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The mechanism of SO_2 effect on NO reduction with propene over In_2O_3/Al_2O_3 catalyst

Chuankui Luo, Junhua Li *, Yongqing Zhu, Jiming Hao

Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Abstract

An In_2O_3/Al_2O_3 catalyst shows high activity for the selective catalytic reduction of NO with propene in the presence of oxygen. The presence of SO_2 in feed gas suppressed the catalytic activity dramatically at high temperatures; however it was enhanced in the low temperature range of 473–573 K. In TPD and FT-IR studies, the formation of sulfate species on the surface of the catalyst caused an inhibition of NO_X adsorption sites, and the absorbance ability of NO was suppressed by the presence of SO_2, and the amount of ad-NO_3^- species decreased obviously. This leads to a decrease of catalytic activity at higher temperatures. However, addition of SO_2 enhanced the formation of carboxylate and formate species, which can explain the promotional effect of SO_2 at low temperature, because active C_3H_6 (partially oxidized C_3H_6) is crucial at low temperature.

Keywords: $DeNO_X$; Selective catalytic reduction; SO_2; In_2O_3/Al_2O_3; Sol–gel method

1. Introduction

Nitrogen oxides are major pollutants in the atmosphere and must 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 engine [1,2]. Indium supported on the zeolite and metal oxide support material has been previously reported to be an active catalyst under lean burn conditions [3–6]. Among them, indium supported on alumina seems to be a promising catalyst for selective catalytic reduction of NO in the presence of oxygen. However, the effect of SO_2 on catalytic activity was seldom investigated. In this study, we investigated the catalytic performance of In_2O_3/Al_2O_3 prepared by the sol–gel method in the absence and presence of H_2O and SO_2, TPD and in situ DRIFTS method were introduced to study the mechanism of SO_2 influence on the formation of some key intermediates.

2. Experimental

5 wt.% In_2O_3/Al_2O_3 catalyst was prepared by a single step sol–gel method which was described in our previous work [7]. Surface areas and pore volumes of the catalyst were 264 $m^2\ g^{-1}$ and 0.416 $cm^3\ g^{-1}$, respectively.

Activity measurements were carried out in a fixed-bed quartz reactor (inner diameter 8 mm) using 0.5 g of catalyst with 60–100 mesh. The feed gas mixture contained 1000 ppm NO, 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 $cm^3\ min^{-1}$. The SO_2-treated catalyst used here is the fresh catalyst pretreated at 873 K for 12 h in a feed of 1000 ppm NO and C_3H_6, 8% O_2, 10% H_2O and 100 ppm SO_2. NO and NO_2 concentration were analyzed with a chemiluminescence NO/NO_2 analyzer (Thermal Environmental, model 42C-HL). Other product gases were analyzed using a Shimadzu GC 17A equipped with Porapak Q and Molecular sieve 5 A columns.

Temperature programmed desorption (TPD) experiments of NO were carried out in a quartz reactor with 5 mm internal diameter. The 100 mg catalyst sample was pre-treated with He until no NO was detected, and then the TPD measurements were then carried out up to 873 K with a heating rate of 10 K min^{-1} in flowing He. The gas flow rate was 50 $cm^3\ min^{-1}$. The desorbed species were continuously monitored by a NO/NO_2 analyzer and mass spectrograph (Omnistar).

Diffuse reflectance FT-IR measurements were carried out in situ in a high-temperature cell fitted with ZnSe windows. Feed gas streamed into the cell at a total flow rate of 100 $cm^3\ min^{-1}$.

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* Corresponding author. Tel.: +86 1062782030; fax: +86 1062785687.
E-mail address: lijunhua@tsinghua.edu.cn (J. Li).

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The temperature in the cell can be programmed from 303 K to 1073 K. Prior to analysis, all the samples were pretreated at 873 K in a mixture of N_2 and O_2 for 60 min, then in N_2 for 30 min to remove surface residents. In all cases, 100 scans were recorded at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Effect of H_2O and SO_2

Fig. 1 shows the effects of H_2O and SO_2 on the activities of In_2O_3/Al_2O_3 catalysts for NO reduction by propene. When 10%H_2O was added to the reaction gas, the maximum NO conversion decreased slightly over the entire temperature range, and the peak temperature shifted to 723 K. An inhibition effect obviously occurred as 100 ppm SO_2 in the reaction gas, and the maximum NO conversion was only about 30%. Co-existing H_2O and SO_2 inhibited catalytic activity to some extent, with the maximum NO conversion decreasing to 76%. However, NO reduction activity in the presence of both SO_2 and H_2O is higher than that in the presence of SO_2 alone. This activity enhancement by coexisting H_2O is probably due to the removal of carbonaceous materials covering the catalytically active sites [8]. It is interesting to note that the activities at low temperature were remarkably enhanced by the presence of SO_2, especially below 623 K. It has been reported that the presence of SO_2 caused the inhibition of NO_X adsorption sites (negative effect) and the creation of Brønsted acid sites (positive effect). The initial activity increase for the C_3H_6-SCR of NO in the presence of SO_2 can be assigned to the creation of Brönsted acid sites on which propene activation is promoted [9].

