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Selective Catalytic Reduction of NO_x with CH_4 over the In/Sulfated TiO_2 Catalyst

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Abstract Tungstated TiO_2 (WTi), tungstated Fe_2O_3 (WFe), tungstated SnO_2 (WSn), sulfated TiO_2 (STi), sulfated Fe_2O_3 (SFe), and sulfated SnO_2 (SSn) are used as the support for the In and Pd catalysts for the SCR of NO with methane. It was found that the In/STi catalyst with a 2% indium loading showed the highest NO_x conversion (39% at 450 °C and 12,000 h^{-1}) among all of the catalysts studied. The acid strength of the STi support was very important for the formation of the InO^+ site, which was thought to be the active site for NO reduction. The activity of the In/STi catalyst can be improved by increasing the surface area of the STi support. The most attractive feature of the In/STi catalyst is its high resistance for SO_2.

Keywords NO reduction · Methane · Superacid · Indium · Sulfated TiO_2

1 Introduction

The selective catalytic reduction (SCR) of nitrogen oxide with methane is the most promising technology for the control of NO_x emissions from natural gas-fired power plants and lean-burning natural-gas engines [1–3]. Low cost and less causticity are the most attractive features for the use of CH_4-SCR compared to other reducing agents. Zeolites based catalysts were found to be very active catalysts for the reaction of CH_4-SCR; however, the poor hydrothermal stability of the zeolite inhibited the application of them [2]. In the past decade, catalysts with superacid supports have drawn a great deal of attention.

SO_4/ZrO_2 (SZr) is the most widely used superacid support [4]. Among all the superacids reported in the literature, the SO_4/ZrO_2 has the highest acid strength. Many elements supported on SZ have been shown to be active for the CH_4-SCR reaction, including Ga [5], Pd [6–9], Rh [10], Co [11], Mn [12], and In [13]. Current research efforts have focused on the mechanism of the reactions over these catalyst [14–16] and on the improvement of the reaction activity of these catalyst by co-loading these element onto the SZr support, such as PdCo/SZr [17, 18]. 2000, Chin et al. reported on the high activity of a Pd/WZr catalyst and its high resistance to H_2O and SO_2 for the reaction [19, 20]. Recently, our group found that an In/WZr catalyst had a higher activity for CH_4-SCR than that of Pd/WZr [21, 22]. SO_4/Al_2O_3 (SAl) was another superacid support used for CH_4-SCR. The reaction activity of Pd/SAl [23] and Co/SAl [24] catalysts has been reported.

Tungstated TiO_2 (WTi), tungstated Fe_2O_3 (WFe), tungstated SnO_2 (WSn), sulfated TiO_2 (STi), sulfated Fe_2O_3 (SFe), and sulfated SnO_2 (SSn) were another type of superacid support which has been used for the skeletal isomerization and cracking of isopentane [25–27]. To our knowledge, the catalysts based on these supports have not been reported on up to now. In this work, the catalysts with Pd and In loaded on these supports were prepared and investigated for the CH_4-SCR reaction. Among these catalysts, In/STi revealed the highest NO reduction activity. So, more attention was focused on the performance of the In/STi catalyst in this paper.

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2 Experimental

2.1 Catalyst Preparation

H_4TiO_4-I, $Fe_2(OH)_3$, and $Sn(OH)_4$ were obtained by hydrolyzing $TiCl_4$, $Fe(NO_3)_3$, and $SnCl_4$ solution with aqueous ammonia. The precipitates were washed with de-ionized water until the washing solution was neutral and without Cl^- ions, and then were dried at 110 °C for 15 h. The STi-I, SFe, and SSn were prepared by treating the dried H_4TiO_4-I, $Fe_2(OH)_3$, and $Sn(OH)_4$ with H_2SO_4 solution for 0.5 h (0.5 M H_2SO_4 for H_4TiO_4-I and $Fe_2(OH)_3$; 3 M H_2SO_4 for $Sn(OH)_4$) with a ratio of 15 ml H_2SO_4 solution per gram hydroxide. Afterwards, the supports were separated by filtration, dried at 110 °C for 15 h and finally calcined in air at 550 °C for 5 h. WTi, WFe, and WSn were obtained by impregnating H_4TiO_4-I, $Fe_2(OH)_3$, and $Sn(OH)_4$ with an aqueous solution of ammonium paratungstate. The W contents in the final supports were 10 wt%. The solids were dried at 110 °C for 15 h and then calcined at 600 °C for 5 h. The loading of Pd and In was accomplished by the impregnation method using $PdCl_2$ and $In(NO_3)_3$ solution, respectively. After being dried at 110 °C overnight, the powder was then calcined at 550 °C for 5 h.

