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Selective catalytic reduction of NO_x with propene over SnO_2/Al_2O_3 catalyst

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ABSTRACT

Selective catalytic reduction of NO_x with propene has been investigated over SnO_2/Al_2O_3 catalysts prepared by impregnation and single step sol–gel methods. Catalyst preparation method exerts significant influence on the catalytic performance, and SnO_2/Al_2O_3 prepared by the sol–gel method is more active than the impregnated catalyst. Moreover, its resistance against water is higher. The high surface area and the strong interaction between SnO_2 and Al_2O_3 may be responsible for the high reduction activity of sol–gel SnO_2/Al_2O_3 catalyst. The presence of oxygen strongly favours the NO_x reduction process. FT-IR results have revealed that the role of oxygen is to contribute to the formation of formate, acetate and nitrate species, all of which are reactive intermediates for NO_x reduction.

1. Introduction

The control of NO_x emission from diesel engine and lean-burn gasoline engine remains to be one of the greatest challenges in environmental catalysis since the conventional three-way catalysts are no longer effective to reduce NO_x under lean-burn conditions. Selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) has become one of the most promising way to solve this problem [1,2] since Held et al. [3] and Iwamoto and Hamada [4] first reported that hydrocarbons could be used to reduce the pollutant NO_x to N_2 in the presence of oxygen.

A variety of effective catalysts, such as metal-exchanged zeolites [4–6], noble metals [7,8] and metal oxide [9,10] catalysts have been investigated so far. Among them the metal oxide catalysts have attracted attention due to their high activities and hydrothermal stabilities. The catalytic activity and selectivity of this type of catalyst are well known to depend strongly on the method of preparation [11,12]. For example, a Ga_2O_3–Al_2O_3 catalyst prepared by sol–gel method showed higher activity than that prepared by impregnation method [13].

SnO_2/Al_2O_3 has appeared to be a promising catalyst for the lean NO_x reduction [14–16]. Park et al. [15] compared the activities of SnO_2/Al_2O_3 catalysts prepared by impregnation and sol–gel methods and found that the catalyst prepared by impregnation method is more active. However, the compared catalysts were of different Sn loading and prepared with different Sn precursors, both of which also affect the performance of lean-NO_x catalyst [11,16,17]. Therefore, the effect of preparation method on the activity of SnO_2/Al_2O_3 catalyst cannot be found exactly. In the present study, we investigated the effect of preparation method on the catalytic performance of SnO_2/Al_2O_3 catalyst in detail and found that the catalyst prepared by sol–gel method is more active. The effects of reducing agent type and oxygen concentration on the activity of sol–gel SnO_2/Al_2O_3 catalyst were also studied. On the basis of in situ IR experiments, the mechanistic cause of the promoting effect of oxygen for NO_x reduction was elucidated.

2. Experimental

2.1. Catalyst preparation

SnO_2/Al_2O_3 catalysts were prepared by impregnation [abbreviated as Sn(IM)] and single step sol–gel [abbreviated as Sn(SG)] methods. 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 proper amount of nitric acid. Then a proper amount of $SnCl_4$ dissolved in ethanol was incorporated into the sol. After 1 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 700 °C for 4 h in air. Sn(IM) was prepared by impregnating the Al_2O_3 powder with an amount of $SnCl_4$ dissolved in ethanol, followed by drying at 120 °C and calcinations at 700 °C for 4 h in air. Alumina powder used here was synthesized from aluminium boehmite sol described

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above. The catalysts were designed by SnX, where X denotes the Sn loading (wt.%).

2.2. Catalytic tests

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, 1000 ppm C_3H_6 or C_3H_8, 0–12% O_2 and helium as the balance gas. The total flow rate of the feed gas was 300 $cm^3 min^{-1}$, corresponding to a GHSV of 32,000 h^{-1}. In order to investigate the effects of H_2O and SO_2 on the activities of SnO_2/Al_2O_3 catalysts, 10% H_2O and/or 100 ppm SO_2 was introduced into the reaction gas mixture. Water was added to the reaction gas by a micropump and removed in a condenser before the gas composition analysis. The reaction temperature was increased from 250 °C to 600 °C in steps of 50 °C.

