

Influence of preparation methods of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst on selective catalytic reduction of NO by propene in the presence of oxygen

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Selective catalytic reduction of NO with propene was investigated over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by three methods, namely, a single sol-gel (SG), impregnation (IM), and co-precipitation method (CP). The catalysts were characterized by means of BET, XRD, XPS, and TPD. The maximum NO conversion over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ prepared by sol-gel method was 95% at 400 °C in the absence of H_2O , and the activity decreased slightly in the presence of H_2O , and it was still 76% even in the presence of H_2O and SO_2 . Although the retarding effect of SO_2 on the activity was observed for the three catalysts, $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) showed relatively high activity. It is found that the high surface area and low average pore diameter are important to the catalytic activity, and the strong interaction between indium and alumina for $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst prepared by sol-gel method may be the reason of high activity for NO reduction. The reaction and surface studies showed that NO_3^- and partially oxidized hydrocarbons (RCOO^- species) are mainly intermediates, and the oxidation C_3H_6 to RCOO^- species maybe the key reaction process in the SCR of NO with C_3H_6 .

KEY WORDS: NO reduction; selective catalytic reduction; lean-burn; de- NO_x catalyst; Indium/Alumina; preparation method.

1. Introduction

Nitrogen oxides are major pollutants in the atmosphere and need to be removed from exhaust gases. Selective catalytic reduction (SCR) of nitrogen oxides is an efficient way to remove NO from lean burn gasoline and diesel exhaust [1,2]. Several precious metal, metal oxide and zeolite catalysts have been reported to efficiently reduce NO. However, the poor hydrothermal stability of zeolite-based catalysts leads to an irreversible deactivation of the catalyst at high temperature in the presence of water vapor [3–5]. Noble metal-based catalysts have high activity and stability at low temperature in the presence of water vapor and SO_2 , but the inevitable greenhouse gas N_2O and narrow operation temperature window are serious problems for practical application [6–9]. Metal-oxide based catalysts have high NO reduction activity over the high temperature range, and have been widely investigated in recent years [10–14].

Indium has previously been reported to be an active element supported on the zeolite and metal oxide support materials under lean burn conditions [15–18]. Among them, indium supported on alumina seems to be a promising catalyst for selective catalytic reduction of NO in the presence of oxygen. Nevertheless, almost all the catalysts reported were prepared by a single method. Apparently, the preparation method is a critical factor to the catalytic activity of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ for NO reduc-

tion by hydrocarbons, and hence a comparison of different catalyst preparation methods is necessary.

In this study, we investigated the catalytic performance of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ prepared by different methods, and found that the catalyst prepared by sol-gel method showed higher activity than other preparation methods, and the high surface area and low average pore diameter are important to the catalytic activity.

2. Experimental

2.1. Catalyst preparation

$\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts were prepared by three methods, namely, single sol-gel [denoted as $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG)], the conventional impregnation [denoted as $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM)], co-precipitation [denoted as $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP)]. The loading of In_2O_3 on all the catalysts was fixed at 5% in mass fraction. Details of the procedure of preparation catalysts are described as follows.

For the single step sol-gel catalyst, aluminium boehmite sol was first prepared by hydrolysis of aluminium(III) iso-propoxide(AIP) in hot water (85 °C) with a small amount of nitric acid until it formed the sol, and then a proper indium nitrate solution was incorporated to the sol. After 6 h 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, 800 and 1000 °C, respectively, for 6 h in air.

The impregnation $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM) catalyst was prepared by impregnating the Al_2O_3 powder with

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aqueous solution containing indium nitrate. The alumina used here was synthesized from aluminium boethmite sol described above, stirred at room temperature for 6 h, followed by drying at 120 °C and calcination at 600 °C for 6 h in air.

The co-precipitation $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP) catalyst was produced by mixing 10% NH_4OH with an aqueous solution of aluminium nitrate and indium nitrate. In this procedure, the pH of the mixed solution was kept at 10. The sediment was washed with distilled water, followed by drying at 120 °C and calcination at 600 °C for 6 h in air.

2.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor (inner diameter 8 mm) using a 0.5 g catalyst of 60–100 meshes. The feed gas mixture contained 1000 ppm NO or NO_2 , 1000 ppm C_3H_6 , 8% O_2 , 0 or 100 ppm SO_2 , 0 or 10% H_2O , and helium as the balance gas. The total flow rate of the feed gas was $300 \text{ cm}^3 \text{ min}^{-1}$, corresponding to a space velocity of about $30,000 \text{ h}^{-1}$. NO and NO_2 concentration were analyzed with a chemiluminescence NO/ NO_2 analyzer (Thermal Environmental Instruments, model 42C). Other product gases were analyzed using a Shimadzu GC 17A equipped with Porapak Q and Molecular sieve 5A columns. A molecular-sieve 5A column was used for the analysis of N_2 and CO and Porapak Q column for that of N_2O , CO_2 and C_3H_6 . The activity data were collected when the catalytic reaction practically reached steady-state conditions for half an hour at each temperature. The formation of N_2O was found negligible ($< 10 \text{ ppm}$) and for this reason this product will not be further discussed.

