

## High Activity SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Catalyst for NO Reduction in the Presence of Oxygen

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**Abstract:** The novel sol-gel SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts for selective catalytic reduction NO by propene under lean burn condition were investigated. The results showed that the maximum NO conversion was 82% on the SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) catalyst, and the presence of H<sub>2</sub>O and SO<sub>2</sub> improved the catalytic activity at low temperature. The catalytic activity of NO<sub>2</sub> reduction by propene is much higher than that of NO at the entire temperature range, and the maximum NO<sub>2</sub> conversion reached nearly 100% around the temperature 425°C.

**Keywords:** Selective catalytic reduction, De-NOx, lean burn, SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

The removal of nitrogen oxides from lean burn engine is a major environmental concern in order to meet the stringent emission regulation<sup>1</sup>. Selective catalytic reduction (SCR) of nitrogen oxides is an efficient way to remove NOx from lean burn gasoline and diesel exhaust<sup>2,3</sup>. The metal oxide catalysts have attracted much attention because they are more stable than zeolites in hydrothermal conditions<sup>4,5</sup>. Tin supported on alumina was reported to be a good metal oxide catalyst for NO reduction by hydrocarbons in the presence of oxygen by some investigators. Kung *et al.*<sup>6,7</sup> reported the SCR of NO over Sn/Al<sub>2</sub>O<sub>3</sub> catalysts, prepared by impregnation method, and the presence of H<sub>2</sub>O and SO<sub>2</sub> inhibited the catalytic activities in some extent. In this work, the SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with various Sn loading were prepared by sol-gel technique that is a useful method to prepare catalysts with highly dispersed species as compared to impregnation method. The catalytic activities for NO reduction by propene in the absence and presence of H<sub>2</sub>O and SO<sub>2</sub> were investigated; the results showed that the SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) was effective catalyst for NO reduction even in the presence of H<sub>2</sub>O and SO<sub>2</sub>.

### Experimental

The SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by single step sol-gel method. Aluminum tri-isopropoxide (AIP) was hydrolyzed at 85°C on the evaporator with a small amount of nitric acid, and then the necessary amount of SnCl<sub>4</sub>·5H<sub>2</sub>O dissolved in ethylene glycol was added to the sol solution, the solvents were evaporated by heating under reduced

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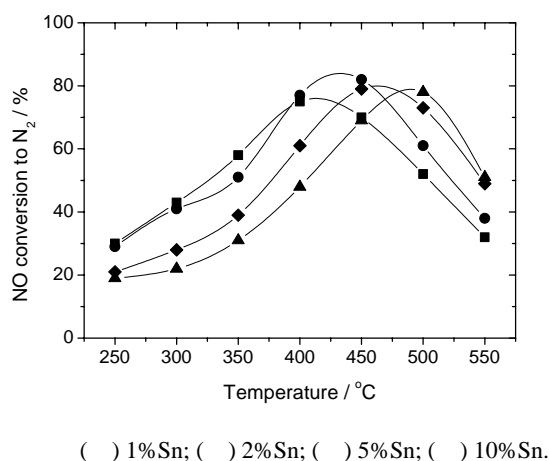
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pressure. The obtained gel was dried at 110°C over 24 hours and calcined at 600°C for 5 hours. Tin loading was changed from 1wt% to 10wt% as Sn metal.

The catalytic reduction activity was carried out in a quartz reactor with an internal diameter of 8 mm. The feed gas mixture consisted of 1000 ppm NO (or 1000 ppm NO<sub>2</sub>), 1000 ppm C<sub>3</sub>H<sub>6</sub>, 8% O<sub>2</sub>, 10% H<sub>2</sub>O (when used), and 100 ppm SO<sub>2</sub> (when used). The total gas flow rate of 300 mL·min<sup>-1</sup> was maintained using helium as the carrier gas.

NO and NO<sub>2</sub> concentrations were continuously determined by chemiluminescent NOx analyzer (Thermo Environmental, Model 42H), and the gas chromatograph (Shimadzu GC 17A) is equipped with a Parapak Q column for the separation of CO<sub>2</sub>, N<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub>. N<sub>2</sub>O formation was not observed in the experiment.

**Figure 1** The effect of Sn loading on NOx and C<sub>3</sub>H<sub>6</sub> conversion over SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) catalysts in the absence of H<sub>2</sub>O and SO<sub>2</sub>.

