

Novel Sn–Ce/Al₂O₃ catalyst for the selective catalytic reduction of NO_x under lean conditions

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Received 12 May 2005; accepted 21 September 2005

Effect of additives, Ce and Mn, on the catalytic performance of Sn/Al₂O₃ catalyst prepared by sol–gel method for the selective reduction of NO_x with propene under lean conditions was studied. Sn–Ce/Al₂O₃ catalysts exhibited higher activity than Sn/Al₂O₃ catalyst and the optimum Ce loading is 0.5–1%. The promoting effect of Ce is to enhance the oxidation of NO to NO₂ and facilitate the activation of propene, both of which are important steps for the NO_x reduction. The presence of oxygen contributes to the oxidation of NO and shows a promoting effect.

KEY WORDS: Sn–Ce/Al₂O₃; selective reduction of NO_x; propene.

1. Introduction

Selective catalytic reduction of NO_x with hydrocarbons as reducing agents (HC-SCR) has received much attention as one of potential technology for reducing NO_x emissions in the presence of excess oxygen. Since the pioneer work of Held et al. [1] and Iwamoto et al. [2] quiet a few different catalyst systems have been investigated for HC-SCR [3–10]. Among them, the metal oxide catalysts are more desirable because they exhibit high activities at high temperatures, besides they are more stable than zeolite-based catalysts in the hydrothermal conditions [11–13].

Since SnO₂ was firstly reported to be an active catalyst for the NO_x reduction by hydrocarbons in the presence of oxygen [14], some research was focused on Sn/Al₂O₃ catalyst [15–19]. For Sn/Al₂O₃ catalyst, the major disadvantage is that the NO_x conversion is low at low-temperature region (250–400 °C). However, there is little report about enhancing the low-temperature activity of Sn/Al₂O₃ catalyst. In the previous research, the higher activity can be observed when feeding NO₂ instead of NO during the HC-SCR over Sn/Al₂O₃ catalyst [20]. That means the NO oxidation might be a limiting step in NO reduction and strengthening the NO oxidation function of Sn/Al₂O₃ catalyst should enhance its activity for the NO reduction. CeO₂ was chosen as one of the active components for favouring the NO oxidation because of its well-known function as oxygen storage/activator in three-way catalysts [21]. And recently, Krishna et al. [22] reported that mixed CeO₂

with H-FER zeolite catalyst showed high activity for HC-SCR. Besides CeO₂, manganese oxide also served as an oxidation catalyst to promote the performance of deNO_x catalyst [23,24]. So the present work attempts to improve the activity of Sn/Al₂O₃ catalyst by adding cerium oxide and manganese oxide.

2. Experimental

2.1. Catalyst preparation

Metal oxide-doped Sn/Al₂O₃ catalysts were prepared by single step sol–gel method. Ce and Mn were selected as an additive. Aluminium boehmite sol was first prepared by hydrolysis of aluminium(III) iso-propoxide(AIP) in hot water(85 °C) with a proper amount of nitric acid, and then mixed with a solution of tin chloride and metal nitrate of the doped metal oxide. After one day of stirring, the solvents were eliminated by heating under reduced pressure to form a gel. The obtained gel was dried at 120 °C for 24 h, followed by calcinations at 600 °C for 4 h in air. The loading of Sn was fixed at 5% since previous research showed that the optimum Sn loading is 5% for Sn/Al₂O₃ catalyst [19]. While that of Ce additive varies from 0.5 to 5%. A 5%Sn/Al₂O₃ was also prepared as a reference sample by the same sol–gel method.

The SBA15 support was synthesized according to a procedure described in the literature [25]. Pluronic P123 triblock copolymer surfactant (EO₂₀PO₇₀EO₂₀) was used as a template, which was dissolved in hydrochloric acid solution. After stirring for a few hours, a suitable amount of TEOS (tetraethyl orthosilicate) was added.

