

DECOMPOSITION OF NO ON THE ALKALIZED Pt/Al₂O₃

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ABSTRACT

Catalytic decomposition of NO on platinum catalysts at 873-1173 K was investigated in the present work. The yield of N₂ in the NO decomposition process was significantly increased on the alkalizing Pt/Al₂O₃ catalyst. The enhancement may be attributed to a trap of additional NO molecules by basic sites of the alkalized catalyst. The interstitially adsorbed species (NaOH(NO)/Pt) might increase the NO adsorption strength during the catalytic NO reduction process. Pt on the high acidity HY was also active for catalytic decomposition of NO. Nevertheless, its activity decreased at higher temperatures (>1073 K) because of the distortion of the HY framework. Combined results of XPS (X-ray photoelectron spectra) and TPR (temperature programmed reduction) showed that PtO and PtO₂ were the main active species on the alkalized Al₂O₃ and HY during NO reduction.

Keywords: Platinum, TPR, NO decomposition.

INTRODUCTION

Emissions of nitrogen oxides (NO_x) from stationary and automotive sources cause many environmental problems including formation of acid rain, smog and degradation in atmospheric visibility. Different methods of NO_x abatement have been academically investigated and practically used [1]. The direct decomposition of NO to nitrogen and oxygen molecules is very attractive in NO emission controls mainly due to its chemical simplicity [2-5].

Thermodynamically, NO molecules ($\Delta G^\circ = 86.7 \text{ kJ mol}^{-1}$) are unstable towards decomposition into N₂ and O₂. However, homogeneous decomposition of NO does not proceed appreciably at <1473 K because of its high activation energy ($E_a > 254 \text{ kJ mol}^{-1}$) [6]. Therefore, many catalysts have been suggested to enhance the decomposition of NO at moderate reaction conditions [7-13]. Cu/ZSM-5 catalysts exhibit a decent activity for the direct decomposition of NO at a temperature of around 773 K [2-4]. However, the susceptibility of Cu to SO₂ poisoning and the rapid deactivation by H₂O severely limit the potential of Cu/ZSM-5 for practical applications [14].

Platinum and palladium have been widely used in exhaust-emission controls of conventional petroleum engines [15,16]. Palladium is active for catalytic oxidation of

hydrocarbons. However, a low NO_x reduction activity on palladium in the oxygen-rich exhaust has generally been found. Therefore, platinum and rhodium are usually used as the major components in converter catalysts [17,18]. Platinum oxides on Al₂O₃ with various chemical states such as PtO₂ [19,20], Pt₂O₄ [21], PtO [22], Pt₂O [23], PtAl₂O₄ [24] and Pt(NO_x) (430 K) [25] have been reported. In separated experiments, we found that decomposition of NO on Pd/Al₂O₃ catalysts at 825-1000 K was remarkably enhanced by a modification with NaOH [26,27]. The modifications have been attributed to a formation of NO_x (with $x > 2$) at the interface between palladium crystallites and NaOH during the catalytic decomposition in this temperature range. Platinum has a higher catalytic activity for decomposition of NO than palladium [28]. Thus, the aim of this work was to investigate the catalytic decomposition of NO on the alkalized Pt/Al₂O₃. For comparison, platinum supported on the acidic zeolite HY was also studied.

EXPERIMENTAL

γ -Al₂O₃ support (Merck, surface area = 108 m²g⁻¹) was alkalized with a NaOH solution (13 wt%) at 300 K. The alkalized Al₂O₃ was dried at 383 K and calcined at 823 K for four hours. The Pt catalysts were prepared by impregnation

of an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Strem, purity >99%) onto Al_2O_3 (1%Pt/ Al_2O_3), alkalinized $\gamma\text{-Al}_2\text{O}_3$ (1%alkalinized-Pt/ Al_2O_3) or zeolite HY (1%Pt/HY) (Tosoh, Si/Al = 5.6). These Pt catalysts were calcined at 823 K for four hours. Catalytic decomposition of NO (4% NO/He) was carried out at catalyst weight/gas volumetric flow rate (W/F) = 2 g sl⁻¹ in a fixed-bed flow reactor at 873-1173 K. Product gases were analyzed by a gas chromatography (GC) using a column of molecular sieve 5A. Yields of N_2 and O_2 during NO decomposition were expressed in $2[\text{N}_2]/[\text{NO}]_0$ and $2[\text{O}_2]/[\text{NO}]_0$ (where $[\text{NO}]_0$, $[\text{N}_2]$ and $[\text{O}_2]$ denote concentrations of NO in reactant and N_2 and O_2 in products, respectively).

