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Catalysis Today 111 (2006) 229–235

CATALYSIS TODAY

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Selective catalytic reduction of NOx with propene over double wash-coat monolith catalysts

Chan-Soon Kang [a], Young-Jae You [a], Ki-Joong Kim [a], Tae-hee Kim [a],
Seong-Jun Ahn [a], Kyong-Hwan Chung [b], Nam-Cook Park [c],
Shoichi Kimura [d], Ho-Geun Ahn [a,*]

[a] *Department of Chemical Engineering, Sunchon National University, 315 Maegok-dong, Suncheon-si, Jeonnam 540-742, Republic of Korea*
[b] *Korea Institute of Culture Technology, Gokseong-kun, Jeonnam 516-853, Republic of Korea*
[c] *Department of Chemical Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea*
[d] *Department of Chemical Engineering, Oregon State University, 102 Gleeson Hall, Corvallis 97331-2702, USA*

Abstract

Selective catalytic reduction (SCR) among the approaches for alleviating NOx emission was much attracted. Zeolites have the advantage for adsorption of propene, and noble metal catalyst has the advantage for oxidation of NO to NO_2. Pt (or Au)/Al_2O_3 (or SiO_2) were used as the lower layer of double wash-coated monolith catalysts. Zeolites (H-mordenite or ZSM-5) were coated as the upper layer. The catalytic performance of the double wash-coated catalyst was, remarkably, improved. Also, temperature window was shifted to lower temperature and broadened. It was known that the combined noble metal monolith catalyst with zeolite was very effective in removing NOx by SCR with hydrocarbons.

Keywords: NOx; Double wash-coat; Monolith; SCR; Propene

1. Introduction

Nitrogen oxides (NOx) in the exhaust of both automobile and stationary sources are of critical concern because these byproducts are toxic environmental pollutants that lead to acid rain and technological challenges have been poured to remove them [1]. To alleviate NOx emission, variety of approaches has been applied such as direct catalytic decomposition of NOx, selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), adsorption, and wet absorption, etc.

Especially, SCR was much attracted to us because it has much advantage such as lower operation temperature and the efficiency. Addition of reducing agent is required for the selective conversion of NOx to N_2 in the presence of oxygen [2–7]. Noble metals, zeolites, and metal oxides were used as the catalysts for SCR, and ammonia, urea, carbon monoxide, methane, ethylene, propene, and methanol, etc., were introduced into reactants as the reducing agents. However, most catalysts have the narrow temperature window and low conversion of NOx at lower temperature.

Obuchi et al. [8] have applied double-layered catalysts to SCR of NOx with hydrocarbon. In general, zeolite is advantageous in the adsorption of propene, and noble metal catalysts have the advantages in the oxidation of NO to NO_2. If two kinds of catalysts were separately coated on monolith, new catalyst system would be developed [9,10].

In this study, Pt (or Au)/Al_2O_3 (or SiO_2) catalysts were coated as a lower layer on monolith. Zeolites of the upper layer were mordenite and HZSM-5. The double wash-coat monolith catalyst was applied to SCR of NOx with propene. The SCR activity of NOx was investigated under the presence of oxygen. Also, the role of two layers was discussed with the results from temperature-programmed desorption of NO and propene.

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* Corresponding author. Tel.: +82 61 750 3583; fax: +82 61 750 3580.
E-mail address: hgahn@sunchon.ac.kr (H.-G. Ahn).

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doi:10.1016/j.cattod.2005.10.031

2. Experimental

2.1. Catalyst preparation

Mini-size monolith (M) as a substrate was prepared by cutting out of a honeycomb with 400 cell/in^2. Diameter of the monolith was ca. 20 mm (12 g). The monoliths were coated by first immersing it into 50% (w/w) solution of aluminum nitrate or silica, followed by drying at 100 °C for 2 h and calcining at 600 °C for 3 h. Loading of Al_2O_3 or SiO_2 was ca. 9 wt.% with respect to monolith.

Gold on Al_2O_3/M (or SiO_2/M) was coated by deposition method (DP) using ammonium hydrogen carbonate (NH_4HCO_3, Junsei Chem.). Precursor of gold was chloroauric acid ($HAuCl_4 \cdot 6H_2O$, Aldrich Chem.). The resulting monolith was dried at 100 °C overnight, and calcined at 400 °C for 3 h. Consequently, Au/Al_2O_3/M (or Au/SiO_2/M) catalyst was prepared. Also, Pt/Al_2O_3/M (or Pt/SiO_2/M) catalyst was prepared by impregnation method (IMP). Precursor of platinum was chloroplatinic acid ($H_2PtCl_6 \cdot 5.1H_2O$, Aldrich Chem.). The obtained monoliths were dried at 100 °C overnight, and calcined at 400 °C for 3 h.

