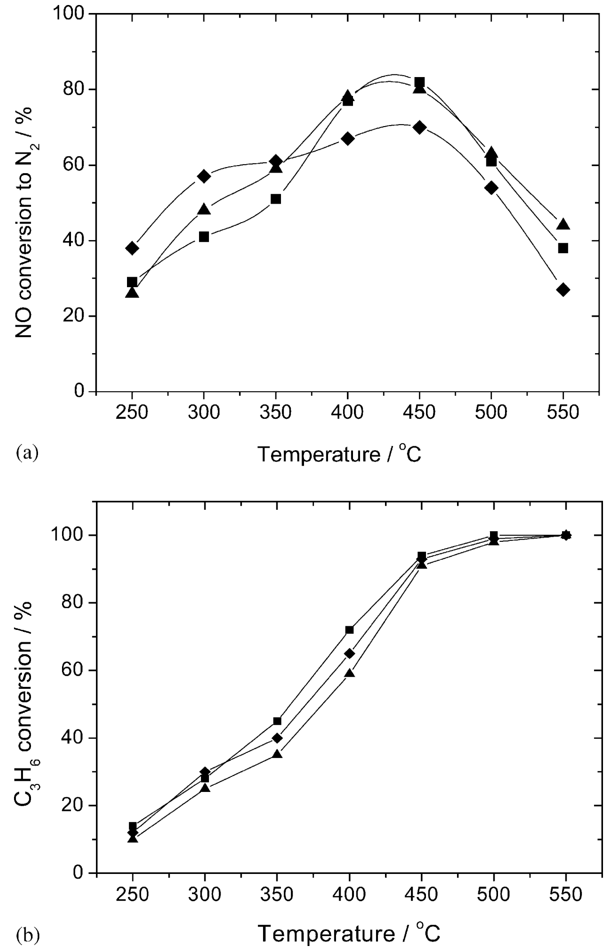

Fig. 9. The effect of H_2O and SO_2 on 5% Sn/Al_2O_3 (SG) catalyst for NO reduction by propene. (■) without H_2O and SO_2; (▲) with 10% H_2O without SO_2; (◆) with 10% H_2O and 100 ppm SO_2. Reaction gas: 1000 ppm NO, 1000 ppm C_3H_6, 8% O_2, He as the balance. $W/F = 0.1\,g\,s\,cm^{-3}$.

by H_2O of the reaction steps resulting in propene oxidation to CO_2 and the removal of carbonaceous materials covering the catalytically active sites by H_2O [32]. Furthermore, on introduction of 100 ppm SO_2, the catalytic activity was inhibited at the high temperature in the presence of water vapor and SO_2, the maximum NO conversion decreased to 72% at 450 °C. However, an enhancement effect was observed at the lower temperature range of 250–350 °C, and the temperature window was also broadened, more than 50% NO conversion was observed at the temperature range of 300–500 °C. It was also found that the propene conversion over Sn/Al_2O_3 was also depressed in the presence of water vapor and SO_2, meanwhile the curve of propene conversion was shifted to the higher temperature.

In order to further investigate the effect of SO_2 on the catalyst, we tested the catalytic activity of spent catalyst (after the reaction of NO reduction in the presence of 10% H_2O and 100 ppm SO_2) and treated catalyst, the results is given in Fig. 10. Both for spent and treated catalysts, the catalytic activities were depressed at the entire temperature as com-

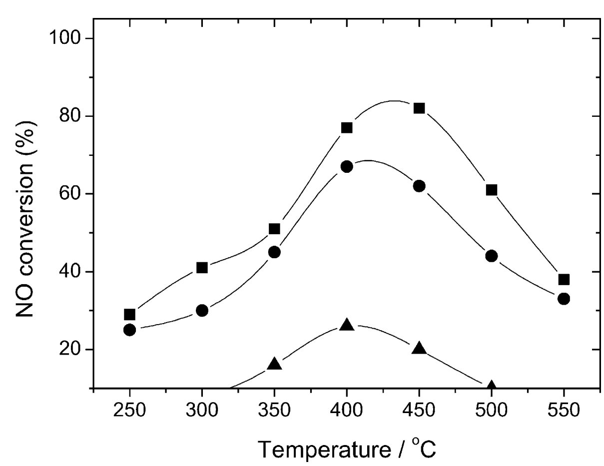

Fig. 10. Catalytic activity of NO reduction over fresh and spent and treated 5% Sn/Al_2O_3 (SG) catalysts in the absence of H_2O and SO_2. (■) fresh catalyst; (●) spent catalyst; (▲) 300 ppm SO_2 treated catalyst. Reaction gas: 1000 ppm NO, 1000 ppm C_3H_6, 8% O_2, He as the balance. $W/F = 0.1\,g\,s\,cm^{-3}$.

pared to the fresh catalyst. As for spent catalyst, the maximum NO conversion is still above 60%. In comparison, as for treated catalyst, the maximum of NO conversion sharply decreased to 33%. The decrease of NO on spent and treated catalyst due to formation of sulfate species (Fig. 2), which resulted in the poisoning of NO_x adsorption sites on which NO reduction proceeds (Fig. 5). It is obviously that more ${SO_4}^{2-}$ species were accumulated on the treated catalyst than those on spent catalyst, so the catalytic activity of treated catalyst dramatically decreased. When the SO_2 was in the reaction gas, it is probably that the strong adsorption of SO_2 on the basic oxygen sites of the catalyst surface compared with NO_2, and then formed ${SO_4}^{2-}$ species on the surface, the ${SO_4}^{2-}$ species might be inhibiting the formation and adsorption of ${NO_3}^-$, which is known to play an essential role in the NO reduction by hydrocarbon.

4. Conclusions

The Sn/Al_2O_3 catalysts prepared by single sol–gel method for NO_x reduction by propene showed higher activities than those prepared by impregnation method in the absence of water vapor and SO_2. The presence of oxygen played an essential role in NO reduction; the activity of the 5% Sn/Al_2O_3 (SG) was not depressed in the presence of large oxygen. The maximum NO conversion was 82% on the 5% Sn/Al_2O_3 (SG) catalyst, the reactivity of NO_2 is much higher than that of NO at the entire temperature range, the maximum NO_2 conversion reached nearly 100% at the range of 400–450 °C. It is of interesting that the effect of addition of water vapor for NO reduction was not depressed but enhanced obviously; When the SO_2 added to the reaction gas, the catalytic activity was enhanced remarkably at the low temperature, and the temperature window was also broadened, more than 50% NO conversion was observed at the temperature range of 300–500 °C. But for 300 ppm SO_2 treated catalyst, the NO_x desorption and NO conversion decreased dramatically in comparison with that of fresh catalyst. The reason is known that the catalytic activity is inhibited by the presence SO_2 due to formation of sulfate species (${SO_4}^{2-}$) on the catalysts.

Acknowledgements

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