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 Diffractometer with $\text{CuK}\alpha$ radiation. XPS measurements were conducted on a PHI15300/ESCA system with Al K α radiation (1484.6 eV), calibrated internally by carbon deposit C 1 s binding energy (BE) at 284.6 eV.

Temperature programmed desorption (TPD) experiments of NO were carried out by using 100 mg catalyst sample. The desorbed species were continuously monitored by a NO/ NO_2 analyzer. Prior to the NO TPD experiment, the catalyst sample was pre-treated in a flow of 8% O_2/He at 600 °C for 1 h and then cooled down to room temperature. Chemisorption of NO was performed by passing a flow of 1000 ppm NO and 8% O_2 diluted in He through the sample bed at room temperature for 1 h. After the sample was purged with He until no NO was detected, the TPD measurements were carried out up to 600 °C with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in flowing He. The gas flow rate was fixed at

$50 \text{ cm}^3 \text{ min}^{-1}$. The amount of NO desorbed from the catalyst was quantified by calibrating the peak area against that of a standard NO pulse.

In situ DRIFTS spectra were recorded on a NEXUS 870-FTIR equipped with a smart collector and an MCT/A detector cooled by liquid N_2 . The samples for studies was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalysts were heated in a flow of 10 vol% $\text{O}_2 + \text{N}_2$ for 60 min at 873 K, then cooled to the desired temperature, and a spectrum of the catalyst in the flow of $\text{N}_2 + \text{O}_2$ serving as the background was recorded. All spectra were measured under real reaction conditions with a resolution of 4 cm^{-1} and an accumulation of 100 scans.

3. Results

3.1. Effect of preparation method on catalytic activity

Figure 1 shows the catalytic activities of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by the three methods. It can be seen that the curves of NO conversion are similar. However, it is interesting to note that the catalysts preparation method exerts significant influence on the catalyst performance. The catalyst prepared by a single step so-gel method showed the highest activity and the widest operating temperature window, followed by the co-precipitated catalyst, while the catalyst prepared by the impregnation method showed poor activity. The decrease order of catalytic activities with various preparation methods is as follows: $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) $>$ $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP) $>$ $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM).

3.2. Influence of calcination temperature

It is known that the calcination temperature is one of the factors affecting the catalytic performance. Since the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst showed the highest activity among the three catalysts, the performances of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst calcined at 600, 800, and 1000 °C were investigated and the results are presented in figure 2. As the calcination temperature increases from 600 to 800 °C, the maximum NO conversion decrease slightly. When the catalyst calcined at 1000 °C, the maximum NO conversion decreases significantly and the operation temperature window shifts to the higher temperature range. The curves of propene conversion shifted to high temperature reign with increasing the calcinations temperature from 600 to 1000 °C. The maximum NO conversion on the 1000 °C calcined catalyst decreased by 30% compared to the one calcined at 600 °C. Therefore, the optimum calcination temperature of 600 °C is suggested for the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst.

3.3. Effect of H_2O and SO_2

Figure 3 shows the effects of H_2O and SO_2 on the activities of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by the three methods. Figure 3(a,b,c) are the results on $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$

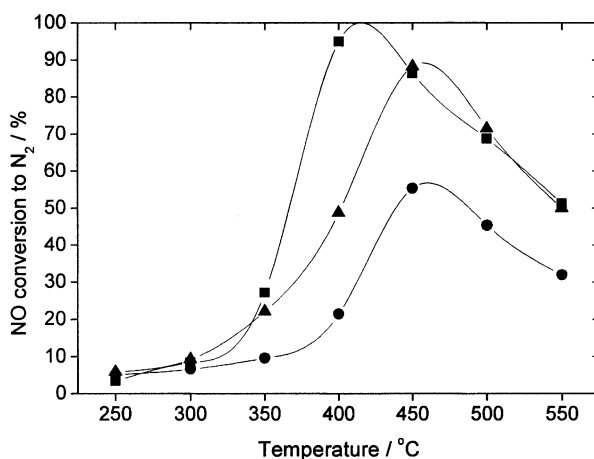


Figure 1. Effect of preparation method on the activity of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst for the NO reduction by propene. (■) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG); (▲) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP); (●) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM). Reaction conditions: 1000 ppm NO, 1000 ppm C_3H_6 , 8% O_2 , He as balance, $W/F = 0.1 \text{ g s cm}^{-3}$.