The upper layer was coated by immersing the lower layered monolith into well-mixed water slurry that was composed of 3 g of a zeolite and 5 cc of colloidal silica (Aldrich Chem.), followed by drying at 100 °C and calcining at 500 °C for 3 h. The used zeolites as the upper layer were H-mordenite (HM), Cu-mordenite (CuM), HZSM-5 and CuZSM-5. HM, JRC-Z-HM15(2) of Japanese reference catalyst. Cu-mordenite (CuM) was prepared by ion exchange of HM [11,12].

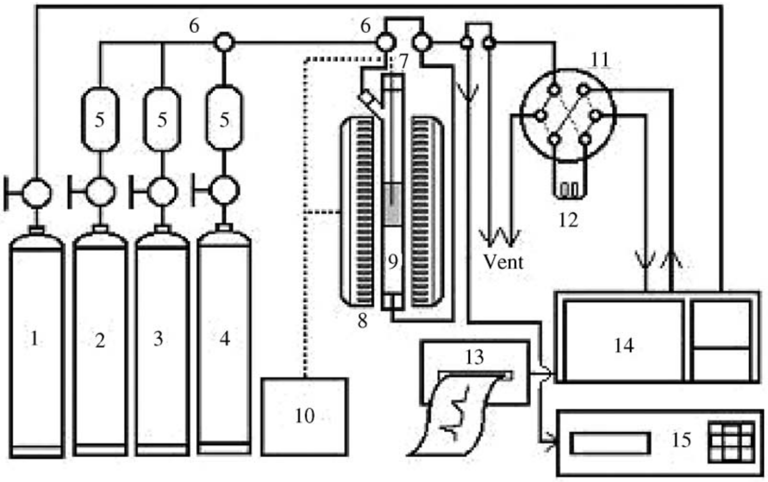
The particles of platinum or gold on lower layer and coated zeolites were observed with TEM and SEM, respectively. The contents of platinum or gold in lower layer were determined by means of Inductively Coupled Plasma Spectrometer (ICP, D-TIME 3000DC, Perkin-Elmer).

2.2. Catalytic activity

The schematic apparatus for measuring the activity of double wash-coat monolith catalyst in SCR with propene is shown in Fig. 1. Catalytic activity was measured by using a flow-type reactor under atmospheric pressure. The reactor was made of the Pyrex with a diameter 22 mm and length 350 mm. Reactant was composed of 5000 ppm NO, 2.5 mol% O_2, and 5000 ppm C_3H_6 balanced with helium. The reaction temperature was controlled by inserting thermocouple (Al–Cr) of ϕ0.2 mm into a centered cell of monolith. Total flow rate of the mixed gas was mainly 60 cc/min. The concentration of NOx (NO, NO_2) was measured by using a NOx analyzer (CLD-700EL, ECO Physics), and C_3H_6 in reactants and products were analyzed by using Gas Chromatograph (GC-14B, Shimadzu).

2.3. Temperature-programmed desorption of NO and propene

Temperature-programmed desorption (TPD) experiments were carried out by using a stainless steel tube of U type (i.d.



1. Helium Cylinder
2. C_3H_6/O_2/He Cylinder
3. NO/He Cylinder
4. Helium Cylinder
5. Mass Flow Controller
6. 3-way Valve
7. Thermocouple
8. Electric Furnace
9. Reactor
10. Temp. Controller
11. 6-way Valve
12. Sampling Loop
13. Data Processor
14. Gas Chromatograph
15. NOX analyrer

Fig. 1. Schematic diagram of experimental apparatus for measuring the activity of SCR catalyst.

ϕ4.35 mm). The catalyst (0.5 g) was put in the tube, and pretreated under helium stream (30 cc/min) at 300 °C. The adsorption of propene or NO on the double wash-coat monolith catalyst was performed with feeding NO (1 mol%, He bal.) gas or propene (1 mol%, He bal.) gas at room temperature. After attained the adsorption equilibrium, the catalyst was sufficiently purged by helium stream. The TPD responses were obtained as thermal conductivity detector (TCD) signal of Gas Chromatograph (GC-14B, Shimadzu). When the response became to be constant, temperature of the catalyst was raised with rate of 6.5 °C/min to 600 °C by using temperature programmer (Han-Young, NP200).