The composition of the product gas was analyzed by using gas chromatograph (Shimadzu GC 17A equipped with Porapak Q and Molecular sieve 5A columns) and a chemiluminescence NO/NO_2 analyzer (Thermal environmental instruments, model 42C). 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 at each temperature. The formation of N_2O was found negligible (<10 ppm) and for this reason this product will not be further discussed. Selective catalytic reduction of NO_x rather than C_3H_6 combustion (S_{SCR}) was calculated as follows: S_{SCR} = [(moles of N_2 formed)/(moles of C_3H_6 converted)] × 100% [18].

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 Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a surface system (LHS-10, SPECS GmbH) equipped with a multi-plate channel detector using Mg Kα radiation. Binding energy was referenced to C 1s at 284.5 eV.

2.4. FT-IR measurements

In situ FT-IR spectra were acquired using an in situ cell installed in a Nicolet Magna 560 FT-IR spectrometer with a MCT detector. Prior to each experiment, the catalyst was pressed into a self-supported disc and pretreated in 3% O_2/He at 400 °C for 1 h, followed by cooling to the desired temperature before taking a reference spectrum. A gas mixture was then fed into the cell at a flow rate of 25 $cm^3 min^{-1}$. The concentrations of NO, C_3H_6 and O_2 in the gas mixture were 2000 ppm, 2700 ppm and 3%, respectively. All spectra reported here were taken at a resolution of 4 cm^{-1} for 100 scans.

3. Results and discussion

3.1. Effect of Sn loading and preparation method

Fig. 1 shows the catalytic activities of SnO_2/Al_2O_3 catalysts prepared by the two different methods in the absence of H_2O and SO_2. For the Sn(IM) catalyst, the Sn1(IM) catalyst shows the lowest NO conversion activity below 500 °C. Increasing Sn loading to 5% results in a dramatic increase in activity with a peak NO conversion of 55% occurring at 450 °C. When the Sn loading was further increased, no more improvement of maximum NO_x conversion was observed, but the temperature window for NO reduction shifted to a lower temperature region. Kung et al. [14] also found that the N_2 yield increased sharply from 1% to 5% Sn loading, but beyond that the temperature window does not shift to a lower temperature region and the NO_x conversion was even declined as Sn loading reached 15%. The difference could be ascribed to the different test conditions. In their research, the activity measurement is conducted in the presence of water and the oxygen concentration is higher.

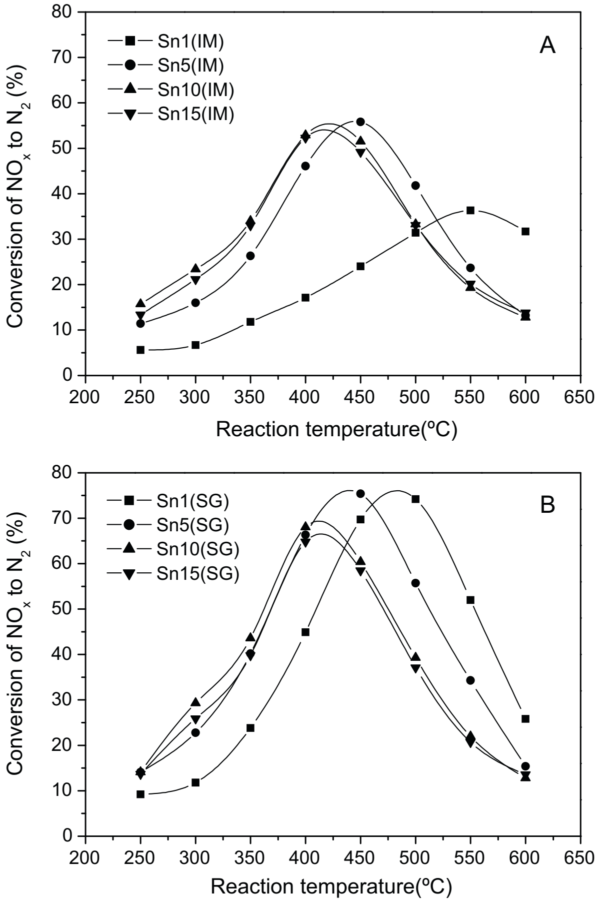

Fig. 1. The effect of Sn loading on the activities of Sn(IM) (A) and Sn(SG) (B) catalysts for NO_x reduction with propene in the absence of H_2O and SO_2. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 8%, GHSV = 32,000 h^{-1}.