(SG), (CP), and (IM), respectively. It can be seen that there are some similarities in the NO conversion curves in the absence and also in the presence of H_2O and SO_2 . For example, when H_2O and SO_2 were introduced to the reactant gas mixture, the maximum NO conversion

decreased and the operation temperature window shifted to the higher temperature range.

However, as for the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) (figure 3(a)), when 10% H_2O was added to the reaction gas, the maximum NO conversion decreased slightly over the entire temperature range, although the peak temperature shifted to 450 °C. Furthermore, the presence of H_2O and SO_2 inhibited the catalytic activity in some extent, the maximum NO conversion decreased to 76% in the presence of H_2O and SO_2 . The effects of H_2O and SO_2 over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM) are similar to that of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG), the maximum NO conversion decreases by 20% after introducing H_2O and SO_2 . Although H_2O and SO_2 have an inhibition effect over all three catalysts, this effect is more pronounced for $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP) catalysts. The maximum conversion decreased to 67% (from 89%) in the presence of H_2O , and only about half of the maximum conversion was observed in the presence of both H_2O and SO_2 . In comparison, $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst shows much higher resistance against H_2O and SO_2 than $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP). More interestingly, an enhancement effect was observed at the lower temperature of 250–350 °C over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst. The addition of H_2O to the feed leads to the inhibition of C_3H_6 conversion and the inhibition becomes more serious in the co-presence of SO_2 and H_2O for the three catalysts (not shown here).

3.4. Effect of O_2

Figure 4 shows the NO conversions with respect to O_2 concentration at 400 °C over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG), (CP), and (IM) catalyst. For all three catalysts, little NO conversion to N_2 was observed in the absence of oxygen, but NO conversion increased sharply with the increase in oxygen concentration up to 2%. With the O_2 concentration increase from 2% to 10%, NO conversion increased over all catalysts, especially for the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst. The maximum NO conversion

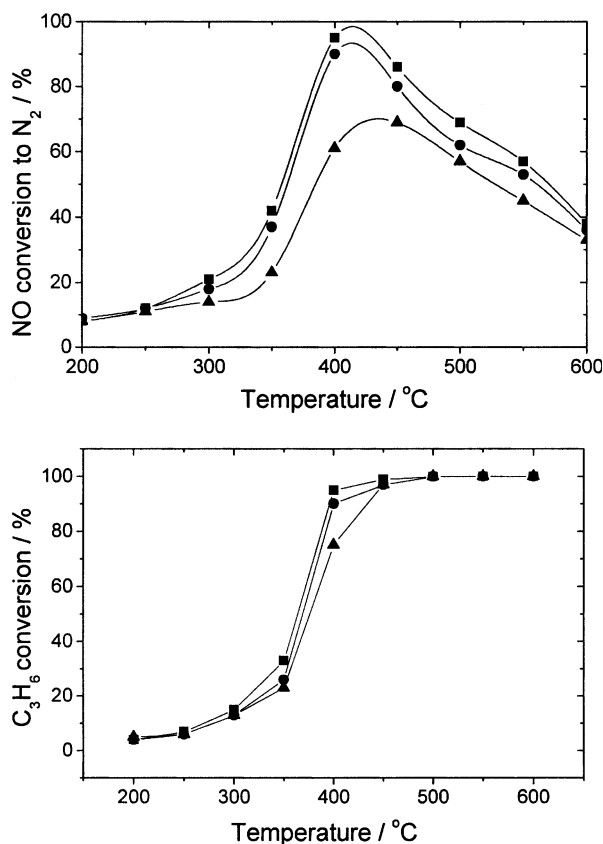


Figure 2. Effect of calcination temperature on the performance of the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst. (■) 600 °C; (●) 800 °C; (▲) 1000 °C. Reaction conditions: 1000 ppm NO, 1000 ppm C_3H_6 , 8% O_2 , He as balance, $W/F = 0.1 \text{ g s cm}^{-3}$.