In the temperature programmed reduction (TPR) experiments, fresh and used catalysts (alkalinized-Pt/ Al_2O_3 and Pt/HY) were reduced in a flow of 10% H_2 /He at a heating rate of 10 Kmin⁻¹. A thermogravimetry analyzer (TGA) (SDT 2960 simultaneous TGA-DTA) was used to monitor the weight change of the catalysts in the reduction process. NMR spectra of catalysts were recorded at 9.4 T in on Bruker Avance DSX 400 spectrometer. Zirconia rotors (4 mm outside diameter) were spun up to 5 kHz by dried compressed air. The ²⁷Al MAS NMR spectra were recorded at 104 MHz. X-ray photoelectron spectra (XPS) of catalysts were also measured

on a Physical Electronics PHI 1600 photoelectron spectrometer with a $\text{MgK}\alpha$ X-ray (1253.6 eV) at 400 W.

RESULTS AND DISCUSSION

Experimentally, catalytic decomposition of NO on Pt/ Al_2O_3 , alkalinized Pt/ Al_2O_3 , and Pt/HY catalysts was conducted at 873-1173 K. In Figure 1(a), the yield of N_2 on the Pt/ Al_2O_3 catalyst increases with the rising reaction temperature and reaches 30% at 1173 K. Generally, NO can be adsorbed on the surfaces of platinum and dissociated into nitrogen and oxygen atoms ($\text{NO}_{(g)} \rightleftharpoons \text{NO}_{(ad)} \rightleftharpoons \text{N}_{(ad)} + \text{O}_{(ad)}$). The adsorbed nitrogen and oxygen formed nitrogen and oxygen molecules ($2 \text{N}_{(ad)} \rightleftharpoons \text{N}_{2(g)}$; $2 \text{O}_{(ad)} \rightleftharpoons \text{O}_{2(g)}$), respectively [6].

Platinum in zeolite HY (acidic support) also exhibited an excellent activity towards decomposition of NO at 873-1073 K (Figure 2(a)). Observed high N_2 yields may result from the high dispersion of platinum in the channels/cages of HY. The N_2 yield for catalytic decomposition of NO on the Pt/HY catalyst reached 65% at 1073 K. However, the structure of the zeolite in the Pt/HY catalyst was not preserved at high temperatures during decomposition of NO and an abrupt reduction of activity was noted at $T > 1073$ K.