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The resulting mixture was stirred for 12 h at 30 °C and then at 100 °C for 24 h. The white product was filtered, washed and dried. Finally, the product was calcined at 550 °C for 4 h to remove the template. A1SBA15 was obtained by impregnating SBA15 with a proper amount Al(NO₃)₃ solution and the Al percentage is 1.3, dried at 120 °C for 12 h, followed by calcinations at 300 °C for 3 h in air. Then A1SBA15 was impregnated with H₂PtCl₆ solution, dried at 120 °C for 12 h, followed by calcinations at 500 °C for 3 h in air and yield the Pt/A1SBA15 catalyst, which was compared with metal oxide-doped Sn1Al₂O₃ catalyst.

2.2. Evaluation of catalyst activity

The activity measurements were carried out in a fixed-bed quartz reactor using a 0.2 g catalyst of 60–80 mesh. The feed gas mixture contained 2000 ppm NO_x, 2700 ppm C₃H₆, 3% O₂ and helium as the balance gas. Unless noted, the total flow rate of the feed gas was 100 cm³ min⁻¹, which corresponded to a space velocity of 26,000 h⁻¹. The reaction temperature was increased from 250 to 550 °C in steps of 50 °C. All the catalysts were pretreated in the reaction feed gas at 600 °C for 2 h before the activity test, In the previous research we compared the activities of two different 5%Sn/Al₂O₃ catalysts, one was only calcined in air and the other was pre-treated in the reaction gas after calcining in air. It was found that the 5%Sn/Al₂O₃ catalyst pre-treated in the reaction feed gas showed much higher activity than that without pre-treatment below 450 °C. And above this temperature there is almost no deactivation after feed gas treatment [19]. For Sn/Al₂O₃ catalyst, besides SnO₂, Al₂O₃ is an active site and contributes to the NO_x reduction but could be prevented from doing so when its active centers are covered by dispersed SnO₂ [17]. From the TEM photographs it can be seen that pre-treatment leads to the crystallization and growth of the SnO₂ species [19]. Due to the agglomeration, Al₂O₃ surface sites previously covered by dispersed SnO₂ species are re-exposed. So the activity of Sn/Al₂O₃ catalyst was improved after pre-treatment in the reaction gas.

The composition of the product gas was analyzed by using gas chromatograph (equipped with Porapak Q and Molecular sieve 5A columns). A molecular-sieve 5A column was used for the analysis of N₂ and CO and Porapak Q column for that of N₂O, CO₂ and C₃H₆. The activity data were collected when the catalytic reaction practically reached steady-state conditions at each temperature. The formation of N₂O was found negligible in the present study. Thus, NO_x conversion was determined by the N₂ produced.

2.3. Catalyst characterization

BET surface areas were measured by N₂ adsorption using a NOVA4200 automated gas sorption system. X-

ray diffraction (XRD) measurements were carried out on a Bruker D8 Discover DADDS X-ray Diffractometer with CuKα radiation.

3. Results and discussion

3.1. Catalyst characterization

The BET surface areas of all the catalysts are summarized in table 1. No significant difference of surface area can be observed over Sn/Al₂O₃, Sn–Ce/Al₂O₃ and Sn–Mn/Al₂O₃ catalysts. Figure 1 shows the XRD patterns of 5%Sn/Al₂O₃ and Sn–Ce/Al₂O₃ catalysts. Except for 5%Sn–5%Ce/Al₂O₃ catalyst, only the characteristic lines of γ-Al₂O₃ can be observed. In addition to the γ-Al₂O₃ phase, small peak assigned to CeO₂ is identified over 5%Sn–5%Ce/Al₂O₃ catalyst. The peak ascribed to SnO₂ was not observed over all the catalysts. This fact suggests the presence of small SnO₂ species on Al₂O₃.