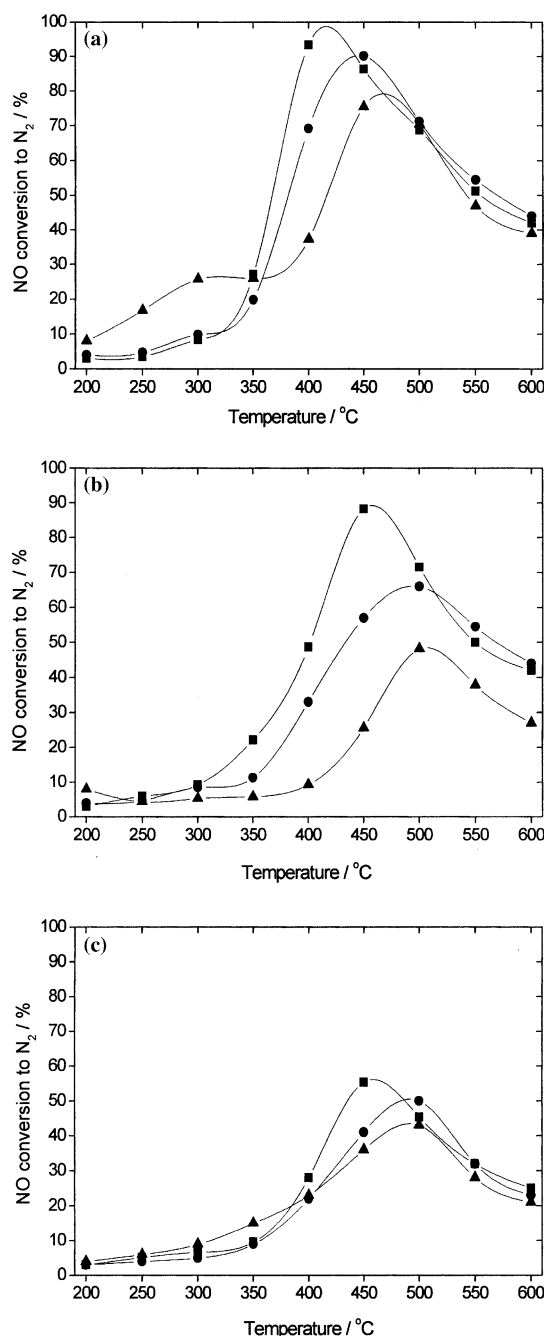


Figure 3. NO conversion as a function of temperature over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by different methods under various reaction conditions. (a) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG), (b) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP), (c) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM). (■) without H_2O and SO_2 ; (●) with 10% H_2O and without SO_2 ; (▲) with 10% H_2O and 100 ppm SO_2 .

reached nearly 100%, which is higher than those measured for the other preparation methods. These results indicate that the oxygen plays a key role in the selective catalytic reduction of NO by propene. Oxygen could 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.

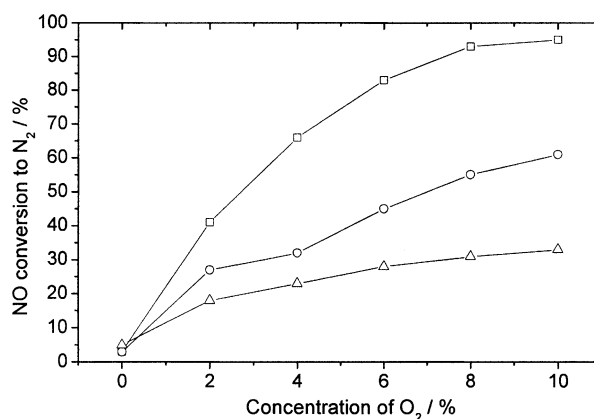


Figure 4. Effect of O_2 concentration on the activities of catalyst prepared by the different methods. Reaction temperature at 400 °C. (□) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG); (○) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP); (△) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM). Reaction conditions are the same as in figure 1 except for the O_2 concentration.

3.5. Comparison of reactivity between NO and NO_2

The most active $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst was further tested in the reaction system of $\text{NO}-\text{C}_3\text{H}_6-\text{O}_2$ and $\text{NO}_2-\text{C}_3\text{H}_6-\text{O}_2$. Figure 5 shows the results of NO_x conversion for NO and NO_2 both in the absence and in the presence of H_2O and SO_2 . Comparing the reactivities of NO and NO_2 , we found that the reactivity of NO_2 was much higher than that of NO, especially below the maximum NO reduction temperature of 450 °C. The propene conversion was also enhanced considerably by using NO_2 instead of NO.

In the presence of H_2O and SO_2 , the catalytic activity of NO_2 was also much higher than that of NO. As for $\text{C}_3\text{H}_6-\text{NO}_2-\text{O}_2$, the maximum NO_2 conversion is still above 90%, although the NO_2 conversion decreased at the temperature range of 300–450 °C in some extent. In comparison, for the $\text{C}_3\text{H}_6-\text{NO}-\text{O}_2$ reactant mixture, the maximum NO conversion decreased from 95 to 76%, although the reduction activity increased slightly over the low temperature range. The propene oxidation in each reaction system was decreased considerably in the presence of H_2O and SO_2 , indicating that they inhibited mainly the procedure of active propene to the key intermediates.