Compared with the Sn (IM) catalysts, the activities of Sn (SG) catalysts are much higher for the same Sn loading over a wide range of Sn content (1–15%). Over the Sn5(SG) catalyst, the maximum NO conversions is 75%, which is much higher than that obtained over Sn5(IM) catalyst. Therefore, the catalyst preparation method exerts significant influence on the catalytic performance of SnO_2/Al_2O_3 catalyst. Based on the above results of the catalytic activities of SnO_2/Al_2O_3 with various Sn loading, we focused on the Sn5 catalyst in the following study.

Besides the activity, the selectivity S_{SCR} is also important because higher selectivity means the utility of the reducing agent is effectively improved and less additional reducing agent needs to be injected in practical application. It can be seen that the selectivity of propene over Sn5(SG) catalyst is noticeably higher than that over Sn5(IM), especially in the low temperature range (see Fig. 2). For the two catalysts, the similarity is that the selectivity decreases with increasing reaction temperature. At high temperatures, the unselective combustion of propene becomes predominant, resulting in the low selectivity.

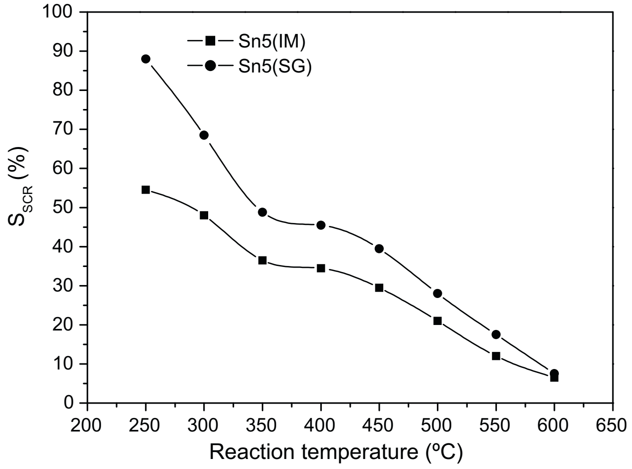

Fig. 2. The effect of preparation method on the S_{SCR} of Sn5 catalysts for NO_x reduction with propene in the absence of H_2O and SO_2. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 8%, GHSV = 32,000 h^{-1}.

3.2. Effects of H_2O and SO_2

A high resistance against H_2O and SO_2 is required because they are typically present in exhaust gases. Fig. 3 illustrates the effect of H_2O on the activities of differently prepared SnO_2/Al_2O_3 catalysts. Both the windows were shifted to higher temperatures due to the presence of H_2O. Competitive adsorption between H_2O and reactant on the catalyst surface was suggested to result in a decrease of the catalytic activity and a shift of activity window to high temperatures [19,20]. Compared with Sn5(IM), only a minor inhibition effect was observed on Sn5(SG) catalyst, over which the shift of temperature window is to a less degree and the maximum NO_x conversion is about 74%. It is evident that Sn5(SG) is more active than Sn5(IM) below 500 °C in the presence of H_2O. In the case of Sn5(IM) catalyst, an increase in the catalytic activity above 450 °C due to the presence of H_2O can be observed. One reason could be that the unselective combustion of propene was suppressed by H_2O, resulting in more reducing agent available for the NO_x reduction [21]. The coexisting H_2O also promotes the removal of carbonaceous materials covering the catalytically active sites [22], thus showing a promoting effect.