3.2. Activity test

3.2.1. Effect of additives on the activity of 5%Sn/Al₂O₃ catalyst

The effect of metal additives on the activity of 5%Sn/Al₂O₃ catalyst is presented in figure 2. It can be seen

Table 1
The specific surface area of the catalysts

Catalyst	Specific surface area (m ² g ⁻¹)
5%Sn/Al ₂ O ₃	170
5%Sn–0.5%Ce/Al ₂ O ₃	185
5%Sn–1%Ce/Al ₂ O ₃	177
5%Sn–2%Ce/Al ₂ O ₃	175
5%Sn–5%Ce/Al ₂ O ₃	178
5%Sn–1%Mn/Al ₂ O ₃	176

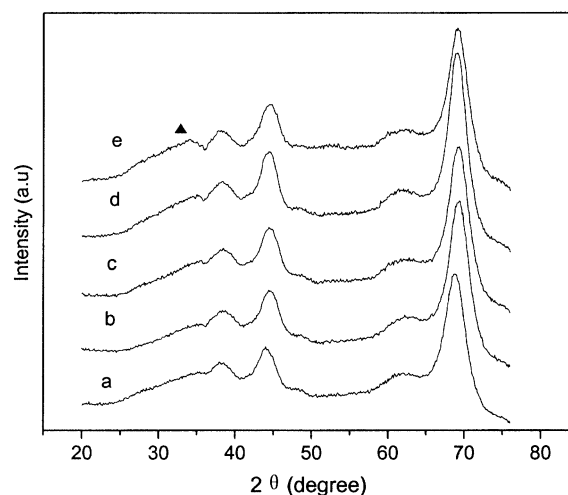


Figure 1. XRD patterns of catalysts: (a) 5%Sn/Al₂O₃; (b) 5%Sn–0.5%Ce/Al₂O₃; (c) 5%Sn–1%Ce/Al₂O₃; (d) 5%Sn–2%Ce/Al₂O₃ and (e) 5%Sn–5%Ce/Al₂O₃. (▲)CeO₂

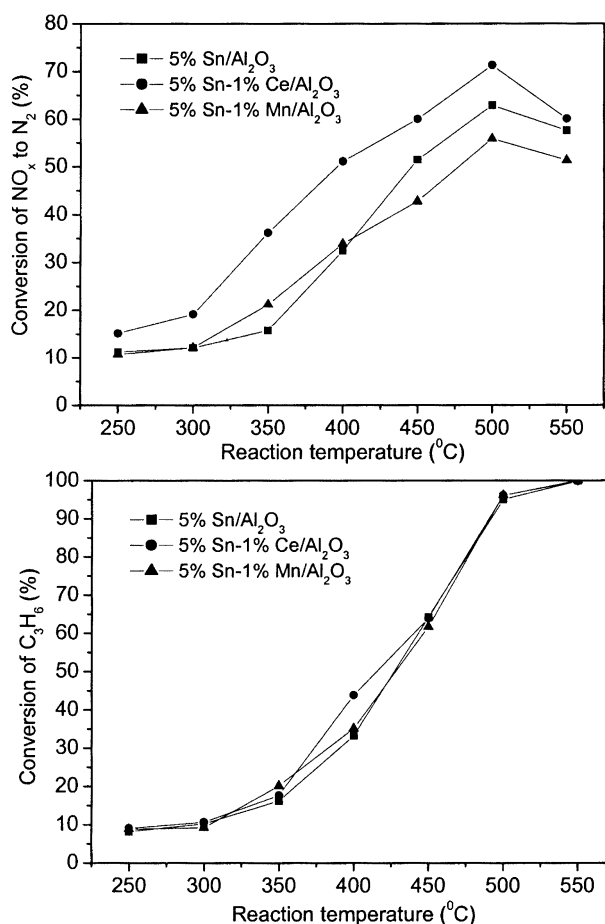


Figure 2. Activities of different metal modified 5% Sn/Al₂O₃ catalysts for NO reduction at different reaction temperatures (reaction conditions: NO = 2000 ppm, C₃H₆ = 2700 ppm, O₂ = 3%, GHSV = 26,000 h⁻¹).

that the addition of Mn causes a pronounced decrease in the catalytic activity of 5%Sn/Al₂O₃ catalyst above 400 °C, although the activity of added Mn catalyst at 350 °C was slightly higher than that of 5%Sn/Al₂O₃ catalyst. On the other hand, the addition of Ce showed a remarkable promoting effect. The added Ce catalyst exhibited higher activity than 5%Sn/Al₂O₃ catalyst over the whole temperature range. Over the three catalysts, the maximum NO_x conversion were all obtained at 500 °C, at which the propene was almost completely converted. The facts confirm that the temperature of maximum NO_x conversion temperature was closely related to that of almost full combustion of reducing agent.