4. Discussion

The physical properties of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by three methods are summarized in table 1. It can be seen that the surface areas of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ prepared by sol-gel method and co-precipitation method are both higher than that of impregnation, and the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst have the largest surface area while the surface area of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM) is the lowest. The average pore diameter of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) is the smallest among the three catalysts studied. From the

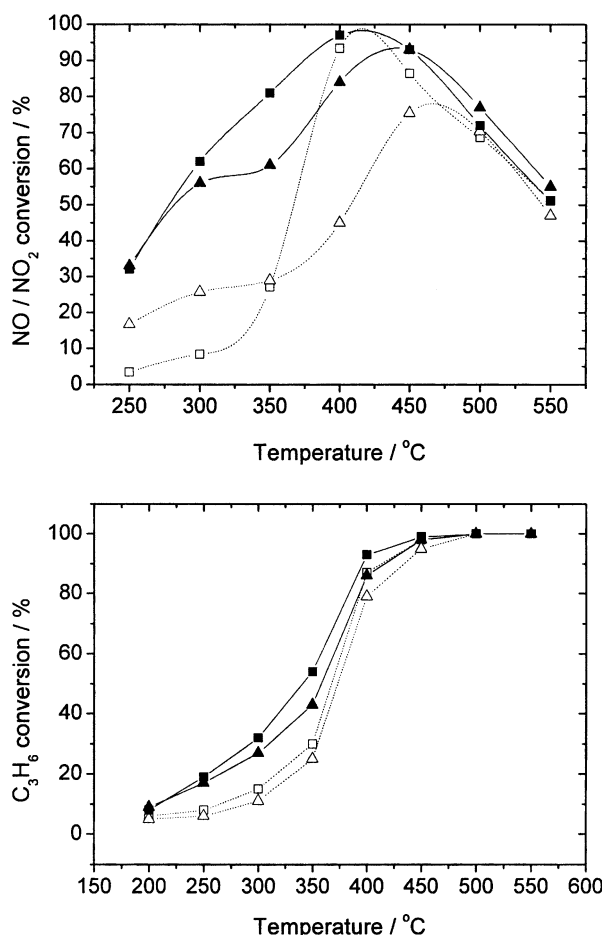


Figure 5. Comparison of reactivity between NO and NO_2 for the selective reduction over $\text{In}/\text{Al}_2\text{O}_3$ in the absence or presence of 10% H_2O and 100 ppm SO_2 . Reaction gas: 1000 ppm NO (or NO_2), 1000 ppm C_3H_6 , 8% O_2 , He as balance, $\text{W}/\text{F} = 0.1 \text{ g s cm}^{-3}$. (■□) without H_2O and SO_2 , (▲△) with 10% H_2O and 100 ppm SO_2 . (□△) $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$, (■▲) $\text{NO}_2 + \text{C}_3\text{H}_6 + \text{O}_2$

results of activities for NO reduction (see figure 1), the decrease order of catalytic activities is in accordance with the order of the surface area. Haneda and his colleagues reported that the high surface area accounted for the high catalytic activity of $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst prepared by the sol-gel method for NO reduction with C_3H_6 [19]. We suggest that the high activity of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst was also due to the large surface area compared with other catalysts prepared by CP and IM methods.

Figure 6 shows XRD patterns of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by three methods. As for the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$

(SG) and $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP), only the characteristic lines of $\gamma\text{-Al}_2\text{O}_3$ can be observed. In comparison, the peaks assigned to In_2O_3 were determined on the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM) catalyst. The mainly reason is due to the catalyst preparation methods. For the sol-gel and co-precipitation methods, the active component In_2O_3 are highly dispersed in the bulk of Al_2O_3 support, so the crystallite size were too small or too disordered to be detected by XRD. On the contrary, the In_2O_3 was probably dispersed on the surface of the catalyst which prepared by impregnation method, and the In_2O_3 contents on catalyst surface is enough to be detected by XRD.

Figure 7 shows the XRD patterns of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst calcined at different temperature (500, 600, 700, 800, and 1000 °C), respectively. It is obvious that the XRD peak intensities of the catalyst increase with the increasing calcination temperature, and only the diffraction peaks attributed to $\gamma\text{-Al}_2\text{O}_3$ are observed at the calcination temperatures below 800 °C. When the catalyst was calcined at 1000 °C, the In_2O_3 peaks are detected due to the increase in crystallite size. Table 2 summarizes the surface area and average pore diameter for various calcination temperatures of the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst. With the increase of calcination temperature, the surface area decreases, while the average pore diameter increases. As shown in figure 2, the NO conversion decreases with increasing calcination temperature, in accord with the physical structure parameters change of the catalyst. It is evident that the high surface area and low average pore diameter are crucial to the catalytic activity.