3.2. TPD studies

TPD profiles of NO and NO_2 on fresh (full symbols) and SO_2-treated (empty symbols) are shown in Fig. 2. Two desorption peaks were observed both for NO and NO_2, one is a low-temperature desorption of NO and NO_2, and the other is a high-temperature desorption of NO and NO_2. The first peak is centered at about 473 K and the second one is about 623 K. It is noted that the main desorption species is NO at low temperature and NO_2 in the high temperature range. The former peak might be due to the decomposition of nitrite species (ad-NO_2^-) which was observed at low temperature in DRIFTS spectra. The desorption of O_2 accompanied by desorption of NO_2 was observed at temperatures above 623 K in our research [10]. It is noted that the NO ad-species (ad-NO_3^-) decomposes to NO_2 and O_2 at high temperatures. The desorption of NO and NO_2 decreased remarkably on the SO_2 treated catalyst, and only one desorption peak was obtained for NO and NO_2. Since ad-NO_3^- species formed on the catalyst surface are known to play an important role in NO reduction [11], ad-NO_3^- species desorbed above 623 K are presumed to participate in NO reduction. This suggests that the presence of SO_2 in the reaction gas probably inhibited NO_X adsorption and the formation of ad-NO_3^- species; therefore, the catalytic activity decreased.

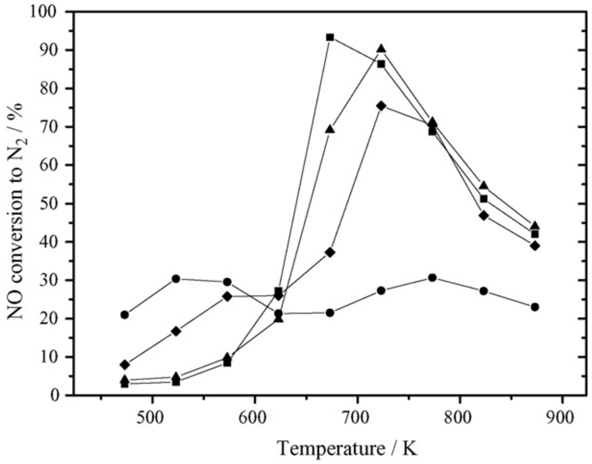

Fig. 1. NO conversion as a function of temperature over In_2O_3/Al_2O_3 catalyst under various reaction conditions. (■) without H_2O and SO_2; (●) with 100 ppm SO_2 and without H_2O; (▲) with 10%H_2O and without SO_2; (◆) with 10%H_2O and 100 ppmSO_2.

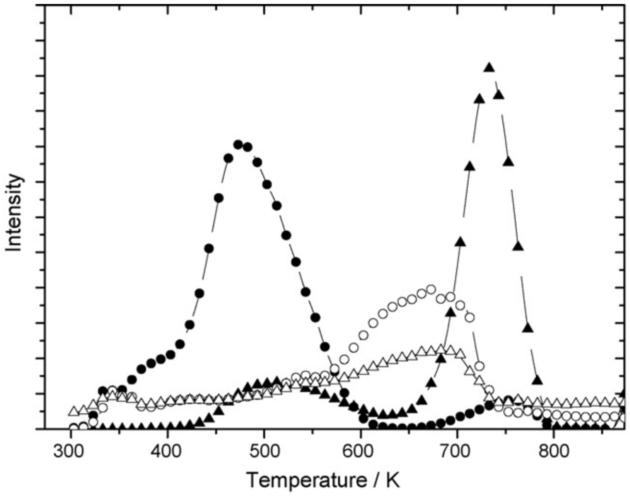

Fig. 2. TPD profiles of NO and NO_2 on fresh and SO_2-treated In_2O_3/Al_2O_3 catalysts. (○●) TPD of NO, (△▲) TPD of NO_2; (●▲) fresh sample, (○△) SO_2-treated sample.