3.2.2. Effect of Ce loading on the activity of 5%Sn/Al₂O₃ catalyst

Since the additive of Ce showed a beneficial effect on the activity of 5%Sn/Al₂O₃ catalyst, the effect of varying the Ce content on the performance of 5%Sn/Al₂O₃ catalyst was further investigated and the results are shown in figure 3. The activity of 5%Sn/Al₂O₃ catalyst hardly changed with increase in the Ce loading from 0.5

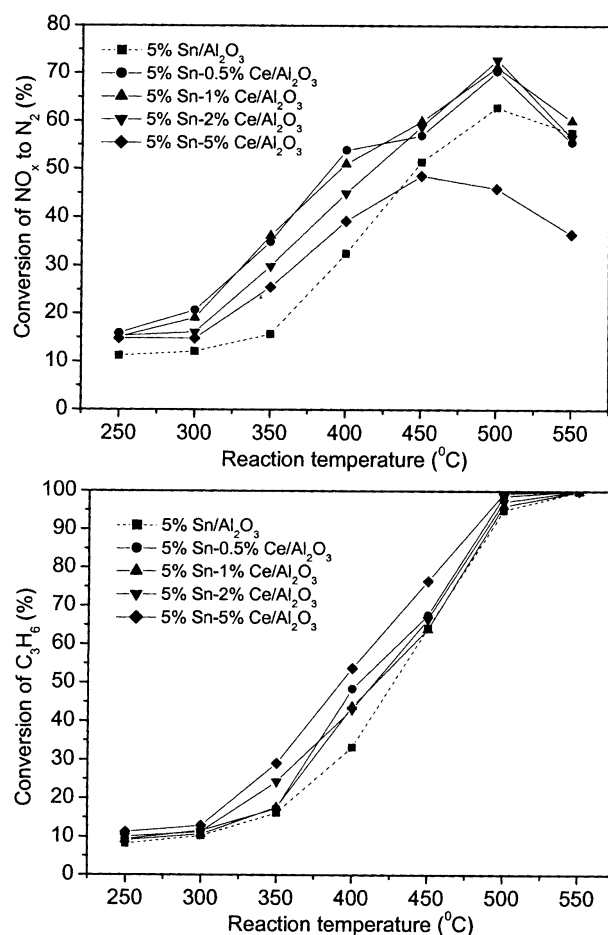


Figure 3. Effect of Ce loading on NO_x conversion over 5%Sn-x%Ce/Al₂O₃ catalysts for NO reduction by propene: (Reaction conditions: NO = 2000 ppm, C₃H₆ = 2700 ppm, O₂ = 3%, GHSV = 26,000 h⁻¹).

to 1%. Further increasing the Ce loading leads to the decreased activity and when the Ce loading reached 5%, the NO conversion was even lower than that over 5%Sn/Al₂O₃ catalyst above 450 °C. However, the low temperature activity of 5%Sn/Al₂O₃ catalyst was still improved. Thus, a small amount of Ce (0.5–1%) provide the maximum promotion of the SCR reaction. When the Ce loading was low, no peak ascribed to CeO₂ was observed from the XRD patterns. So high-dispersed Ce was present on the catalyst. At higher Ce loading, large CeO₂ particles were formed, which were active for the combustion of propene as a side reaction. Above 450 °C, the side reaction predominated and there was not enough reductant to reduce NO_x, so the conversion of NO_x over 5%Sn-5%Ce/Al₂O₃ catalyst was even lower than that over 5%Sn/Al₂O₃ catalyst.

