

## Highly Active Bifunctional Catalyst for SCR of NO with Methane

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Selective catalytic reduction (SCR) of NO with hydrocarbon has received much attention because of its potential application in the removal of NO from exhaust gases. Natural gas is a favourable alternative to automotive fuel due to its easy availability, low price and high hydrogen to carbon ratio. Natural gas fuelled vehicles (NGVs) appear to be attractive to solve the transportation problems and also to reduce the pollution since compared to diesel, the NGV engines produce less emission of NO<sub>x</sub> and particulates. A SCR system which can use methane as a reductant would be beneficial for not only natural gas fuelled facilities, but also stationary NO<sub>x</sub> emission sources where natural gas supply is available. Several metal ion-exchanged zeolites, such as Co-,<sup>1,2</sup> Mn-,<sup>3</sup> Ga-,<sup>4</sup> In-,<sup>5,6</sup> Pd-,<sup>7,8</sup> and Ce-Ag-ZSM-5<sup>9</sup> have shown to be active for the SCR of NO with methane. However, water vapor and SO<sub>2</sub> present in combustion exhausts may cause severe deactivation of catalyst during the SCR reaction<sup>10,11</sup>

In this report, preliminary results on the SCR of NO with methane over catalyst prepared by simple physical mixing of modified layered oxide and Pd/H-ZSM-5 are dealt with. NO<sub>x</sub> conversion of > 85% was observed in the range of 450–520 °C in the presence of 3% O<sub>2</sub>, 3% H<sub>2</sub>O, and 30 ppm SO<sub>2</sub> with GHSV 20,000 h<sup>-1</sup>.

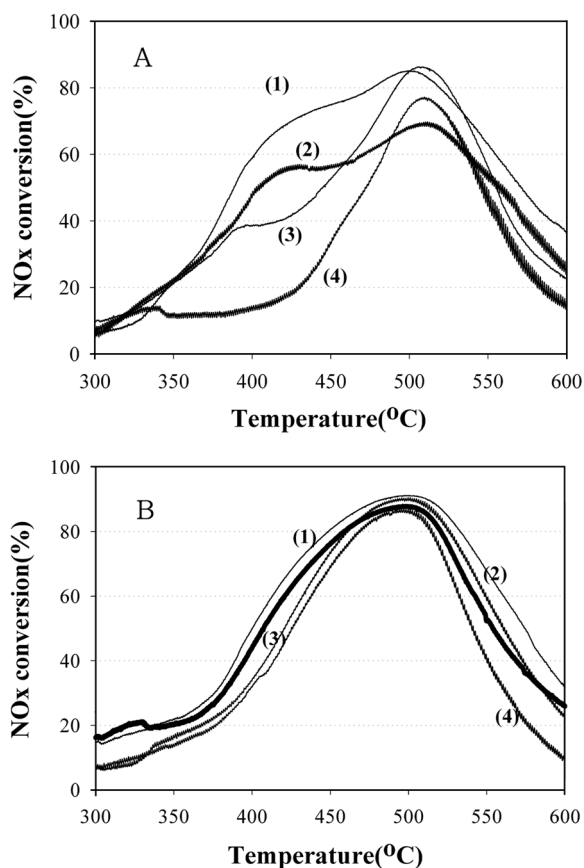
The Pd/H-ZSM-5 catalyst was prepared using NH<sub>4</sub>-ZSM-5 (Zeobuilder, Si/Al=20) by a conventional ion-exchange method using an aqueous PdCl<sub>2</sub> and NH<sub>4</sub>OH solution at 80 °C, followed by calcination at 500 °C in He for 4h. After filtration, the sample was washed with distilled water and dried at 110 °C. For the synthesis of modified layered oxide catalyst, a commercial MgAl<sub>2</sub>O<sub>4</sub> (SASOL MG50) was used as a support. MgO/MgAl<sub>2</sub>O<sub>4</sub> and CeO<sub>2</sub>-MgO/MgAl<sub>2</sub>O<sub>4</sub> were prepared by impregnating with Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution. The contents of CeO<sub>2</sub> and MgO were 12.3 and 5 wt%, respectively. After oven drying at 110 °C, the dried powder was calcined in air at 500 °C for 5 h. The catalytic study of NO<sub>x</sub> reduction was performed in a fixed-bed flow reactor at atmospheric pressure. The reaction gas contains a mixture of 1250 ppm NO, 4500 ppm CH<sub>4</sub>, 3–10% O<sub>2</sub>, 30 ppm SO<sub>2</sub> and 3% H<sub>2</sub>O in He flow and was fed over a catalyst (*ca.* 0.18 g) at a total flow-rate of 100 cm<sup>3</sup>/min, corresponding to a GHSV=20,000 h<sup>-1</sup>. The exit gases were analysed by a GC (HP 5890 series II) and a NO/NO<sub>x</sub> analyser (Kimoto Model 272). The NO<sub>x</sub> conversion is determined by the difference between the NO<sub>x</sub> concentration

before and after reaction. ESR spectra was recorded at 77 K with a Bruker ESP 300.

