Chinese Chemical Letters Vol. 16, No. 11, pp 1535-1538, 2005
http://www.imm.ac.cn/journal/ccl.html

Enhancement of Activity of SnO_2-doped In_2O_3/Al_2O_3 Catalyst for NO Reduction with Propene in the Presence of H_2O and SO_2

Xiang Yu CUI, Jun Hua LI*, Ji Ming HAO, Li Xin FU

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

Abstract: The novel bimetallic Sn-In/Al_2O_3 catalysts prepared by three methods for NO reduction by propene were investigated. The results showed that the catalytic activity was enhanced significantly in the presence of H_2O on sol-gel catalyst, and the maximum NO conversion increased from 46% to 92%, even in the presence of 100 ppm SO_2, NO conversion was still 80%.

Keywords: Selective catalytic reduction, De-NOx, lean burn, In_2O_3/Al_2O_3, Sn-In/Al_2O_3.

The selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) has attracted much attention as an efficient way to remove NO in the presence of excess oxygen[1-2]. The metal oxides are the most promising catalysts for the SCR of NO because of their high activity and selectivity[3-5]. In the previous work, the metal oxides such as Ag, Sn, In, Co supported on alumina for NO reduction were investigated[6-8], however, the HC-SCR is usually suppressed in the presence of H_2O and SO_2, which inevitably exist in the exhaust gas, resulting in a difficulty for the utilization of the catalysts. In this study, the bimetallic Sn-In/Al_2O_3 catalysts were prepared by the sol-gel (SG-Cat), impregnation (IM-Cat) and co-precipitation (CP-Cat), and their activities for NO reduction by propene were investigated, and the effect of preparation method on the activities were also investigated in the absence and presence of H_2O and SO_2.

Experimental

The catalysts were prepared by three methods, one is single step sol-gel, and aluminium boehmite sol was first prepared by hydrolysis of aluminium *iso*-propoxide (AIP) in water at 85℃ with a proper amount of nitric acid, and then mixed with a solution of indium nitrate and tin chloride dissolved in ethanol. Co-impregnation method is using alumina powder to immerse the aqueous solution containing indium nitrate and tin chloride. The co-precipitation catalyst was produced by mixing 10% NH_4OH and an aqueous solution of indium nitrate and tin chloride. For all the preparation methods, the following step was drying at 110℃ and calcinations at 600℃ for 5 h in air.

---

* E-mail: lijunhua@tsinghua.edu.cn

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 mesh. The feed gas mixture contained 1000 ppm NO, 1000 ppm C_3H_6, 8% O_2, 0 or 10% H_2O, 0 or 100 ppm SO_2, and helium as the balance gas. The total flow rate of the feed gas was 300 $cm^3 \cdot min^{-1}$.

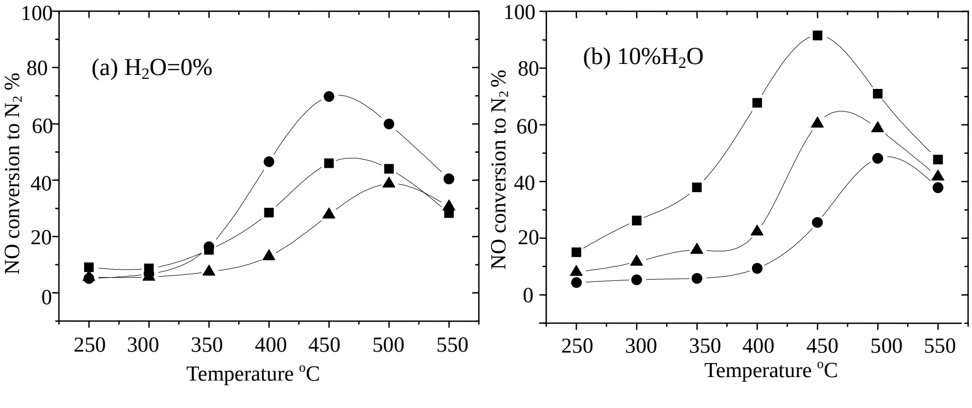
NO and NO_2 concentrations were continuously determined by NOx analyzer (Thermo Environmental, Model 42H), the gas chromatograph (Shimadzu GC 17A) is equipped with a Parapak Q column for the separation of CO_2, N_2O and C_3H_6. N_2O formation was not observed in test of the catalysts.

Results and Discussion

Figure 1 shows the catalytic activity of the Sn-In/Al_2O_3 catalysts prepared by three methods for NO reduction in the absence and presence of H_2O, it can be seen that the great difference were observed with the various preparation methods, CP-Cat showed the highest activity, the NO conversion was 70% at 450 ℃, and the activity decreased in the order of CP-Cat > SG-Cat >IM-Cat. However, when the 10% H_2O was injected into the reaction gas, an interesting catalytic behavior was observed depending on the catalyst preparation method. It is found that coexisting H_2O caused activity depression of CP-Cat over the entire temperature range, and the maximum NO conversion decreased from 70% to 48%, meanwhile the temperature window became narrow and shifted to the higher temperature region. On the contrary, the activity of SG-Cat and IM-Cat were enhanced considerably by coexisting H_2O, especially for SG-Cat catalyst, the maximum NO conversion increased from 46% up to 92% in the presence of 10%H_2O.