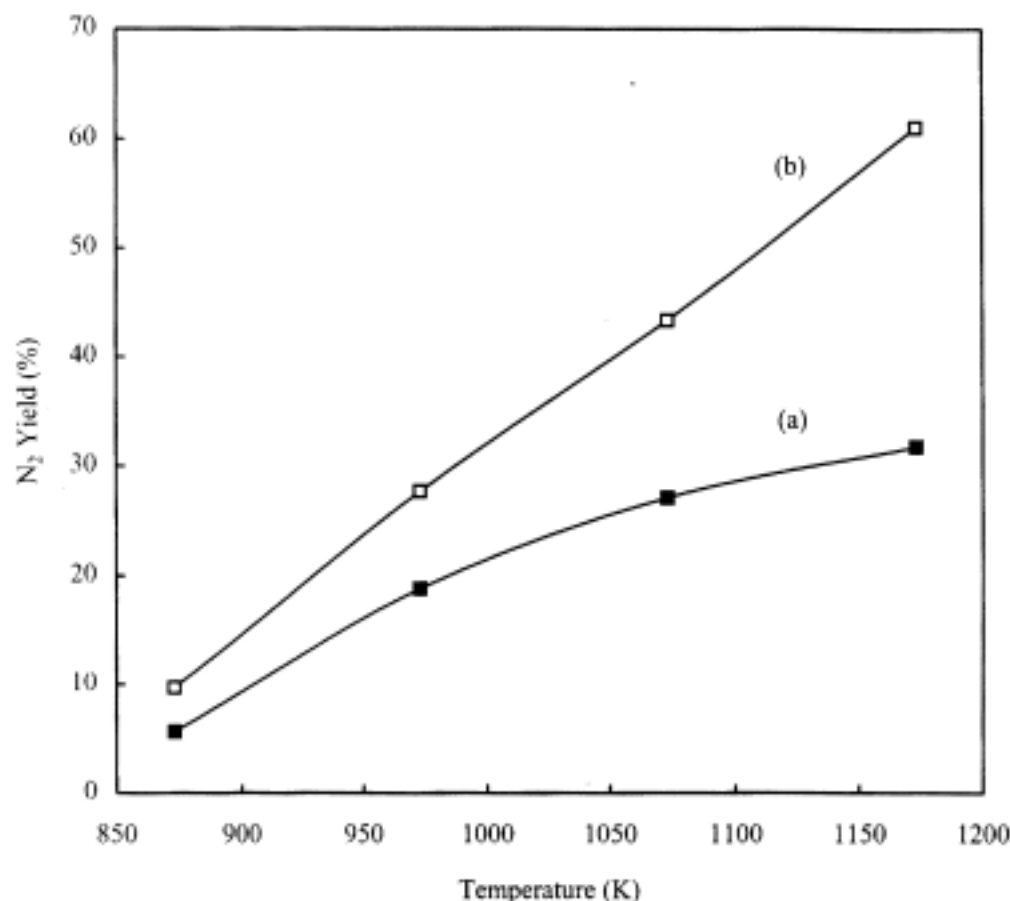


Figure 1. N_2 yields for decomposition of NO on (a) Pt/ Al_2O_3 and (b) alkalinized Pt/ Al_2O_3 .

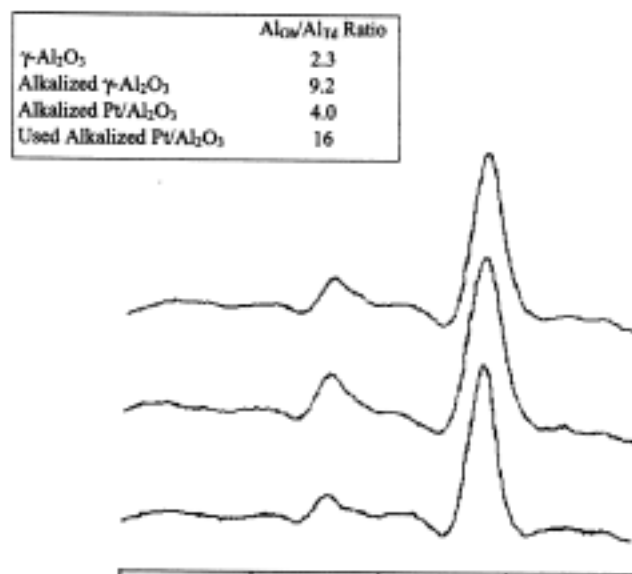


Figure 3. ²⁷Al NMR spectra of (a) used alkalized Pt/Al₂O₃ (obtained from the catalytic decomposition of NO at 1173 K for 40 min), (b) alkalized Pt/Al₂O₃, and (c) alkalized Al₂O₃.

catalysts were also studied. PtO and PtO₂ with binding energies ($Pt_{4d_{5/2}}$) of 317 and 315 eV, respectively, were found on the alkalized Al₂O₃ and Pt/HY catalysts. About 30% of PtO on the alkalized Pt/Al₂O₃ catalyst were oxidized to PtO₂ during catalytic decomposition of NO at (1173 K) for 40

minutes. PtO and PtO₂ were also the main surface species on the fresh and used Pt/HY catalyst.

Figure 4(a) shows that PtO and PtAl₂O₄ are the main platinum species of the alkalized Al₂O₃ that were reduced at 330 K and 500 K, respectively. TPR data also show that the