Figure 1 shows the influence of reaction temperature on the activity of Pd/H-ZSM-5 catalyst for the reduction of NO with methane. Over Pd/H-ZSM-5, two maximum peaks are observed at temperatures, 425 and 500 °C, indicating the existence of at least two different active sites on the catalyst surface. In our previous work,<sup>12</sup> both highly dispersed PdO and Pd<sup>2+</sup> or the protonic sites were shown to be catalytically active for the abatement of NO by methane and a synergistic activity was anticipated when they were combined properly.

The rise in NO<sub>x</sub> conversion follows that of CH<sub>4</sub> conversion and reaches a broad maximum where CH<sub>4</sub> conversion is close to completion. This indicates that CH<sub>4</sub> is used as a reducing agent during SCR of NO.

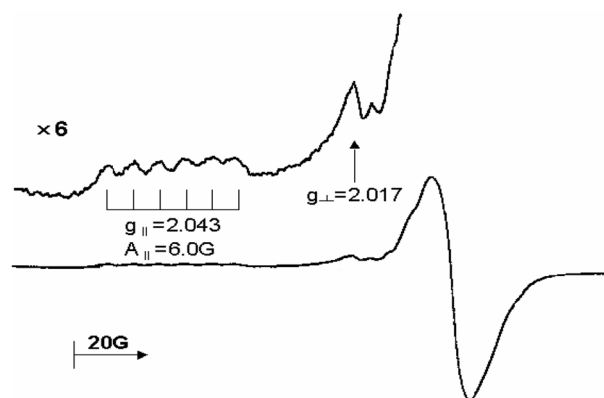
It is evident from Figure 1[A]-curve (2) that in presence of water vapor, NO<sub>x</sub> conversion is suppressed in the entire temperature range from 350 to 600 °C. At 500 °C, the conversion falls from 85% to 68%. Deleterious effect of water vapor on the activity of Ga-, In-, Co-exchanged zeolites for NO<sub>x</sub> reduction with methane had been commonly observed whereas a better water tolerance had been achieved for Pd-ZSM-5 catalysts containing the second metal ions including Rh<sup>13</sup> or Co.<sup>14</sup> Also, it is observed that in the presence of SO<sub>2</sub>, the NO<sub>x</sub> conversion is drastically suppressed at lower temperatures. At 425 °C, the NO<sub>x</sub> conversion falls from 70% to 40%. However, at higher temperatures, the effect is not severe, and at 500 °C, the NO<sub>x</sub> conversion is almost same even in the presence of SO<sub>2</sub>. Z. Li *et al.*<sup>15</sup> have reported that inhibition of the SCR reaction at low temperatures is caused by SO<sub>2</sub> adsorption on the active sites over Ce-Ag-ZSM-5 catalyst. However, this is fully reversible with temperature. In the presence of both H<sub>2</sub>O and SO<sub>2</sub>, Figure 1[A]-curve-4, the catalytic activity of Pd/H-ZSM-5 is reduced considerably at lower temperatures and remains active only at higher temperature. Figure 1[B] shows the activity of mixed catalyst for the reduction of NO<sub>x</sub> with methane. This mixed catalyst is made by physically mixing the 1 wt% Pd/HZSM-5 with 12.3 wt% CeO<sub>2</sub>-5 wt% MgO/MgAl<sub>2</sub>O<sub>4</sub> (1 : 1 weight ratio). The mixed catalyst showed a maximum activity (91%) at 497 °C in the absence of SO<sub>2</sub> and H<sub>2</sub>O. In the presence of water vapor, the NO<sub>x</sub> conversion is almost the same (90%). However, the temperature window becomes narrower than the dry condition. In the presence of SO<sub>2</sub>, the NO<sub>x</sub> conversion decreases to 87%



**Figure 1.** NO<sub>x</sub> conversion as a function of temperature during SCR of NO. [A] 1 wt% Pd/H-ZSM-5, [B] mixed catalyst. (1) NO 1250 ppm, CH<sub>4</sub> 4500 ppm, O<sub>2</sub> 3%. (2) (1) + H<sub>2</sub>O 3%. (3) (1) + SO<sub>2</sub> 30 ppm. (4) (1) + H<sub>2</sub>O 3% + SO<sub>2</sub> 30 ppm, and GHSV = 20,000 h<sup>-1</sup>. The mixed catalyst consists of 50 wt% of 1 wt% Pd/HZSM-5 in the mixture of 1 wt% Pd/HZSM-5 and 12.3 wt% CeO<sub>2</sub>-5 wt% MgO/MgAl<sub>2</sub>O<sub>4</sub>.