Surface structures of the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst were analyzed by XPS and the results are shown in figure 8. A binding energy of 444.7 eV was measured for In $3d_{5/2}$ of sample $\text{In}/\text{Al}_2\text{O}_3(\text{SG})$, which is in good agreement with the value of 444.4 eV reported for indium in In_2O_3 [20]. Indium at the catalyst surface should be in the In_2O_3 bulk phase in accordance with the conclusion drawn from the XRD patterns shown previously.

Figure 9 illustrates TPD profiles of NO and NO_2 obtained on the catalysts prepared by the three methods. All three catalysts show similar TPD profiles in which two distinct desorption peaks of NO are observed. The first peak is centered at about 200 °C and the second one is about 450 °C. The former peak might be due to the decomposition of nitrite species (ad-NO_2^-)[21]. The desorption of O_2 accompanied with the desorption of NO_2 was observed at the high temperature above 350 °C

Table 1
Physical properties of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts prepared by different methods (calcinated at 600 °C)

Catalysts	BET surface area/ $\text{m}^2 \text{ g}^{-1}$	Pore volume/ $\text{cm}^3 \text{ g}^{-1}$	Average pore diameter/nm	BET surface area/ $\text{m}^2 \text{ g}^{-1}$ (spent)
$\text{In}/\text{Al}_2\text{O}_3$ (SG)	264	0.416	4.10	233
$\text{In}/\text{Al}_2\text{O}_3$ (CP)	208	0.375	6.83	179
$\text{In}/\text{Al}_2\text{O}_3$ (IM)	156	0.235	6.16	138

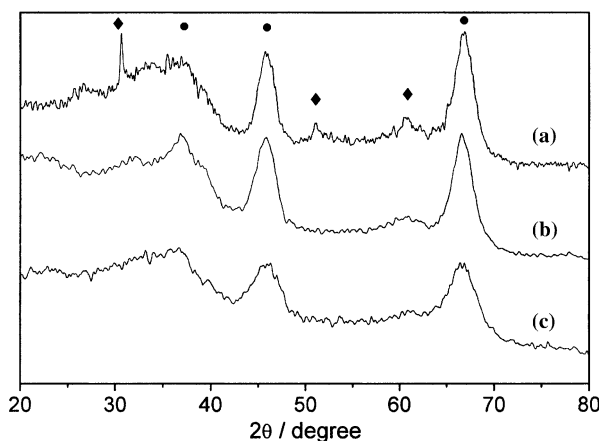


Figure 6. XRD patterns of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst prepared by different methods. (a) IM; (b) SG; (c) CP; (◆) In_2O_3 phase; (●) Al_2O_3 phase.

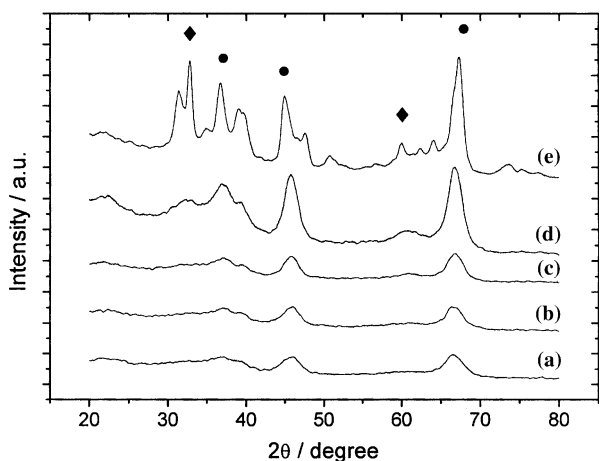


Figure 7. XRD spectra of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) with various calcinations temperatures (◆) In_2O_3 , (●) Al_2O_3 . (a) 500 °C; (b) 600 °C; (c) 700 °C; (d) 800 °C; (e) 1000 °C.

in our previous work [22]. It is noted that the NO ad-species (ad-NO_3^-) decompose to NO_2 and O_2 at high temperature range. Since ad-NO_3^- species formed on the catalyst surface is known to play an important role in NO reduction [21,22], ad-NO_3^- species desorbed above 350 °C are presumed to participate in NO reduction reaction. Based on the different preparation method, the intensities of NO desorption peak are also different, and

Table 2

Specific area of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalysts calcined with various temperatures

