

Hydrocarbon SCR by Plasma Enhanced Catalysis over Nano-Size Gold Supported on Alumina for Lean NO_x Treatment

Dae-Won Lee^{1,2}, Jae-Hong Ryu², Dong-Hoon Jeong², Hyeong-Sang Lee³, Kwang Min Chun^{2,3} and Kwan-Young Lee¹

¹Korea University, Seoul, Korea. ²BluePlanet Co., Seoul, Korea. ³Yonsei University, Seoul, Korea

Introduction

The catalytic reduction of NO_x emission from lean burn or diesel engine exhaust has been a critical issue. Considering the diesel exhaust temperature ranges from 100 °C to 400 °C and a significant portion of NO_x emissions can be generated at 250~350 °C, most of up-to-date tested catalysts were eventually disqualified as DeNO_x catalyst [1,2]. Some researchers suggested “plasma-catalyst” strategy as the alternative of “catalyst only.” The combination of plasma-catalyst for lean DeNO_x has been examined using γ -alumina [3]. The plasma converts NO to NO₂ but doesn't convert SO₂ to SO₃ which is the leading component to poison the catalyst [4]. NO₂ and partially oxidized HC produced by plasma react with each other effectively on γ -alumina and widen the active temperature window but still did not cover low temperatures below 350 °C. In our previous study [5,6], plasma-Ag/Al₂O₃ showed an improved DeNO_x activity in the temperature range of 250~450 °C, where the catalyst was inactive in the case of being used alone. But the reduction activity (N₂ yield) decreased to near zero at the temperature below 250 °C. So we have tried to find other materials to achieve plasma-catalyst activity at this low temperature range.

The gold catalysts have been applied to lean DeNO_x catalysis in Ueda's work previously [7]. In this report, Au/Al₂O₃ was especially effective in producing N₂ but regrettably, it does not solve the aforesaid temperature problems. The catalyst needed high temperature of 350~500 °C to become efficient in NO conversion into N₂. The authors pointed out that the NO conversion into NO₂ is rate-determining and such high temperature was necessary to accelerate this step. The same research group tried to assist SCR activity of Au/Al₂O₃ by mechanically mixing with Mn₂O₃ which is active for NO oxidation to NO₂ and showed high N₂ yield of 70 % at 350 °C [8]. This report did not show reduction activity below 250 °C as well, but we could anticipate for better low-temperature DeNO_x performance by combining this catalyst with plasma activation, which could provide sufficient NO₂ and more active reductants of partially oxidized and organo-nitro hydrocarbons. In this study, we tried to apply nano-size Au supported on alumina to plasma-catalyst lean DeNO_x system.

Experimental

Au/Al₂O₃ catalysts were prepared by deposition-precipitation method. The nano-size distribution of metallic gold on the alumina support was examined by TEM, XRD and XPS. The DeNO_x activity of plasma-Au/Al₂O₃ system was observed using a plasma-catalyst series reactor as follows. A simulated diesel exhaust gas stream containing 1610ppm NO, 10% O₂, 3200ppm C₃H₆ (C₁/N = 6) with helium balance was flowed into the reactor at a rate of 1 L/min. The catalysts of 4.6 mL were packed to adjust space velocity at 13,000/h. The temperature of plasma reactor was fixed at 100 °C and the catalyst activity was tested within the ranges over 100~400 °C with decreasing manner to avoid adsorption effect on the catalysis. The plasma reactor was a dielectric barrier discharge (DBD) type and plasma energy density was 39 J/L.

Results and Discussion

The NO_x removal performance of Au/Al₂O₃ catalysts was successfully improved by being assisted by plasma. For total NO_x conversion and N₂ yield, even 0.2 wt% Au loaded Au/Al₂O₃ showed better plasma-catalyst performance than alumina. From this, it can be confirmed that Au is quite efficient to activate NO_x on its surface. The NO_x reduction into N₂ at low temperatures below 250°C was achieved by using catalysts in which Au amount over 1.0 wt% was included. In particular, the catalysts of more than 2.0 Au wt% showed N₂ yield over 10~20% at even lower temperatures of 100~200°C, which has never been reported yet. For this lower temperature activity, 2.0 wt% Au/Al₂O₃ showed the highest activity as shown in Fig. 1. The low temperature DeNO_x activity of plasma-Au/Al₂O₃ was noteworthy and it can be emphasized that the activity was brought by nano-size distribution of active Au metal. The relatively high value of total NO_x conversion of 40% at temperatures of 100~200°C could be caused by the high adsorption capacity (especially for NO₂) of metallic gold supported on alumina. The bare alumina also exhibited some adsorption but did not reach the case of Au/Al₂O₃. The XRD analysis showed that Au metal on catalysts consisted of (111) crystal phase in the largest portion, which has been recognized as the most active crystal phase of gold metal for NO_x adsorption [9].

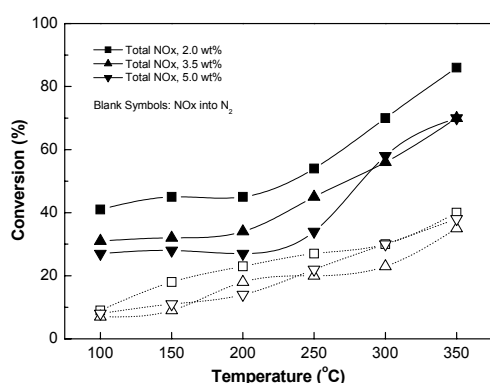


Fig. 1. The Effect of Au Amount on the DeNO_x Activity of Plasma-Au/Al₂O₃.

Even though alumina captures oxygenated hydrocarbons so effectively, alumina alone was supposed not to produce N₂ as much as Au/Al₂O₃ owing to the lack of available NO_x on the surface. The NO_x species on the Au surface would supply this shortage if their supplying rate to hydrocarbons anchored on alumina was fast enough. Taking account that NO_x species can meet adsorbed hydrocarbons on the interface between Au and alumina, the formation of nano-sized Au particles resulted in the increase of Au-alumina interface and consequently, the migration speed of NO_x could be promoted. This is supposed to be the main cause of catalytic activity of Au/Al₂O₃ in the respect of structure.

References

1. Shelef, M., *Chem. Rev.*, **95**(1), 209 (1995).
2. Majewski, W. A., *DieselNet Technology Guide*, Address: http://www.dieselnet.com/tech/cat_lean-nox.html (2001).
3. Penetrante, B. M., Brusasco, R. M., Merritt, B. T., Pitz, W. J., Vogtlin, G. E., Kung, M.C., Kung, H. H., Wan C. Z. and Voss, K. E., *SAE Technical Paper*, 982508 (1998).
4. Penetrante, B. M., Brusasco, R. M., Merritt, B. T. and Vogtlin, G. E., *SAE Technical Paper*, 1999-01-3687 (1999).
5. Chun, B.-H., Lee, H.-S., Nam, C.-S., Ryu, J.-H., Lee, K.-Y., and Chun, K. M., *SAE Technical Paper*, 2000-01-2897 (2000).
6. Lee, H.-S., Chun, K. M., Song, S. J., Ryu, J. H., Lee, D.-W., Lee, K.-Y. and Chun, B. H., *Proceeding of the Combustion Institute*, **28**, 1227 (2000).
7. Ueda, A., Oshima, T. and Haruta, M., *Appl. Catal., B: Envir.*, **12**, 81 (1997).
8. Ueda, A. and Haruta, M., *Appl. Catal., B: Envir.*, **18**, 115 (1998).
9. Wang, J. and Koel, B. E., *J. Phys. Chem., A*, **102**(44), 8573 (1998).