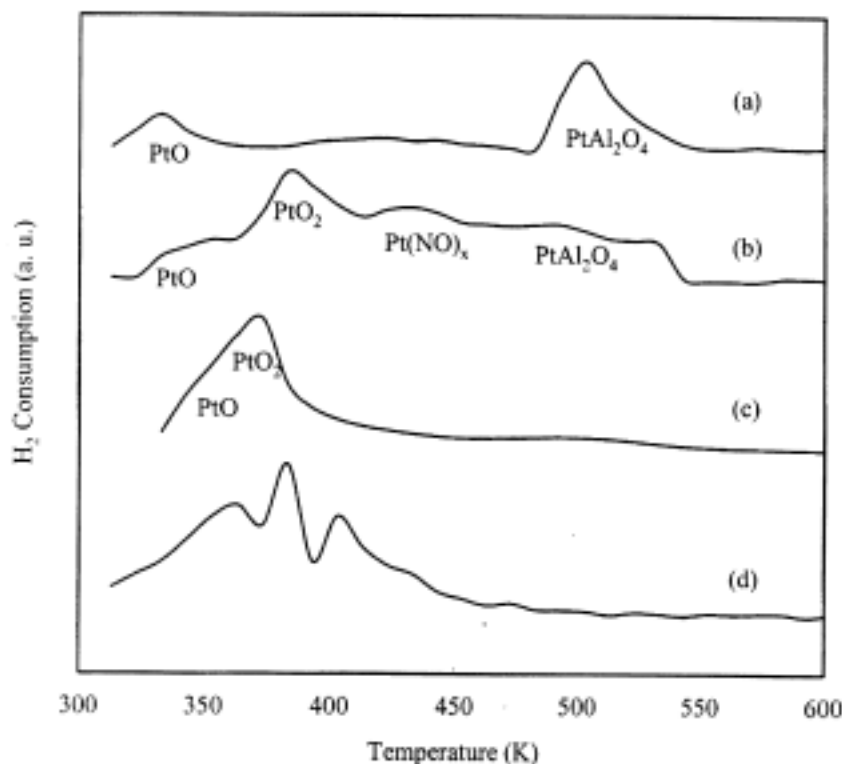


Figure 4. Temperature programmed reduction (TPR) of (a) alkalized Pt/Al₂O₃, (b) used alkalized Pt/Al₂O₃, (c) Pt/Y and (d) used Pt/Y (obtained from the catalytic decomposition of NO at 1173 K for 40 min.)

used alkalinized Pt/Al₂O₃ catalyst contains Pt species such as PtO (330 K), PtO₂ (380 K), Pt(NO₂) (430 K), and PtAl₂O₄ (500 K). Similar observations are reported in the literature [19,20,22,24,25]. The NaOH(NO)Pt species (I) was also observed at 530 K in the TPR feature. PtO and PtO₂ were also the main active species in the HY. PtAl₂O₄ was not observed in the TPR of the used Pt/HY catalyst.

CONCLUSIONS

Decomposition of NO over Pt/Al₂O₃ catalyst at a temperature of around 1000 K was significantly enhanced on alkalization with NaOH. The enhancement may be attributed

to an increase in the adsorption strength of NO. An interstitially adsorbed species (NaOH(NO)Pt) involves in providing extra NO on the alkalinized Pt/Al₂O₃. Decomposition of NO may also effectively catalyzed by the Pt/HY catalyst. By combined XPS and TPR, we found that PtO and PtO₂ were the active species on both catalysts during their catalysis of NO decomposition.