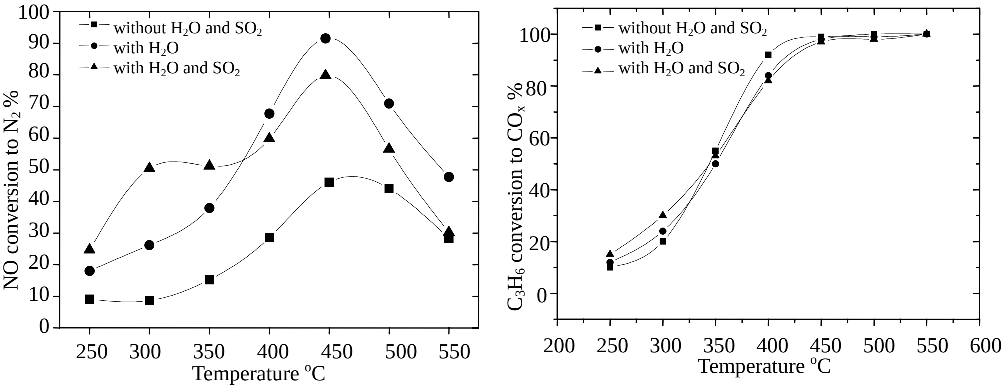
The effect of SO_2 on the activity over SG-Cat was further investigated, and the results of NO and C_3H_6 conversion as a function of temperature are shown in **Figure 2**. On introduction of 100ppm SO_2, the maximum NO conversion decreased slightly around 450℃ compared with that in the presence of H_2O, however, it is significant that the activity was enhanced remarkably at the lower than 350℃, and the temperature window

Figure 1 Effect of preparation method on the NO conversion over Sn-In/Al_2O_3 catalyst by propene in the absence (a) and presence of H_2O (b).



(■) SG-Cat, (▲) IM-Cat, (●) CP-Cat.

Figure 2 Effect of H_2O and SO_2 on the activity of sol-gel Sn-In/Al_2O_3 catalyst for NO reduction by C_3H_6.



was broadened, and the NO conversion was above 50% at the wider temperature range of 300-500℃. Moreover, the activity is higher obviously than that in the absence of H_2O and SO_2 over the whole temperature region, and the maximum NO conversion is still 80% in the co-presence of H_2O and SO_2.

It is evident that the effect of H_2O on the activity is related to the catalyst preparation methods, the difference of pore structure with preparation method seem to be one factor to this phenomenon. It is an important factor but not necessary and permanent property for the activity, the state and the location of SnO_2 and In_2O_3 on alumina and the interaction of them are more significant factor. The sol-gel process for SG-Cat and the alumina support of IM catalyst might be assigned to the enhancement of H_2O.

There are no great difference of propene conversion into COx in the absence and presence of H_2O, it suggests that the role of H_2O seems to improve the utilization of reductant agent. The promotional effect of H_2O reported is of removal of carbonaceous materials deposited on the catalyst surface by H_2O; however the color of the catalysts did not change to brown or black as usual observed in the formation of carbonaceous materials after the reaction test on each catalyst. Therefore, the promotional effect of H_2O is probably based on the different reaction mechanism in the absence and presence of H_2O, the selective inhibition by H_2O of the reaction steps resulting in propene oxidation to CO_2, and the reaction intermediates maybe easy formed and adsorbed on catalyst surface in the presence of H_2O. The introduction of SO_2 probably increased the propene activation ability, the enhancing effect of SO_2 could be assigned to the increase of Brönsted acid site that facilitate the activities of the hydrocarbon[9], and then improved the activity at lower temperature.

In conclusion, there are great difference of coexisting H_2O effect on activity over the catalysts prepared by various preparation methods, the activity were improved remarkably over SG-Cat in the presence of H_2O, and the maximum NO conversion increased from 46% to 92%. Coexisting of SO_2 broadened the temperature window, and the NO conversion was above 50% at a wide temperature range of 300 to 500℃.

Acknowledgments

The work was financially supported by National Natural Science Foundation of China (Grant No.20437010) and National 863 Project. (NO.2004AA649150)

References

1. H. Akama, K. Matsushita, *Catal. Surv. Jpn.*, **1999**，*3*, 139.
2. J. H. Li, J. M. Hao, L. X. Fu, T. L. Zhu, *Topics in Catal.*, **2004**, *30/31*: 81.
3. K. I. Shimizu, A. Satsuma, T. Hattori, *Catal. Surv. Jpn.*, **2000**, *4*, 115.
4. J. H. Li, J. M. Hao, L. X. Fu, X. Y. Cui, *Chin. Chem. Lett.*, **2004**, *15*: 695.
5. P. W. Park, H.H. Kung, D. W. Kim, and. M.C. Kung, *J. of Catal*., **1999**, *184*, 440.
6. J. H. Li, J. M. Hao, L. X. Fu, Z. M. Liu, X.Y. Cui, *Appl. Catal. A.*, **2004**, *265*, 43.
7. J. H. Li, J. M. Hao, L. X. Fu, Z. M. Liu, X.Y. Cui, *Catal. Today,* **2004**, 90, 215.
8. J. H. Li, J. M. Hao, L. X. Fu, T. L. Zhu, X. Y. Cui, *React. Kinet. Catal. Lett.,* 2003, **80**: 75.
9. M. Haneda,Y. Kintaichi, H. Hamada, *Appl.Catal. B.,* **2001**, *31*, 251.

Received 8 February, 2005