than in the absence of SO<sub>2</sub> at a wide temperature range. With H<sub>2</sub>O and SO<sub>2</sub> there is again a little reduction of the catalytic activity (86%) and temperature window becomes narrower. The mixed catalyst shows much higher activity, although it was obtained by physical mixing. The 12.3 wt% CeO<sub>2</sub>/5 wt% MgO/MgAl<sub>2</sub>O<sub>4</sub> itself shows no activity in NO<sub>x</sub> reduction. The highest catalytic activity was observed when the mixed catalyst consist of 50 wt% of 1 wt% Pd/HZSM-5 in the mixture of 1 wt% Pd/HZSM-5 and 12.3 wt% CeO<sub>2</sub>-5 wt% MgO/MgAl<sub>2</sub>O<sub>4</sub>.

An interesting finding in this work is the observation of hyperfine structure of ESR spectrum which is indicated in Figure 2. When oxygen is contacted at 100-200 °C onto Pd/H-ZSM-5 six hyperfine lines is observed due to the interaction between <sup>27</sup>Al nucleus (*I*=5/2) and the unpaired electron of superoxide ion, O<sub>2</sub><sup>-</sup>. ESR parameters, *g*<sub>||</sub> = 2.043, *A*<sub>||</sub> = 6G and *g*<sub>⊥</sub> = 2.017, is similar to the previous report.<sup>17</sup> This result indicates that there are some Lewis acid sites on Pd/H-ZSM-5 zeolite and aluminum atom is involved in the adsorption site for the O<sub>2</sub><sup>-</sup> ion. And also O<sub>2</sub><sup>-</sup> species formed



**Figure 2.** ESR spectra at 77 K of O<sub>2</sub> adsorbed on 1 wt% Pd/H-ZSM-5.

may be adsorbed aluminum site by which methane can be activated to enhance the NO-SCR activity.

Overall, the addition of modified layered oxide to Pd/H-ZSM-5 catalyst can increase the selective catalytic reduction of NO<sub>x</sub> with methane in the presence of excess O<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub>. Not only highly dispersed PdO and Pd<sup>2+</sup> or the Bronsted acid site but also Lewis acid site in Pd/H-ZSM-5 are responsible active sites for SCR of NO. And it seems that modified layered oxide (CeO<sub>2</sub>-MgO/MgAl<sub>2</sub>O<sub>4</sub>) can retard the thermal decomposition of Pd-species and enhance durability against SO<sub>2</sub> poisoning in the presence of excess O<sub>2</sub> and H<sub>2</sub>O.

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## References

- Li, Y.; Armor, J. N. *U.S. Patent* **1992**, 5,149,512.
- Kaucky, D.; Vondrova, A.; Dedecek, J.; Wichterlova, B. *J. Catal.* **2000**, 194, 318.
- Campa, M. C.; Pietrogiaconi, D.; Tuti, S.; Ferraris, G.; Indovina, V. *Appl. Catal. B* **1988**, 18, 151.
- Li, Y.; Armor, J. N. *J. Catal.* **1994**, 145, 1.
- Yogo, K.; Kikuchi, E. *Stud. Surf. Sci. Catal.* **1994**, 84, 1547.
- Wang, X.; Zhang, T.; Xu, C.; Sun, X.; Liang, D.; Lin, L. *Chem. Commun.* **2000**, 279.
- Nishizaka, Y.; Misono, M. *Chem. Lett.* **1994**, 237.
- Wen, B.; Sun, Q.; Sachtler, W. M. H. *J. Catal.* **2001**, 204, 314.
- Li, Z.; Flytzani-Stephanopoulos, M. *Appl. Catal. A* **1997**, 165, 15.
- Li, Y.; Armor, J. N. *Appl. Catal. B* **1993**, 3, L1.
- Li, Y.; Armor, J. N. *Appl. Catal. B* **1995**, 5, L257.
- Park, Y. K.; Lee, J. W.; Lee, C. W.; Park, S. E. *J. Mol. Catal. A* **2000**, 158, 173.
- Misono, M.; Nishizaka, Y.; Kawamoto, M.; Kato, K. *Stud. Surf. Sci. Catal.* **1997**, 105, 1501.
- Ogura, M.; Sugiura, Y.; Hayashi, M.; Kikuchi, E. *Catal. Lett.* **1996**, 42, 185.
- Li, Z.; Flytzani-Stephanopoulos, M. *Appl. Catal. B* **1999**, 22, 35.
- Vaccari, A. *Appl. Clay Sci.* **1999**, 14, 161.
- Wang, K. M.; Lunsford, J. H. *J. Phys. Chem.* **1969**, 73, 2069.