Another H_4TiO_4-II was prepared by dissolving $Ti(OC_4H_9)_4$ in 1 M nitric acid solution and then hydrolyzing with aqueous ammonia followed by washing and drying. The preparation of the STi-II support and the In/STi-II catalyst was done using similar procedures, but H_4TiO_4-II was used instead of H_4TiO_4-I.

In addition, the TiO_2 support was prepared by directly calcinating H_4TiO_4-II at 550 °C for 5 h. The preparation of the In/TiO_2 catalyst was done in the same manner as that of In/STi-I.

The resulting catalysts are hereafter referred to as InaM or PdaM, where In refers to Indium, Pd refers to palladium, and a refers to the weight content of indium or palladium in the catalyst, M represents the support of the catalyst, such as STi-I, STi-II, or WTi.

2.2 Catalytic Activity Measurement

Activity measurements were carried out with a fixed-bed quartz reactor (inner diameter 8 mm) using a 0.5 g catalyst of 60–80 mesh. The feed gas was a mixture containing 1,000 ppm NO or NO_2, 3,000 ppm CH_4, 10% O_2, 0 or 100 ppm SO_2, 0 or 10% H_2O and N_2 as the balance gas. The total flow rate of the feed gas was 100 mL/min, corresponding to a space velocity of about 12,000 h^{-1}. NO and NO_2 concentrations were analyzed with a chemiluminescence NO/NO_2 analyzer (Thermal Environmental Instruments, model 42C). The activity data were collected after the catalytic reactions reached near steady-state conditions for half an hour at each temperature.

2.3 Catalyst Characterization

X-ray diffraction (XRD) patterns were determined using a Rigaku D/max-RB diffractometer. The analyses were performed using a Cu Target (40 KV and 100 mA); a typical scan speed was 6°/min with a step of 0.002° in the range from 20° to 70°. BET surface area, pore size, and pore volume were measured by the N_2 adsorption-desorption method using a NOVA 3200e analyzer.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI15300/ESCA system with Al Ka radiation (1484.6 eV); it was calibrated internally by carbon deposit C1s binding energy (BE) at 284.6 eV.

3 Results and Discussion

3.1 Characterization of the Catalysts

The BET surface areas of different catalysts are summarized in Table 1. It can be seen that STi-II showed higher surface area than STi-I. This fact can be explained by the different hydrolyzation procedures of $TiCl_4$ compared to $Ti(OC_4H_9)_4$. In the preparation process, $TiCl_4$ hydrolyzed faster than $Ti(OC_4H_9)_4$, which resulted in the formation of a denser structure of $Ti(OH)_4$ from $TiCl_4$ than that from $Ti(OC_4H_9)_4$. As a result, STi prepared from $TiCl_4$ had a lower surface area than that from $Ti(OC_4H_9)_4$. It was noticed that sulfated samples such as STi-II and In2STi-II had much greater surface areas than the samples of un-sulfated ones (TiO_2 and In2TiO_2), suggesting that the sulfation process could stabilize the pore structure of TiO_2. On the other hand, the loading of In on the supports all caused a distinct decrease in the surface area. The surface

Table 1 BET surface areas of the catalysts studied

Samples	BET surface area (m^2/g)
STi-I	64.03
In2STi-I	62.14
TiO_2	66.45
In2TiO_2	48.30
STi-II	81.68
In1STi-II	80.64
In2STi-II	77.74
In5STi-II	70.99
In10STi-II	64.91

Table 2 In3d$_{5/2}$ binding energies, In/Ti and S/Ti atomic ratios of InTiO$_2^a$ and InSTi-II^a derived from XPS

Samples	In3d$_{5/2}$ (eV)	In/Ti	S/Ti
InTiO$_2$	444.7	0.049 (0.014)^b	–
InSTi-II	445.5	0.032 (~0.014)^b	0.075

[a] The contents of In over the two catalysts were 2 wt%

[b] The values in parenthesis are the expected ratios when elements are all homogeneously dispersed in the catalysts

area of InTiO$_2$, InSTi-I and InSTi-II catalysts were smaller compared with that of TiO$_2$, STi-I and STi-II, respectively.