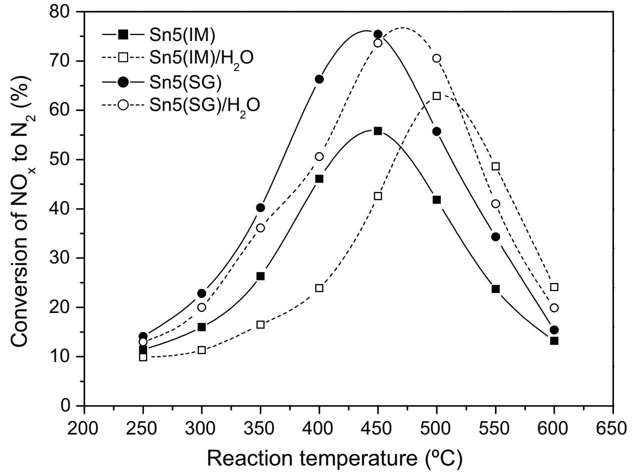

Fig. 3. The effect of H_2O on the activities of Sn5(IM) and Sn5(SG) catalysts: (full lines) in the absence of 10% H_2O and SO_2; (dotted lines) in the presence of 10% H_2O. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 8%, H_2O = 0 or 10%, SO_2 = 0 or 100 ppm, GHSV = 32,000 h^{-1}.

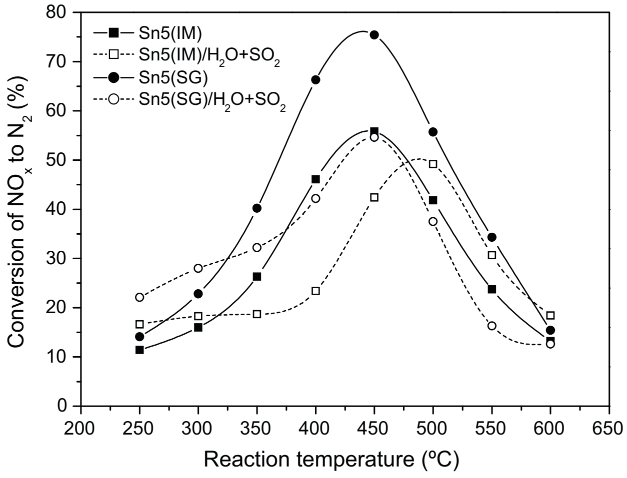

Fig. 4. The effects of H_2O and SO_2 on the activities of Sn5(IM) and Sn5(SG) catalysts: (full lines) in the absence of 10% H_2O and SO_2; (dotted lines) in the presence of 10% H_2O and 100 ppm SO_2. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 8%, H_2O = 0 or 10%, SO_2 = 0 or 100 ppm, GHSV = 32,000 h^{-1}.

The catalytic activities of the two catalysts in the co-presence of H_2O and SO_2 were further examined and the results are shown in Fig. 4. It can be seen that both the activities of the two catalysts are seriously suppressed. But Sn5(SG) is still more active than Sn5(IM). It is worthy to note that the reduction activities of the two catalysts were enhanced slightly in the co-presence of H_2O and SO_2 than those in the presence of H_2O below 350 °C (see Fig. 3). The initial activity increase due to the presence of SO_2 could be attributed to the creation of Brönsted acid site on which propene is more easily activated [23], which contributes to the NO_x reduction to proceed [2]. Above 350 °C, the NO_x conversion over Sn5(SG) was lower than that only in the presence of H_2O. The reason is that the present SO_2 would adsorb on the catalyst surface and form $SO_4{}^{2-}$ species [24]. The sulfation leads to a decrease in the number of sites available for the nitrate species to adsorb and hence in the number of adsorbed nitrate species with which propene derivate species can react. As a result, the NO_x reduction activity decreased. Considering the fact that Sn5(SG) is more active, we will focus on this catalyst in the following study.

3.3. Effect of reducing agent

Previous studies showed that the nature of reducing agent can affect the activity of metal oxide catalyst [2]. Here we compare the abilities of propene and propane to reduce NO_x over Sn5(SG) catalyst and the results are illustrated in Fig. 5. It is evident that the efficiency of propane to reduce NO_x is extremely low. The activity of Sn5(SG) is almost lost below 400 °C. Even the temperature is up to 550 °C, the peak NO_x conversion is only 25%, which is much lower than that (75%) obtained in the case of propene as a reducing agent. From the conversion curve of C_3H_8, it can be seen that C_3H_8 can be activated only above 400 °C. Although the C_3H_8 conversion reaches 63% at 550 °C, the NO_x conversion is still low (25%), indicating that C_3H_8 is not a selective reducing agent for NO_x reduction over Sn5(SG) catalyst. Iliopoulou et al. [25] found that over Ag/Al_2O_3 catalyst propene was more efficient than propane, but the difference between the peak NO_x conversions was much less (48.5% vs 42.7%) and the activity temperature window just shifted to high temperature by about 30 °C in the case of propane as reducing agent instead of propene. These facts suggest that the type of reducing agent is more critical for SnO_2/Al_2O_3 catalyst.