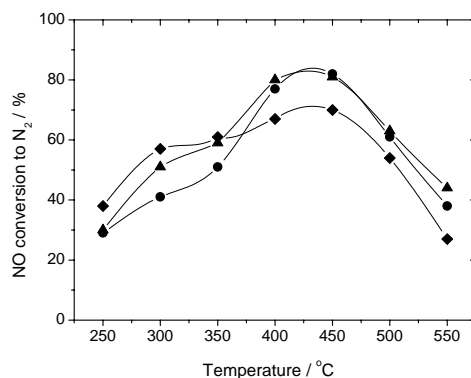


## Results and Discussion

**Figure 1** showed the effect of Sn loadings on catalytic activities for NO conversion by propene. With the increase of Sn loading from 1wt% to 5wt%, the maximum NO conversion increased up to 82% at 450°C, however, when Sn loading reached 10wt%, no further improvement of the NO conversion was observed, although the temperature of the maximum NO conversion shifted to a lower temperature region.

The effect of H<sub>2</sub>O and SO<sub>2</sub> on SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) catalyst for selective catalytic reduction of NO by C<sub>3</sub>H<sub>6</sub> is shown in **Figure 2**. When added 10% H<sub>2</sub>O into the reaction gas, NO conversion enhanced at the low temperature below 400°C. Furthermore the addition of 100 ppm SO<sub>2</sub>, the NO conversion increased at the low temperature of 250-350°C, and the temperature window was broadened, but the maximum NO conversion decreased to 70% at 450°C. The reasons of promotional effect of H<sub>2</sub>O are the selective inhibition by H<sub>2</sub>O of the reaction steps resulting in propene oxidation to CO<sub>2</sub> and the removal of carbonaceous materials covering the catalytically active sites by H<sub>2</sub>O. The enhancing effect of SO<sub>2</sub> could be assigned to the increase of Brönsted acid site that facilitate the activities of the hydrocarbon<sup>8</sup>.

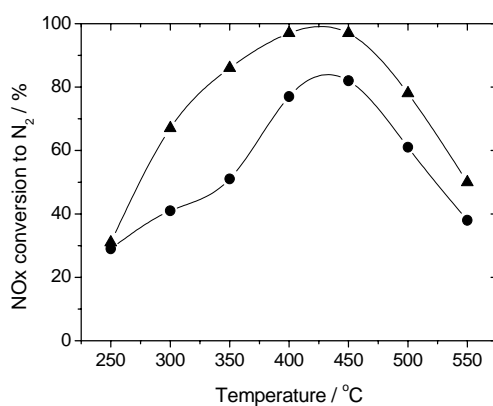
**Figure 2** The effect of H<sub>2</sub>O and SO<sub>2</sub> on SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) catalyst for NO reduction by C<sub>3</sub>H<sub>6</sub>.



( ) without H<sub>2</sub>O and SO<sub>2</sub>; ( ) with 10% H<sub>2</sub>O without SO<sub>2</sub>; ( ) with 10% H<sub>2</sub>O and 100ppm SO<sub>2</sub>.

**Figure 3** shows the activities of SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) for NO and NO<sub>2</sub> reduction by propene. To compare the reactivity between NO and NO<sub>2</sub> found that the reactivity of NO<sub>2</sub> is much higher than that of NO at the entire temperature range, more than 60% NO<sub>2</sub> conversion was observed at a wider temperature range of 300-500°C, and the maximum NO<sub>2</sub> conversion reached nearly 100% at the temperature range of 400-450°C. These findings suggest that NO<sub>2</sub> is more reactive than NO, and the NO oxidation into NO<sub>2</sub> may be a limiting factor in NO reduction, and NO<sub>2</sub> is likely to react more quickly with propene on the surface of the catalyst to form N<sub>2</sub>.

**Figure 3** Comparison of reactivity between NO and NO<sub>2</sub> on SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) catalyst in the absence of H<sub>2</sub>O and SO<sub>2</sub>.



( ) NO conversion to N<sub>2</sub>; ( ) NO<sub>2</sub> conversion to N<sub>2</sub>.

In summary, the SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by sol-gel method for NO reduction by propene showed high activity and stability, the maximum NO conversion was 82% on the SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (5%Sn) catalyst, and the coexisting of H<sub>2</sub>O and SO<sub>2</sub> enhanced the catalytic activity at the low temperature. The maximum NO<sub>2</sub> conversion reached nearly 100% around 450°C. From a practical point of view, the SnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst has a potential application to remove NO<sub>x</sub> in the lean burn gasoline and diesel engine

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