3.2.3. Comparison of activities of 5%Sn-0.5%Ce/Al₂O₃ and 2.3%Pt/AlSBA15 catalysts

Among the catalysts tested for the selective reduction of NO by propene, Pt supported catalysts were extensively studied due to its high low-temperature activity [26–28]. So in this work the activities of 5%Sn-0.5%Ce/

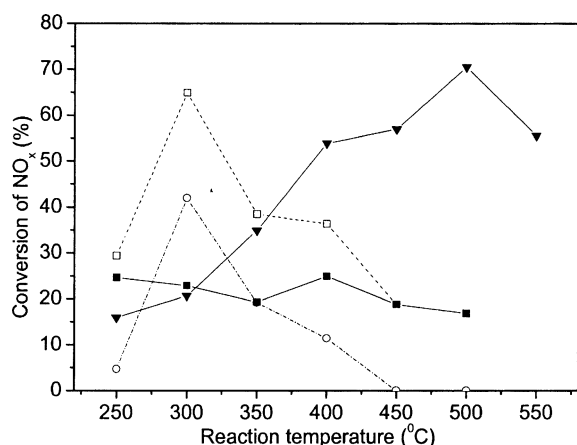


Figure 4. Comparison of activities of 5%Sn–0.5%Ce/Al₂O₃(▼) and 2.3% Pt/AlSBA15(□ total conversion of NO_x; ○: conversion to N₂O; ■: conversion to N₂) catalysts (Reaction conditions: NO=2000 ppm, C₃H₆=2700 ppm, O₂=3%, GHSV=26,000 h⁻¹).

Al₂O₃ and 2.3%Pt/AlSBA15 catalysts were compared under identical reaction conditions. As shown in figure 4, the activity of Pt/AlSBA15 catalyst was high at low temperature region and the maximum NO conversion was obtained at 300 °C. However, the high selectivity to N₂O and the narrow temperature window are the obstacle for practical application. In contrast, the selectivity towards N₂ over 5%Sn–0.5%Ce/Al₂O₃ catalyst is almost 100%. In view of the conversion to N₂, 5%Sn–0.5%Ce/Al₂O₃ catalyst was more active at temperatures above 300 °C and the temperature window was wider, though Pt/AlSBA15 catalyst was slightly more active at 250 °C.

3.2.4. Effect of O₂

Figure 5 illustrates the changes in NO and C₃H₆ conversions with respect to O₂ concentration over 5%Sn/Al₂O₃ and 5%Sn–0.5%Ce/Al₂O₃ catalysts, respectively. At 350 °C, the increase of O₂ concentration was found to be favorable for NO_x reduction over the two catalysts. Especially for 5%Sn–0.5%Ce/Al₂O₃ catalyst, the conversion of NO_x significantly improved with the increase of oxygen concentration from 1 to 3%. With further increase in oxygen concentration the NO_x conversion remained almost unchanged, although the conversion of propene was further increased. At 450 °C, with the O₂ concentration further increasing to 10% from 6%, the NO_x conversion over 5%Sn–0.5%Ce/Al₂O₃ catalyst was slightly decreased, which was a little lower than that over 5%Sn/Al₂O₃ catalyst. The possible reason is that at higher temperatures more reducing agent was combusted and there was not enough reductant to reduce NO_x over 5%Sn–0.5%Ce/Al₂O₃ catalyst. The fact indicates that the oxygen plays an important role in the selective reduction of NO_x. TPD-NO_x results over Sn/Al₂O₃ showed that the amount of desorbed species after adsorption of NO+O₂ were much larger than that of adsorption of NO [20]. This means the NO_x