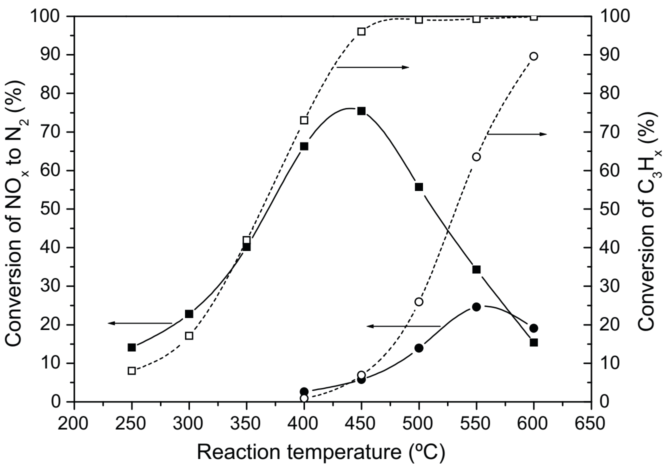

Fig. 5. The effect of reducing agent on the activity of Sn5(SG) catalyst. (■, □) C_3H_6; (●, ○) C_3H_8. Reaction conditions: NO = 1000 ppm, C_3H_6 or C_3H_8 = 1000 ppm, O_2 = 8%, GHSV = 32,000 h^{-1}.

3.4. Effect of oxygen concentration

A noticeable character of the exhaust emitted from diesel engine and lean-burn gasoline engine is that it contains much higher O_2 than that emitted from stoichiometric engine. Thus the effect of oxygen on the activity of Sn5(SG) catalyst was further investigated and the results are shown in Fig. 6. Interestingly, little NO_x conversion to N_2 was observed in the absence of oxygen, but NO_x conversion increased significantly with the oxygen concentration up to 4%. With the O_2 concentration further increasing from 4% to 8%, the maximum NO_x conversion was increased from 58% to 75% and the temperature window was broadened as well. More importantly, the low-temperature activity was noticeably enhanced. A slight increase still can be observed even O_2 concentration increased from 8% to 12%. These facts suggest that the presence of O_2 did not inhibit NO_x reduction but promote it. This observation is different from the previous report [9], where it was found that the NO_x conversion was decreased beyond the optimum partial pressure of 4%.

3.5. Catalysts characterization

Table 1
The specific surface areas of two different SnO_2/Al_2O_3 catalysts.

Catalyst	Surface area ($m^2\ g^{-1}$)
Sn5(IM)	154
Sn5(SG)	186

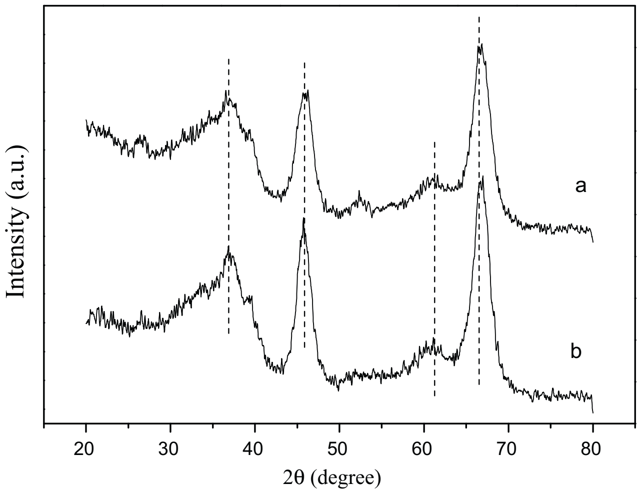

Fig. 7. XRD patterns of the two different SnO_2/Al_2O_3 catalysts. (a) Sn5(IM); (b) Sn5(SG); γ-Al_2O_3: dash line(- - -).

The specific surface areas of two different SnO_2/Al_2O_3 catalysts are summarized in Table 1. It can be seen that the surface area of Sn5(SG) is higher than that of Sn5(IM) catalyst. The high specific surface area contributes to the adsorption of NO_x [13] thus showed high activity. Haneda et al. [13] also attributed the higher activity of Ga_2O_3–Al_2O_3 catalyst prepared by sol–gel method than that of the impregnated Ga_2O_3/Al_2O_3 to its higher surface area.