The XPS results for the InTiO$_2$ and InSTi-II catalysts are given in Table 2 in terms of the binding energies of the In3d$_{5/2}$ and the atomic ratio of In/Ti and S/Ti in the sample surface. As reported in our previous studies [21], the binding energy of 444.7 eV for the InTiO$_2$ catalyst suggested that indium species over a TiO$_2$ support were mainly in the state of In$_2$O$_3$ bulk phase. The binding energy of In3d$_{5/2}$ for the InSTi-II catalyst was shift to a higher value than that for InTiO$_2$ catalyst. As in the case of the In/WZr and In/HZSM-5 catalysts [21, 28–30], the result was attributed to the formation of InO$^+$ species, which was the non-aggregated state of indium in our catalyst. The In/Ti ratio for the InTiO$_2$ and InSTi-II catalysts were both higher than the expected values. This fact can be attributed to the preparation method of impregnation, which always leads to the enrichment of indium over the TiO$_2$ support. It can also be seen from Table 2 that the In/Ti ration for InTiO$_2$ was much higher than that for InSTi-II. This suggested that a more serious aggregation of indium exists on the InTiO$_2$ catalyst surface. This result was attributed to the higher surface area of STi-II compared with TiO$_2$, as well as the dispersion effect of strong acid sites over STi-II support for the formation of the InO$^+$ species.

The XRD patterns of TiO$_2$, In2TiO$_2$, STi-II, and In2STi-II catalysts are shown in Fig. 1. All these samples showed the typical anatase TiO$_2$ phase; no rutile TiO$_2$ phase could be detected. It was noticed that the peaks at 25.26° for the STi-II and In2STi-II catalysts were broader and shorter than those for the TiO$_2$ and In2TiO$_2$ catalysts. This result was in agreement with the BET results; they both showed the stabilization effect caused by the sulfation process on the textural structure of TiO$_2$. No distinct peaks of indium oxide could be observed after loading on the TiO$_2$ and STi-II support with 2% indium. The XRD patterns for STi-I and In2STi-I were also tested (not shown in the figures); they both showed patterns similar to those found with STi-II and In2STi-II. In addition, no In$_2$O$_3$ peak was detected too.

The XRD patterns for InSTi-II with different Indium content were compared; the results were shown in Fig. 1. For the In1STi-II, In2STi-II, and In5STi-II catalysts, only the characteristic lines of anatase TiO$_2$ could be observed. However, in the XRD patterns of the In10STi-II catalyst, a weak peak at 30.56 ° corresponding to In$_2$O$_3$ was observed.

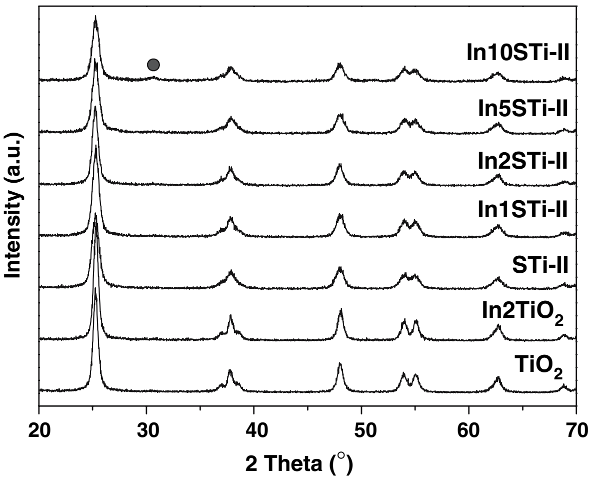

Fig. 1 XRD patterns of TiO$_2$, In2TiO$_2$, STi-II, and InSTi-II with different In content, the dark circle denoted the peak location of In$_2$O$_3$