3.3. XPS studies

Surface structures of the fresh sample and the S2p spectra of the SO_2-treated In_2O_3/Al_2O_3 catalyst were analyzed by XPS and the results are shown in Fig. 3a and b. A binding energy of 444.7 eV was measured for In $3d_{5/2}$ of In_2O_3/Al_2O_3 catalyst, which is in good agreement with the value of 444.4 eV reported for indium in In_2O_3 [12]. 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. Based on the results of the S2p spectra of spent In_2O_3/Al_2O_3 catalyst, the sulfur species on the surface mainly exists as sulfate. It indicates that $In_2(SO_4)_3$ and $Al_2(SO_4)_3$ are formed on the catalyst surface, causing the poisoning of NO adsorption sites on which NO reduction proceeds.

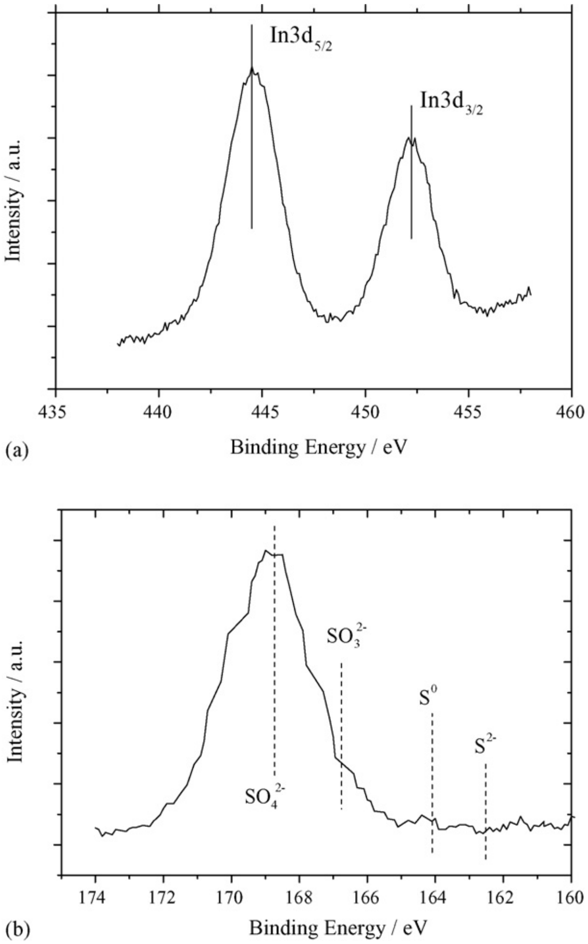

Fig. 3. (a and b) The XPS of the fresh sample and the S2p spectra of the SO_2-treated In_2O_3/Al_2O_3.

3.4. FT-IR studies

Fig. 4 shows the in situ DRIFTS spectra of In_2O_3/Al_2O_3 at various temperatures in the reaction of NO + C_3H_6 + O_2. It can be seen that monodentate nitrate (1254 and 1546 cm^{-1}), bidentate nitrate (1302 and 1595 cm^{-1}), and bridge nitrate (1614 cm^{-1}) bands are weak at a temperature of 423 K. These species reach the highest strength at a temperature of 673 K. Nitrite NO_2^- species (1232 cm^{-1}) and N=O (1470 cm^{-1}) are present below 473 K and disappeared when the temperature increased continually, which shows that NO desorption at low temperatures is due to the decomposition of NO_2^-. The band at 1665 cm^{-1} can be assigned to an organic nitrite compound (Al–ONO) [13,14]. The appearance of adsorbed NO_3^- species is observed even at room temperature, decreases with the temperature increases, and is negligible above 723 K. Formate (3005, 2906, 1394 and 1377 cm^{-1}) species appeared at 473 K and reach the highest strength at a temperature of 573 K. However, the bands of acetate species were not detected at low temperature. Carboxylate species (1454 and 1576 cm^{-1}) appeared at 573 K and the intensity increased with temperature. This indicates that active C_3H_6 (partially oxidized C_3H_6) is may be the key reaction process for the reduction of NO.