Fig. 7 shows the XRD patterns of two different SnO_2/Al_2O_3 catalysts. Only the peaks assigned to γ-Al_2O_3 [10] can be observed. The peak ascribed to SnO_2 [15] was not observed, suggesting that SnO_2 species are highly dispersed on Al_2O_3. Fig. 8 illustrates the Sn $3d_{5/2}$ XPS spectra of Sn5(SG) catalyst. It can be seen that the binding energy is 487.2 eV, which is ascribed to Sn^{4+} [26]. Previous study showed that Sn^{4+} was active for the reduction of NO_x [15].

3.6. FT-IR studies

As described above, the presence of oxygen is favourable for the reduction of NO_x. In order to elucidate the promoting effect

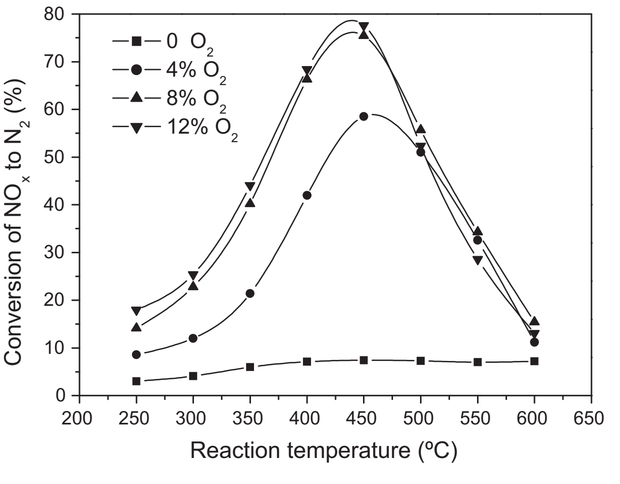

Fig. 6. The effect of O_2 on the NO_x reduction activity of Sn5(SG) catalyst. Reaction conditions: NO = 1000 ppm, C_3H_6 = 1000 ppm, O_2 = 0–12%, GHSV = 32,000 h^{-1}.

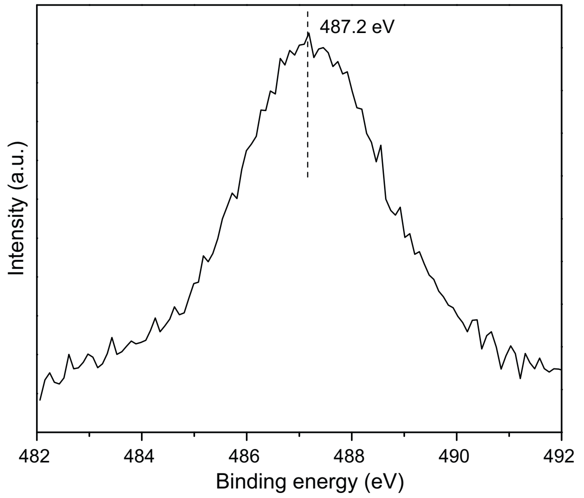

Fig. 8. Sn $3d_{5/2}$ XPS spectra of Sn5(SG) catalyst.

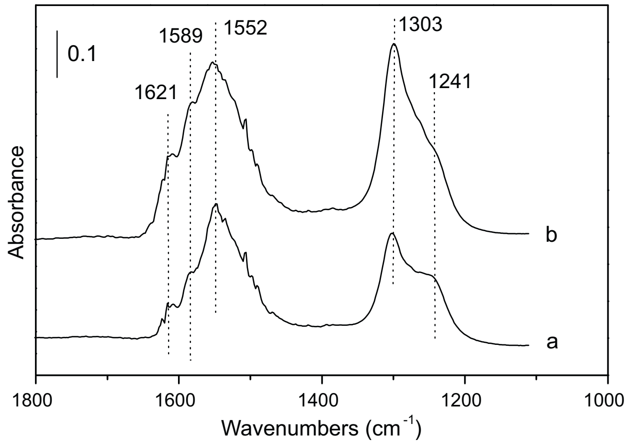

Fig. 9. IR spectra of adsorbed nitrate species over Sn5(SG) catalyst in the absence (a) and presence (b) of oxygen at 300 °C. Conditions: NO = 2000 ppm, O_2 = 0 or 3%.