Calcined temperature / °C	Specific area / $\text{m}^2 \text{g}^{-1}$	Average pore diameter/nm
500	268	3.6
600	264	4.1
700	215	4.2
800	197	4.7
1000	106	7.4

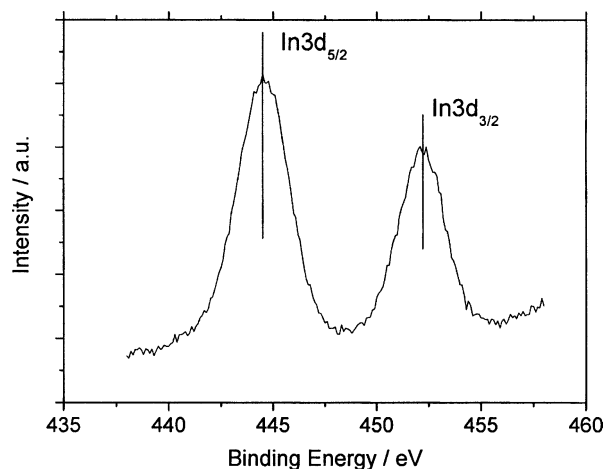


Figure 8. The XPS of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst.

the decrease order of the amount of NO_2 desorption is in accordance with the catalytic activity and the surface area of the catalysts, $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) > $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP) > $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM).

In order to investigate the key intermediate species and reaction mechanism of the NO_x reduction over $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst, we carried out experiments using in situ DRIFTS. Figure 10 shows the IR spectra of the $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst in the flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ in a steady state at various temperatures. Based on previous study [23,24], the bands in figure 10 are assigned to bands of adsorbed nitrates (1300 and 1580 cm^{-1}), formate and acetate (1380 , 1458 cm^{-1}), and adsorbed hydrocarbons C_3H_6 (2904 cm^{-1}), respectively. It is apparent that the NO_3^- and COO^- are the mainly intermediate species. The appearance of adsorbed NO_3^- species was observed even in the room temperature, and decreased with the temperature increases, and was negligible above 450 °C . However, the intensity of acetate species was not detected at low temperature, and it obviously decreased as the temperature increases. It is indicated that the active C_3H_6 to partially oxidized hydrocarbons (RCOO^- species) maybe the key reaction process. The $-\text{NCO}$ on $\text{Ag}/\text{Al}_2\text{O}_3$ is an important reaction intermediate during the SCR of NO by C_3H_6 [24], while the formation of $-\text{CN}$ (2140 cm^{-1}) and $-\text{NCO}$ (2240 cm^{-1}) species was not evidenced on $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG). Possibly, NO_3^- species formed on $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ serves as a strong oxidant for C_3H_6 .

As shown in figure 5, replacing NO with NO_2 in the feed increased the N_2 yield. The fact proved that the oxidation of NO to NO_2 plays an important role for the NO reduction, the influence of oxygen concentration on the NO conversion further explain the important role of NO oxidation to NO_2 (see figure 4). These experimental results indicate that NO_2 is more reactive than NO , and the NO oxidation into NO_2 may be one of limiting factors in NO reduction. As a result, NO_2 is

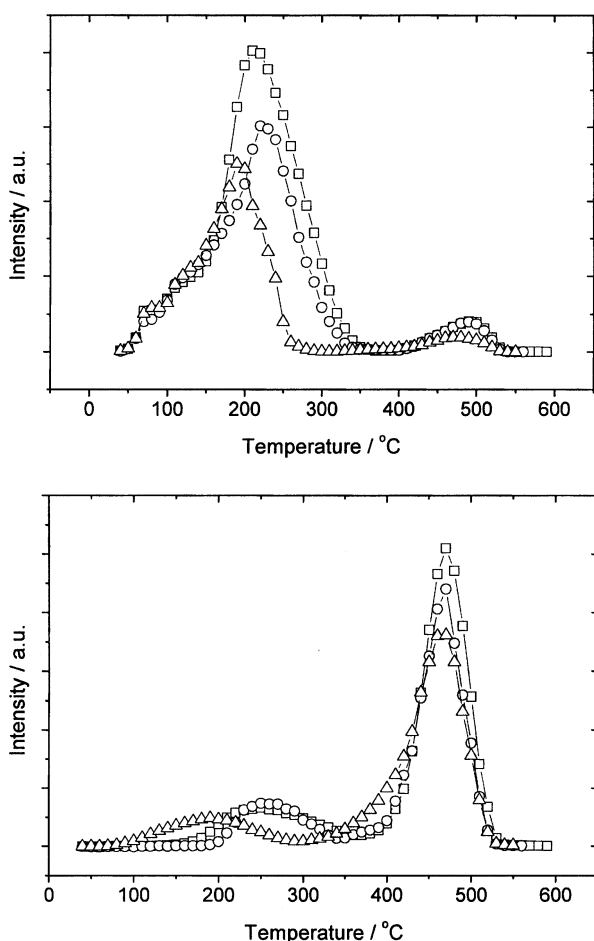


Figure 9. TPD profiles of NO and NO_2 on $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst prepared by different methods. (a) TPD of NO, (b) TPD of NO_2 , (\square) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG); (\circ) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (CP); (\triangle) $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (IM).