3.2 CH$_4$-SCR Activity Test

The NO$_x$ conversion activities of Pd or In loaded on the WTi, WSn, and WFe catalysts at 500 °C are compared in Fig. 2a. The highest activity, 17%, was obtained over the InWTi catalyst, while the NO$_x$ conversions over all other catalysts were lower than 10%. Fig. 2b shows the activities of Pd or In loaded on STi-I, SSn, and SFe supports. It can be seen that these sulfated catalysts were obviously more active for NO$_x$ conversion than that of the tungstated catalysts. The conversion of NO$_x$ over the PdSTi-I, PdSFe, InSTi-I, and InSFe catalysts were all higher than 10%. InSTi-I showed the highest activity of a 33% NO$_x$ conversion ratio in all these catalysts. The main effect of these supports on the catalytic activity of Pd or In loaded catalysts might come from the difference in their acid strength. It has been reported that the acid strength of the sulfated supports was stronger than that of the corresponding tungstated supports, and that the H$_0$ of all WTi, WSn, and WFe supports was higher than −14.52, while the H$_0$ of all STi, SSn, and SFe supports was lower than −14.52 [25, 27]. The stronger acid strength of these sulfated supports might be important for the formation of the active species of Pd^{2+} or InO$^+$. As a result, the sulfated catalysts were more active for NO$_x$ conversion than the corresponding tungstated catalysts. It was noticed that the reaction activity for the NO$_x$ conversion of SnO$_2$ based catalysts, including PdWSn, InWSn, PdSSn, and InSSn, were very poor. SnO$_2$ has been reported to be easily form solid solution with several other elements [31]. For these catalyst, Pd and In may be doped into the lattice of SnO$_2$, but they will not

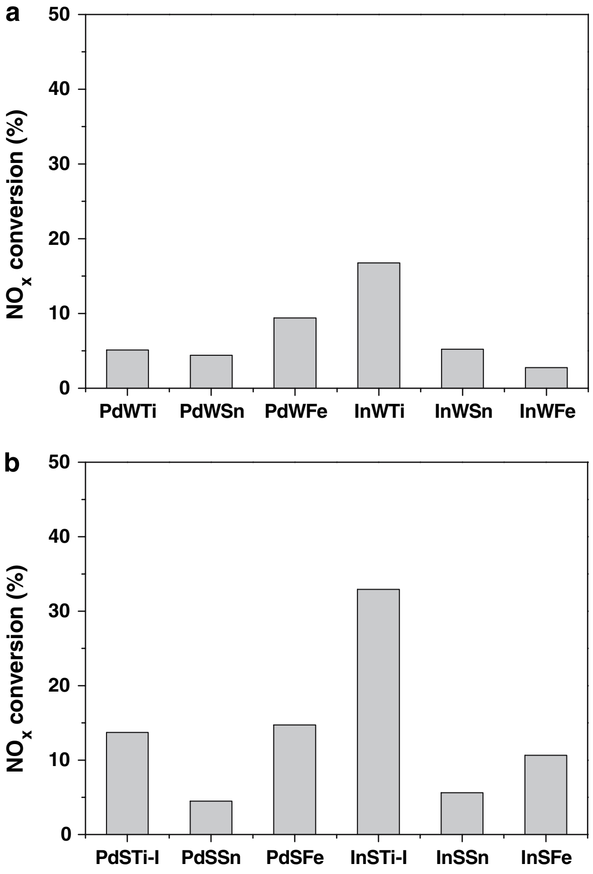

Fig. 2 NO_x conversions over Pd or In loaded WTi, WSn, and WFe catalysts (**a**), over Pd or In loaded STi-I, SSn, and SFe catalysts (**b**) at 500 °C. The contents of Pd and In were 0.1 wt% and 2 wt%, respectively. Reaction conditions: 1,000 ppm NO, 3,000 ppm CH_4, 10% O_2, N_2 as balance; GHSV = 12,000 h^{-1}

interact with the superacid sites over WO_3/SnO_2 and SO_4/SnO_2 to form the active site of Pd^{2+} and InO^+. The following investigations focused on the InSTi catalyst due to its high activity for NO_x conversion.

Figure 3 shows the activities for the In2STi-I and In2STi-II catalysts prepared using different sources of Ti, including $TiCl_4$ and $Ti(OC_4H_9)_4$. The In2STi-II catalyst prepared from $Ti(OC_4H_9)_4$ has a much higher NO_x conversion activity than the In2STi-I prepared from $TiCl_4$. The reason for this difference was the higher surface area of STi-II compared to that of STi-I, and more active species of InO^+ might be formed over surface of the STi-II.