of oxygen, the effect of oxygen on the formation of nitrate species and oxygenated hydrocarbon species was investigated. Fig. 9 shows the IR spectra of adsorbed nitrate species over Sn5(SG) catalyst in the absence and presence of oxygen at 300 °C. The main adsorbed species in the flowing of NO or NO + O_2 are monodentate nitrate (1241 and 1552 cm^{-1}), bidentate (1303 and 1589 cm^{-1}) and bridging (1621 cm^{-1}) nitrates [27–29]. By comparing Fig. 9a and b, it is evident that the nitrate peaks are more intense in the case of NO + O_2, indicating that the presence of O_2 promotes the formation of nitrates. Fig. 10 shows the IR spectra of adsorbed oxygenated hydrocarbon species over Sn5(SG) catalyst in the absence and presence of oxygen at 300 °C. In the absence of oxygen, although the peaks at 1376, 1392, 1446, 1474, 1590 and 1670 cm^{-1} can be observed, they appear to be very weak. The peaks at 1446 and 1670 cm^{-1} can be assigned to ν_s(COO) of acrylate [30] and acrolein [31], respectively. The characteristic peak at 1474 cm^{-1} can be assigned to δ_{as} (CH_3) of propionate [32]. The peaks ascribed to formate (1376, 1392 and 1590 cm^{-1}) [33,34] are very weak. These facts indicate that in the absence of oxygen propene is hard to be activated to form oxygenated hydrocarbons. In contrast, in the presence of oxygen the peaks assigned to formate are much higher than those in the absence of oxygen and the acetate peak (1462 cm^{-1}) [35] is noticeably observed. Therefore, the presence of oxygen is necessary for the activation of propene to form formate and acetate species. According to the proposed reaction mechanism [1,2,36], initial formation of intermediate active species (formate and acetate) from partial oxidation of hydrocarbons is the crucial reaction step for NO_x reduction. The activation of hydrocarbon over Sn5(SG) catalyst is difficult in the absence of oxygen. As a result, the NO_x conversion is very low as shown in Fig. 6. The presence of oxygen not only contributes to the activation of propene to form formate and acetate but also contributes to the formation of nitrate species, thus favours the NO_x reduction to proceed. Propane, a saturated hydrocarbon, is hard to be activated even in the presence of oxygen, resulting in very low NO_x conversion.

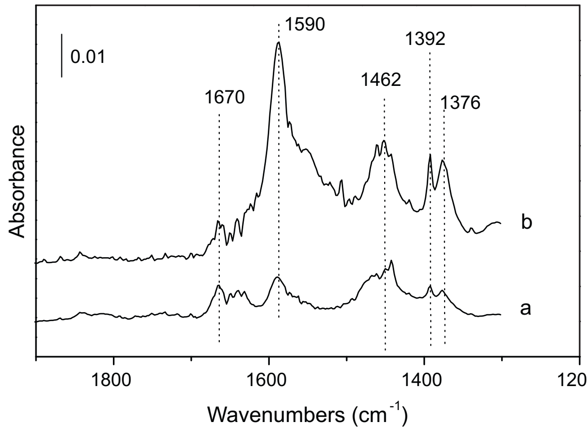

Fig. 10. IR spectra of adsorbed oxygenated hydrocarbon species over Sn5(SG) catalyst in the absence (a) and presence (b) of oxygen at 300 °C. Conditions: C_3H_6 = 2700 ppm, O_2 = 0 or 3%.

Catalyst characterization showed that Sn5(SG) catalyst was of higher surface area. The high specific surface area contributes to the adsorption of NO_x [10] thus showed high activity. Haneda et al. [37] proposed that the strong interaction between the active metal and Al_2O_3 was necessary for the high NO_x reduction activity. Sol–gel technique is one of the most useful methods capable of preparing catalysts with highly dispersed species through the formation of M_1–O–M_2 bonding [22]. Previous research showed that the strong interaction between indium and alumina for In_2O_3/Al_2O_3 prepared by sol–gel method leads to its higher activity than that prepared by impregnation method [38]. In the present study, it is presumed that Sn(SG) catalyst includes a lot of Sn–O–Al bonding at the fringe of catalysts particles. The intimate contact between SnO_2 and Al_2O_3 may be related to the high deNO_x activity of Sn(SG) catalyst.