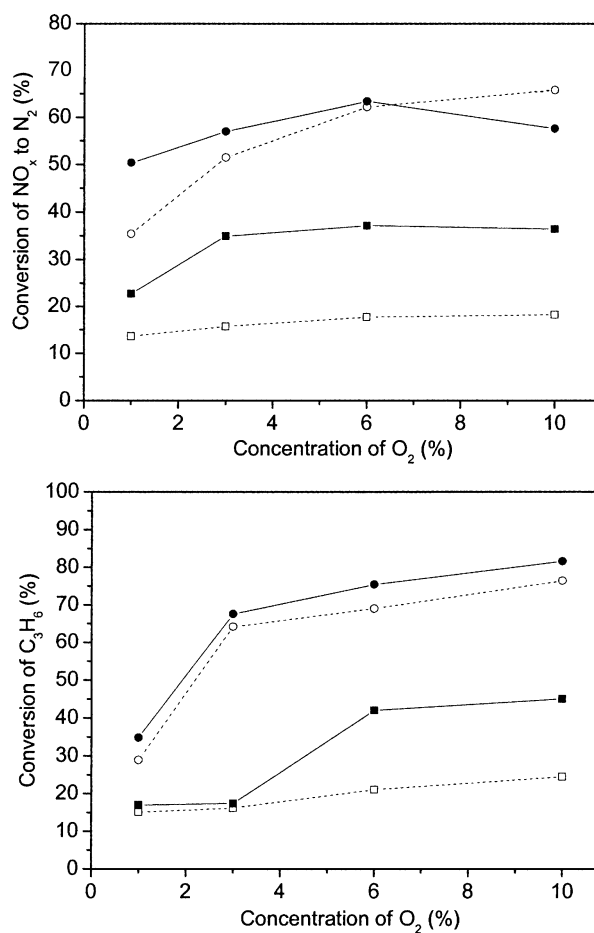


Figure 5. Effect of O₂ concentration on the activities of 5%Sn/Al₂O₃ (dashed line) and 5%Sn–0.5%Ce/Al₂O₃ (Solid line) catalysts at 350 °C(□, ■) and 450 °C(○, ●) (Reaction conditions: NO=2000 ppm, C₃H₆=2700 ppm, O₂=1–10%, GHSV=26,000 h⁻¹).

species are more easily adsorbed on the surface of the catalyst in the presence of oxygen and further converted to surface nitrates, which is an important reaction intermediate for NO_x reduction [9]. The presence of oxygen also contributes to the oxidation of NO to NO₂, which is more reactive than NO and as a result is more likely to react quickly with some other key reaction intermediates to form N₂.

3.2.5. Effect of C₃H₆

Figure 6 presents the effect of C₃H₆ on the activities of 5%Sn/Al₂O₃ and 5%Sn–0.5%Ce/Al₂O₃ catalysts. Over the latter catalyst, the NO_x conversion was increased when the concentration of propene was increased from 1000 to 4000 ppm. This result indicates that high concentration of reductant is beneficial to the reduction of NO_x. The effect is in accordance with the previous research [29,30] and is attributed to the fact that the larger amount of reducing agent makes more reaction intermediates species formed to facilitate the NO reduction. On the other hand, the NO_x conversion appeared to decrease over 5%Sn/Al₂O₃ catalyst as the

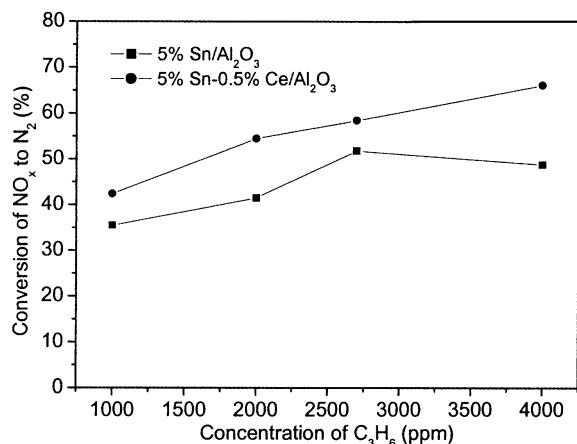


Figure 6. Effect of C₃H₆ on the activities of 5%Sn/Al₂O₃ and 5%Sn-0.5%Ce/Al₂O₃ catalysts at 450 °C. (Reaction conditions: NO=2000 ppm, C₃H₆=1000–4000 ppm, O₂=3%, GHSV=26,000 h⁻¹).

propene concentration was increased from 2700 to 4000 ppm. This phenomenon is similar to the report by L.F.Córdoba et al. [31]. It was speculated that the carbonaceous deposits were more easily formed on the catalyst surface when the propene concentration was high and inhibited the NO_x reduction [12].