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REFERENCES

1. Curtin T., Grange P. and Delmon B., The effect of pretreatments on different copper exchanged ZSM-5 for the decomposition of NO. *Catal. Today*, **36**, 57-64 (1997).
2. Curtin T., Grange P. and Delmon B., The direct decomposition of nitrogen monoxide. *Catal. Today*, **35**, 121-127 (1997).
3. Zhang Y.P. and Flytzanistephanopoulos M., Hydrothermal stability of cerium modified Cu-ZSM-5 catalyst for nitric-oxide decomposition. *J. Catal.*, **164**, 131-145 (1996).
4. Gervasini A., Desorption study of NO and O₂ on Cu-ZSM-5. *Appl. Catal. B*, **14**, 147-159 (1997).
5. Nakanishi Y., Yoshihara Y. and Nishiwaki K., Non-catalytic reduction of NO in diesel exhaust with the addition of methylamine. *JSAE Rev.*, **21**, 4, 561-566 (2000).
6. Wu R.J. and Yeh C.T., Activation-energy for thermal-decomposition of nitric-oxide. *Int. J. Chem. Kinet.*, **28**, 89-94 (1996).
7. Lim K.J. and Boudart M., Nitrogen desorption in the reaction of nitric-oxide on carbon-supported platinum catalysts. *J. Catal.*, **105**, 263-265 (1987).
8. Wu R.J., Chou T.Y. and Yeh C.T., Enhancement effect of gold and silver on nitric-oxide decomposition over Pd/Al₂O₃ catalysts. *Appl. Catal. B*, **16**, 105-116 (1995).
9. Haruta M., Size-dependency and support-dependency in the catalysis of gold. *Catal. Today*, **36**, 153-166 (1997).
10. Teraoka Y., Fukuda H. and Kagawa S., Catalytic activity of perovskite-type oxides for the direct decomposition of nitrogen monoxide. *Chem. Lett.*, 1-4 (1990).
11. Vannice M.A., Walters A.B. and Zhang X., The kinetics of NO_x decomposition and NO reduction by CH₄ over La₂O₃ and Sr/La₂O₃. *J. Catal.*, **159**, 119-126 (1996).
12. Iwamoto M., Yahiro H., Mine Y. and Kagawa S., Excessively copper ion-exchanged ZSM-5 zeolites as highly-active catalysts for direct decomposition of nitrogen monoxide. *Chem. Lett.*, 213-216 (1989).
13. Valyon J. and Hall W.K. Studies of the desorption of oxygen from Cu-Zeolites during NO decomposition. *J. Catal.*, **143**, 520-532 (1993).
14. Fritz A. and Pitchon V., The current state of research on automotive lean NO_x catalysis. *Appl. Catal. B*, **13**, 1-15 (1997).
15. Burch R. and Watling T.C., The effect of promoters on Pt/Al₂O₃ catalysts for the reduction of NO by C₂H₆ under lean-burn conditions. *Appl. Catal. B*, **11**, 207-216 (1997).
16. Plisanu A.M. and Gigola C.E., NO decomposition and NO reduction by CO over Pd/ α -Al₂O₃. *Appl. Catal. B*, **20**, 179-189 (1999).
17. Chuang S.S.C., and Tan C.D., Promotion of oxygen desorption to enhance direct NO decomposition over Tb-Pt/Al₂O₃ catalyst. *J. Phys. Chem. B*, **101**, 3000-3004 (1997).
18. Kyomasu A., Okuhara T. and Misono M., Effects of additives to Pt/Al₂O₃ on catalytic decomposition of NO. *Nippon Kagaku Kaishi*, 651-652 (1991).
19. Lieske H., Lietz G., Spindler H. and Volter J., Reactions of platinum in oxygen- and hydrogen-treated Pt/ γ -Al₂O₃ catalysts/ - temperature programmed reduction and redispersion of platinum. *J. Catal.*, **81**, 8-16 (1983).
20. Lietz G., Lieske H., Spindler H., Hanke W. and Volter J., Reactions of platinum in oxygen- and hydrogen-treated Pt/ γ -Al₂O₃ catalysts/ - ultraviolet - visible studies, sintering of platinum and soluble platinum. *J. Catal.*, **81**, 17-25 (1983).
21. Caben D., Ibers J.A. and Mueller M.H., Platinum bronzes. II. Crystal structures of CaPt₂O₄ and Cd_{1-x}Pt_xO₄. *Inorg. Chem.*, **13**, 110-115 (1974).

22. Yao H.C., Sieg M. and Plummer H.K., Surface interactions in the Pt/ γ -Al₂O₃ system. *J. Catal.* **59**, 365-374 (1979).
23. Otter G.J.D. and Dautzenberg F.M., Metal-support interaction in Pt/Al₂O₃ catalysts. *J. Catal.*, **53**, 116-125 (1978).
24. Hwang C.P. and Yeh C.T., Platinum-oxide species formed by oxidation of platinum crystallites supported on alumina. *J. Molec. Catal. A*, **112**, 295-302 (1996).
25. Lin T.W., The behavior of Platinum species supported on NaY. BS Thesis, National Tsinghua University, Hsinchu, Taiwan, (1998).
26. Wang C.B., Chang J.G., Wu R.C. and Yeh C.T., Promotion effect of coating alumina-supported palladium with sodium-hydroxide on the catalytic conversion of nitric-oxide. *Appl. Catal. B*, **17**, 51-62 (1998).
27. Huang Y.J., Yeh C.T., Wang H.P., Tai C.C. and Peng, C.Y., Enhanced decomposition of NO on the alkalinized PdO/Al₂O₃ catalyst. *Chemosphere*, **39**, 2279-2287 (1999).
28. Bamwenda G.R., Ogata A., Obuchi A., Oi J., Mizuno K. and Skrzypek J., Selective reduction of nitric-oxide with propene over platinum-group based catalysts - studies of surface species and catalytic activity. *Appl. Catal. B*, **6**, 311-323 (1995).
29. Lee M.H., Cheng C.F., Heine V., Klinowaki J., Distribution of tetrahedral and octahedral Al sites in gamma-alumina. *Chem. Phys. Lett.*, **265**, 673-676 (1997).