NO_x conversion activities over the TiO_2, STi-II, In2TiO$_2$, and In2STi-II catalysts are compared in Fig. 4. The TiO_2 and In2TiO$_2$ catalysts were totally inactive for the reduction of NO_x in the temperature range from 300–550 °C. This result suggested that the TiO_2 catalyst can not provide active oxygen, which was the key reactant for the conversion of NO_x as shown for the La_2O_3 or ZrO_2 catalyst [3, 21, 32]. On the other hand, In_2O_3 bulk phase over the In2TiO$_2$ catalyst, as detected by XPS, was also inactive for CH_4-SCR. This result was in agreement with our previous studies on the In/ZrO_2 catalyst [21]. After sulfation, the STi-II catalyst showed a low activity at 500–550 °C. However, when 2% In was loaded on STi-II, the NO_x conversion activity were significantly improved. These results suggested that the sulfation of the support TiO_2 is essential for the high activity of the In2STi-II catalyst, because it provided sufficient acid strength over the STi-II support for the formation of the active species of InO^+ over the In2STi-II catalyst.

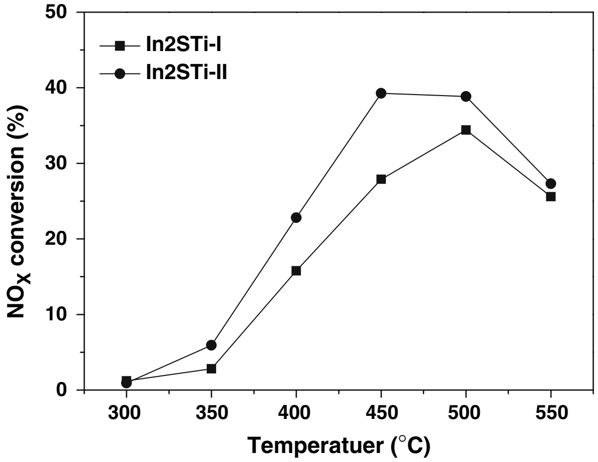

Fig. 3 NO_x conversion over In2STi-I and In2STi-II catalysts prepared from $TiCl_4$ and $Ti(OC_4H_9)_4$, respectively. Reaction conditions: 1,000 ppm NO, 3,000 ppm CH_4, 10% O_2, N_2 as balance; GHSV = 12,000 h^{-1}

The influence of the In contents on the NO_x conversion activity of the InSTi-II catalyst is shown in Fig. 5. When the In loading is increased from 1% to 2%, the NO_x conversion over the InSTi-II catalyst increased in the full

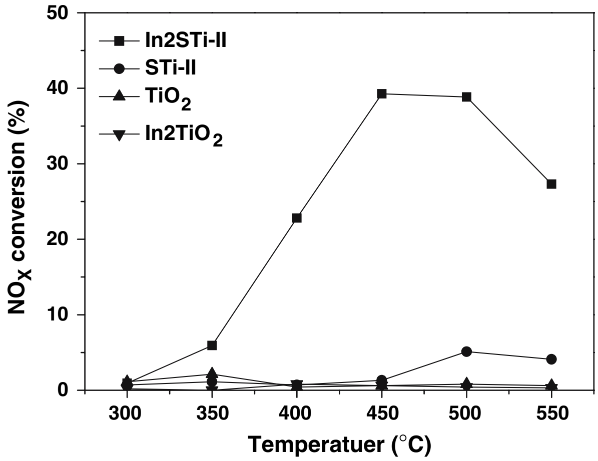

Fig. 4 NO_x conversion over TiO_2, STi-II, In2TiO$_2$, and In2STi-II. Reaction conditions: 1,000 ppm NO, 3,000 ppm CH_4, 10% O_2, N_2 as balance; GHSV = 12,000 h^{-1}