3.2.6. Effect of space velocity

Figure 7 shows the effect of space velocity of feed gas on the activity of 5%Sn-0.5%Ce/Al₂O₃ catalyst. When the GHSV was 13,000 h⁻¹, it showed very high activity, 53% NO_x conversion can be obtained at temperature as low as 350 °C. As expected, the conversion of NO_x to N₂ decreased with increasing space velocity. However, the maximum NO_x conversion was only slightly decreased at a space velocity of 39,000 h⁻¹.

For the C₃H₆-SCR of NO_x over Sn/Al₂O₃ catalyst, SnO₂ was found to promote the formation of acetaldehyde from propene and subsequently the acetaldehyde was oxidized to form acetates[33]. The acetate species are then believed to react with the surface adsorbed nitrates to yield organo-nitrogen species. The formation of the organo-nitrogen species is likely to be the rate-determining step of the reaction. The organo-nitrogen species will be decomposed to CN and/or NH₃ species, which then react with NO and/or NO₂ to form N₂ [9,33]. Kung et al. [33] proposed that acetate species react with the surface adsorbed nitrates to yield organo-nitrogen species and the formation of N₂ occurred over Al₂O₃ sites.

For bifunctional catalyst, a key issue related to the development of the NO oxidation function is to avoid the oxidation of hydrocarbon with oxygen. Sn/Al₂O₃ catalyst was regarded as a unique kind of lean NO_x catalysts [17,32] due to its poor ability to activate hydrocarbons. So a small amount of CeO₂ addition to Sn/Al₂O₃ catalyst did not lead to the combustion of propene but contributed to the activation of the reductant to form hydrocarbon intermediates such as acetal-

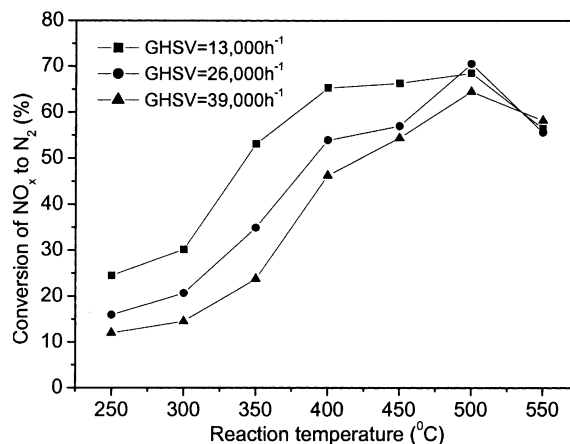


Figure 7. Effect of space velocity of feed gas on the activities of 5%Sn-0.5%Ce/Al₂O₃ catalyst. (Reaction conditions: NO=2000 ppm, C₃H₆=2700 ppm, O₂=3%, GHSV=13,000–39,000 h⁻¹).

dehyde, which is an important step for the NO_x reduction to proceed [6,33]. At the same time, CeO₂ catalyze the oxidation of NO to NO₂ [34,35], which is more active species. Both aspects facilitate the formation of N₂. So Sn-Ce/Al₂O₃ catalyst exhibited higher activity than Sn/Al₂O₃ catalyst.

4. Conclusions

Sn-Ce/Al₂O₃ catalysts were more active than Sn/Al₂O₃ catalyst for the selective reduction of NO_x and the optimum Ce loading is 0.5–1%. The oxygen dependency of these catalysts is desirable for NO_x removal of a lean burn engine. The addition of Ce to Sn/Al₂O₃ catalyst contributes to the oxidation of NO to NO₂ and the activation of propene, thus improving the yield of the whole NO reduction reaction.

Acknowledgements

This research was funded by Center for Ultramicrochemical Process Systems (CUPS) supported by KOSEF(2004) and Z. Liu was supported by BK21 postdoctoral fellowship.

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