3.7. Comparison with other lean-deNO_x catalysts

Ag/Al_2O_3 [11,19,25] and Co/Al_2O_3 [39,40] catalysts have been extensively studied for the selective catalytic reduction of NO_x by propene under lean conditions. And their activities were sensitive to the loading of the active metal. For example, the NO_x conversion was decreased from 92% to 38% as the Ag loading of Ag/Al_2O_3 increased from 5% to 9% [11]. High Ag loading produced higher rates of propene combustion with O_2, at the expense of its reaction with NO_x. This is ascribed to the detrimental effect of increasing the particle size of silver oxide entities, yielding reducible entities (Ag^0) with high oxidation activity [19]. The effectiveness of the Co/Al_2O_3 catalyst also depends greatly on the Co loading, best catalytic activity being achieved with relatively low loading (1–2%) [40]. Different from Ag/Al_2O_3 and Co/Al_2O_3 catalysts, the activity of SnO_2/Al_2O_3 catalyst changed to a less degree as the Sn loading increased from 5% to 15% (as shown in Fig. 1). One peculiar characteristic of SnO_2/Al_2O_3 is its poor ability to activate hydrocarbon [15]. So even with high Sn loading, the activity for the combustion of hydrocarbon with O_2 seldom improved. Thus SnO_2/Al_2O_3 still exhibits high NO_x conversion even with the Sn loading up to 15%. High concentration of O_2 contributes to the activation of propene to form the oxygenated hydrocarbons, which were regarded as key intermediates in the selective reduction of NO_x over SnO_2/Al_2O_3 [41]. Therefore, oxygen is essential for NO_x reduction over SnO_2/Al_2O_3 and its activity increased with increasing oxygen concentration even up to 12% (as shown in Fig. 6).

Compared with SnO_2/Al_2O_3, Ag/Al_2O_3 and Co/Al_2O_3 are more active for the activation of hydrocarbon. Over Ag/Al_2O_3 the peak NO_x conversion just slightly decreased with propane used as reductant instead of propene [25]. In the case of Co/Al_2O_3 catalyst, both propene and propane were highly effective for the reduction of NO_x [39]. While over SnO_2/Al_2O_3, significant decrease of NO_x conversion was observed using propane as reductant instead (see Figs. 1 and 5). The type of hydrocarbon reducing agent is also critical for In_2O_3/Al_2O_3 catalyst [42]. And Park et al. [42,43] suggested that the partial oxidation of propene was essential for the promotion of NO_x reduction over this catalyst. FT-IR results described above also showed that the activation of propene to form formate and acetate species is crucial for the NO_x conversion over SnO_2/Al_2O_3 catalyst. Similar to SnO_2/Al_2O_3, high NO_x conversion can be obtained even if the In_2O_3 loading reached 20% in the case of In_2O_3/Al_2O_3 [37].

Therefore, SnO_2/Al_2O_3 and In_2O_3/Al_2O_3, over which hydrocarbon is not easily activated compared with Ag/Al_2O_3 and Co/Al_2O_3, can be classified to a type of lean $deNO_x$ catalyst.

4. Conclusions

SnO_2/Al_2O_3 catalyst prepared by two different preparation methods have been evaluated for the reduction of NO_x under lean conditions and Sn5(SG) is more active than Sn5(IM). The presence of water shows a minor inhibiting effect over Sn5(SG) catalyst while the inhibition effect was noticeable over Sn5(IM). Even in the co-presence of H_2O and SO_2, Sn5(SG) catalyst still showed higher activity. The high activity of Sn5(SG) catalyst may be ascribed to its high surface area and the strong interaction between SnO_2 and Al_2O_3. Compared with propene, propane is not an effective and selective reducing agent for NO_x reduction over SnO_2/Al_2O_3 catalyst. The role of O_2 is to contribute to the formation of hydrocarbon-derived species (formate and acetate) and nitrate species, thus promoting NO_x reduction to proceed.

Acknowledgements

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