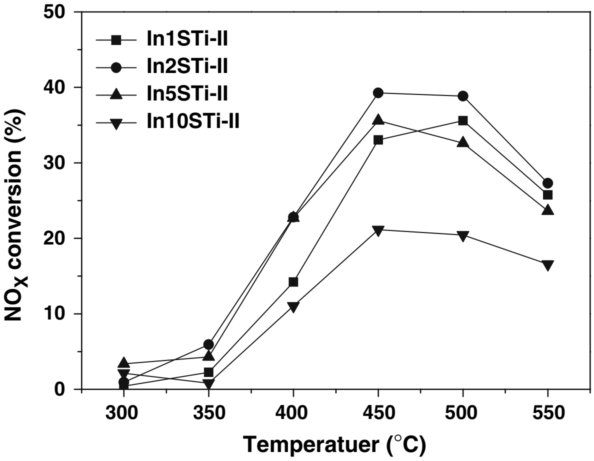

Fig. 5 Effect of indium content on the NO_x conversion over InSTi-II catalysts. Reaction conditions: 1,000 ppm NO, 3,000 ppm CH_4, 10% O_2, N_2 as balance; GHSV = 12,000 h^{-1}

temperature range. More active sites (InO^+) might be formed over the In2STi-II catalyst than that over the In1STi-II catalyst. Further increases of In loading from 2% to 10% led to a decrease of the NO_x conversion activity, and when the In content was above 5%, the activity decreases seriously with the increased In content. The In_2O_3 phase, formed in the In10STi-II catalyst as detected by XRD, might inhibit its activity for NO_x conversion.

The influence of H_2O and SO_2 in the reaction flow on the NO_x conversion activity of the In2STi-II catalyst was tested and is shown in Fig. 6. When SO_2 was added to the reaction gas, the maximum NO_x conversion decreased from 39% to 32%, and the maximum conversion was also achieved at 450 °C. This result suggested that the InSTi catalyst appeared to be more resistant to SO_2 than the InWZr catalyst did. Over the InWZr catalyst, the maximum NO_x conversion decreased from 70% to 33% in the presence of SO_2 [21]. The inhibition effect of H_2O on the activity of In2STi-II was more pronounced than that of SO_2. The maximum NO_x conversion decreased to only 11%, while the temperature window for reduction shifted by 50 °C to higher temperatures. When H_2O and SO_2 were co-added into the reaction gas, the activity was similar to the case that only H_2O was added.

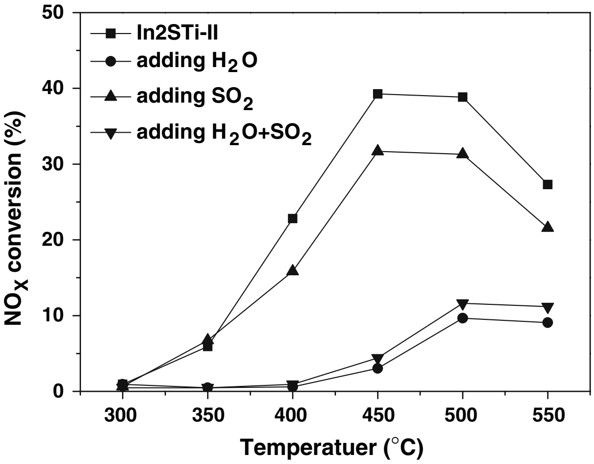

Fig. 6 Effect of H_2O and SO_2 on the NO_x conversion over In2STi-II catalyst. Reaction conditions: 1,000 ppm NO, 3,000 ppm CH_4, 10% O_2, 0 or 100 ppm SO_2, 0 or 10% H_2O, N_2 as balance; GHSV = 12,000 h^{-1}

An attempt was made to improve the activity of the In2STi-II catalyst by adding additives such as Ce. Unfortunately, the promotion effect was not found until now, and further studies are in progress to determine the mechanism for CH_4-SCR over the InSTi catalyst.

4 Conclusion

In this paper, the CH_4-SCR performances of Pd or In loaded on different superacid supports, including WTi, WFe, WSn, STi, SFe, and SSn, were investigated. It is demonstrated that the In/STi catalyst has the highest activity for NO_x conversion. The STi support, which has stronger acid sites, is essential for the high activity of InSTi. This is because it provides a suitable environment for the formation of InO^+ sites, which were attributed to the active sites over indium based catalysts for CH_4-SCR. The increase of the BET surface area of the STi support was due to the preparation from proper Ti precursor and it was helpful for improving the activity of In/STi catalyst. Moreover, In/STi was more tolerant to SO_2 than the In/WZr catalyst.

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