The dynamic changes of in situ DRIFTS of the In/Al_2O_3 in the dry feed with SO_2 at 573 K are shown in the Fig. 5. According to the literature [15], the band at 1350 cm^{-1} can be attributed to asymmetric stretching vibrations of O=S=O, while the band at 1174 cm^{-1} can be attributed to the symmetric stretching vibrations of O=S=O. The adsorption of SO_2 increased significantly after injecting SO_2 to the feed. Monodentate nitrate (1560 cm^{-1}) and bidentate nitrate (1300 cm^{-1}) disappeared rapidly with 100 ppm SO_2 injection, implying that the addition of SO_2 mainly inhibits adsorption of NO_2 and NO. Al–ONO (1662 cm^{-1}) increases while SO_2 is added, which means that organic nitrite compounds can be formed easily in the presence of SO_2. The adsorption of carboxylate species (1474, 1595 cm^{-1}) and formate species (1394, 1377, 3000 and 2905 cm^{-1}) also increased. It is known that conversion of active C_3H_6 into partially oxidized hydrocarbons is difficult at low temperatures. Addition of SO_2 enhanced formation of carboxylate and formate species,

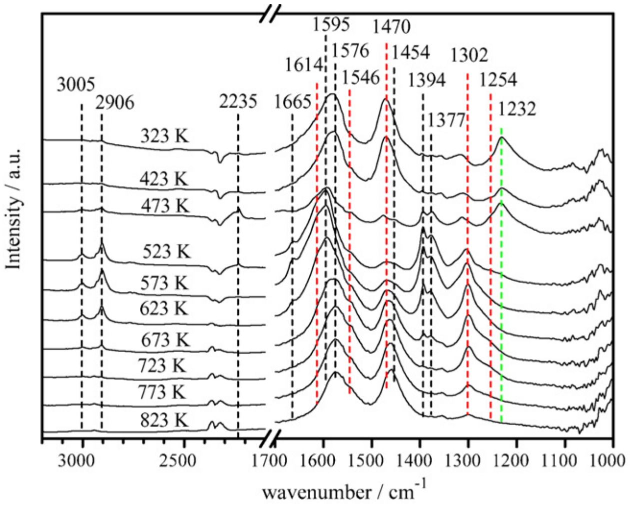

Fig. 4. In situ steady state DRIFTS spectra of In_2O_3/Al_2O_3 at various reaction temperatures. Gas composition: 1000 ppm NO, 1000 ppm C_3H_6, 8%O_2, N_2 balance.

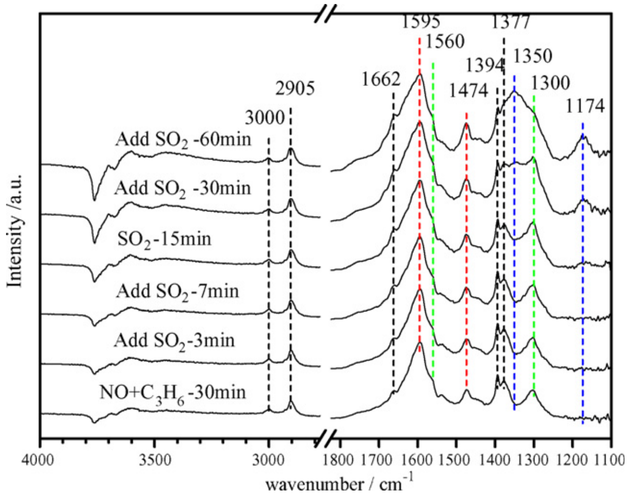

Fig. 5. Dynamic changes of in situ DRIFTS spectra over In_2O_3/Al_2O_3 during the SCR of NO in the presence of SO_2 at 573 K. Gas composition: 1000 ppm NO, 1000 ppm C_3H_6, 100 ppm SO_2, 8%O_2, N_2 balance.

which can explain the promotional effect of SO_2 at low temperature.

4. Conclusions

For the In/Al_2O_3 catalyst, the effect of H_2O on the catalytic activity was low. The presence of SO_2 caused an obvious inhibition of SCR of NO at higher temperatures, while it significantly enhanced NO conversion in the lower temperature range. On the basis of TPD and FT-IR studies it is evident that, in the presence of SO_2, sulfate species form causing a lowering in the NO_X adsorption, suppressing the appropriate IR absorbance, and diminishing the amount of ad-NO_3^- species. These species are desorbed above 623 K and are presumed to participate in the reaction of NO reduction. The bands assigned to NO_3^- and COO^- species were observed in the IR spectra, the peak intensity of these species increasing with rising reaction temperature from 473 to 723 K, and decreasing with temperature above that. This trend is in accordance with the activity curve, suggesting that these species could be the crucial intermediates in the process of reducing NO with C_3H_6. Addition of SO_2 enhances the formation of carboxylate and formate species, which can explain the promotional effect of SO_2 at low temperatures conversion of active C_3H_6 to partially oxidized hydrocarbons is difficult at low temperature.

Acknowledgements

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