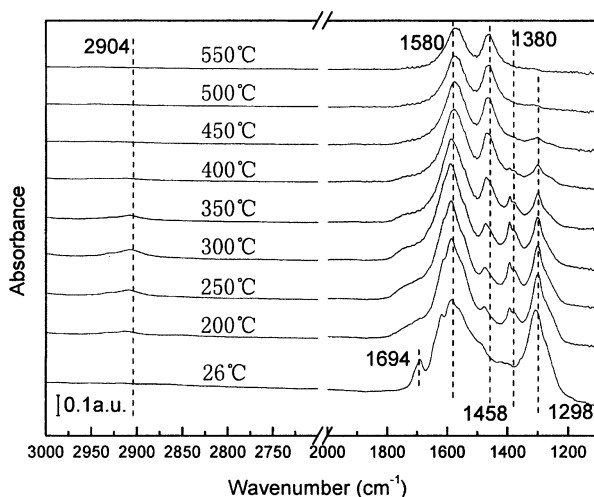


Figure 10. *In-situ* FT-IR spectra of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) during the SCR of NO_x at various reaction temperatures. (Gas composition: 1000 ppm NO, 1000 ppm C_3H_6 , 8% O_2 , N_2 as balance).

more quickly react with the surface of the catalyst to form ad-NO_3^{-1} species which have been proposed as key intermediates in the reaction [25,26].

The inhibition of H_2O on the catalytic activity is probably due to its competitive adsorption with NO and C_3H_6 on the active sites of catalyst, so the propene oxidation curves in all the reaction system are decreased slightly in the presence of H_2O and SO_2 (see figure 5). The inhibition effect of SO_2 on the catalytic activity for NO reduction by hydrocarbons has been reported for many alumina-based catalysts [12,27], the negative effect of SO_2 is due to the formation of SO_4^{2-} species on the catalyst, it maybe $\text{In}_2(\text{SO}_4)_3$ and $\text{Al}_2(\text{SO}_4)_3$ formed on the catalyst surface. The influence is the poisoning of NO adsorption sites on which NO reduction proceeds. In order to acquire the information of sulfur on the spent catalyst (after the reaction of NO reduction in the presence of 10% H_2O and 100 ppm SO_2), the S2p spectra of spent $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst is shown in figure 11. The results showed that the sulfur in the surface mainly exists as sulfate. The formation of SO_4^{2-} species on the catalyst cause the surface areas of the catalysts decrease (see table 1). It is of interest that the reduction activity enhanced slightly on $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) at the lower temperature; Haneda et al. proposed that the initial activity increase for the C_3H_6 -SCR of NO in the presence of SO_2 could be assigned to the creation of Brönsted acid site on which propene activation is promoted [28].

The $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst prepared by sol-gel method shows high activity, moreover, it shows better tolerance to water vapour and SO_2 than those of catalysts prepared by IM or CP method (see figure 3). These are due to high dispersion of active component In_2O_3 on the large surface area, which is associated with high activity and stability. It is evident that there was strong interaction between indium and alumina for In_2O_3 - Al_2O_3 catalyst prepared by sol-gel method. The adsorption of H_2O and SO_2 on the surface of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst were to be suppressed in comparison to the other two catalyst preparation, this way explain why NO

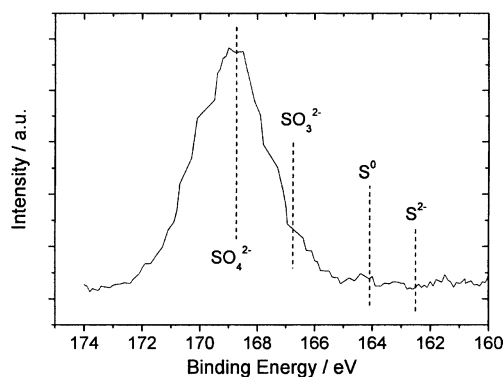


Figure 11. S 2p XPS spectra of $\text{In}_2\text{O}_3/\text{Al}_2\text{O}_3$ (SG) catalyst.

reduction is less affected by the presence of H_2O and SO_2 .

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