3. Results and discussion

3.1. Particle size of gold or platinum

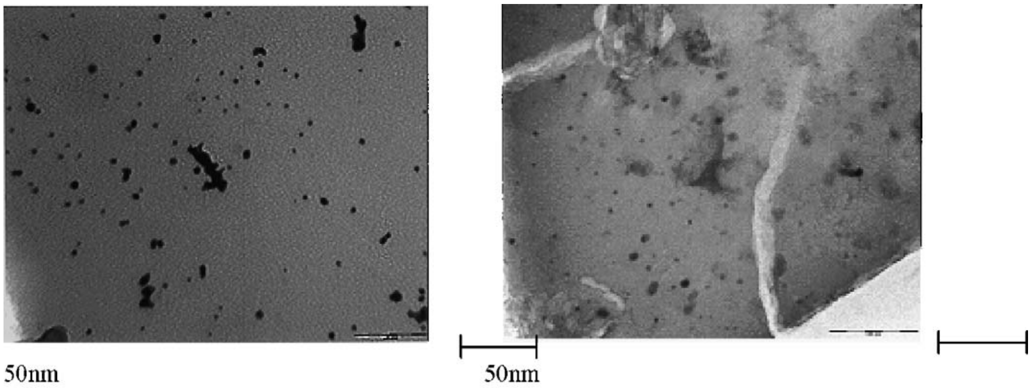
Dispersion state of gold or platinum particles on SiO_2/M and Al_2O_3/M with only lower layer was observed with TEM. Fig. 2 shows TEM images of Au/Al_2O_3/M, Pt/Al_2O_3/M, Au/SiO_2/M, and Pt/SiO_2/M catalysts. The coated gold particles were uniformly dispersed on Al_2O_3/M or SiO_2/M, and its average particle size was about 3–4 nm. The platinum particles were uniformly dispersed on SiO_2/M and Al_2O_3/M in the range of particle sizes below 5 nm. The gold and platinum particles could be highly dispersed on monolith like on power supports.

Surface state of the double wash-coated catalysts was observed by SEM. Fig. 3 shows SEM images for Al_2O_3/M, HM//Pt/Al_2O_3/M, SiO_2/M, and HM//Pt/SiO_2/M. SiO_2 on monolith was present with particles, but Al_2O_3 was cracked by condensation during drying and calcination. H-mordenite powder in upper layer was well coated by colloidal silica as a binder. Also, similar surface state was found on another catalysts.

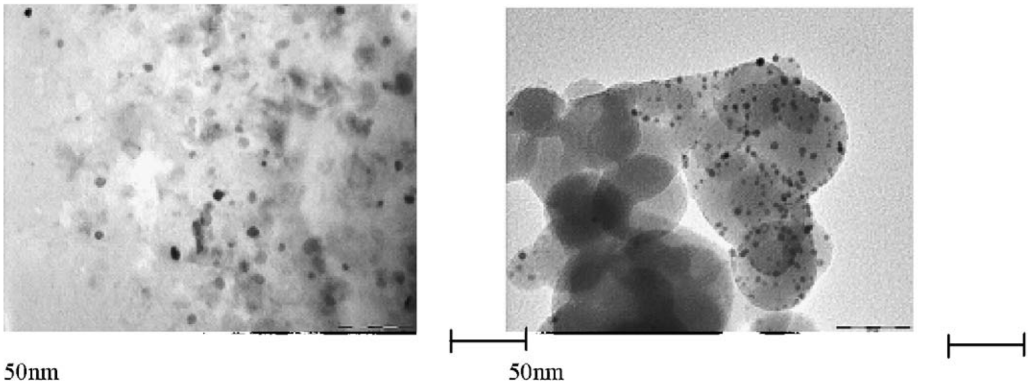
3.2. Catalytic activity of double wash-coat catalysts

When NO and O_2 in feed stream were mixed, NO_2 was formed before reaching to the inlet of the reactor. Concentration of NOx in reactant was measured with bypassing the reactor, and was regarded as the initial concentration in feed.

First of all, effect of NOx removal over the monolith catalysts without the lower layer was investigated. Fig. 4 shows the variation of conversion of NOx and propene over Cu/M and HM/M catalysts with reaction temperature. The conversion of HM/M catalyst at 450 °C was ca. 40%, and that of CuM/M catalysts was greatly increased to 70% even at 400 °C. Concentration of propene was rapidly reduced with increasing the reaction temperature, and oxidized completely at maximum conversion of NOx. This result indicates that maximum activity appears at higher temperature, and that temperature window is very narrow.

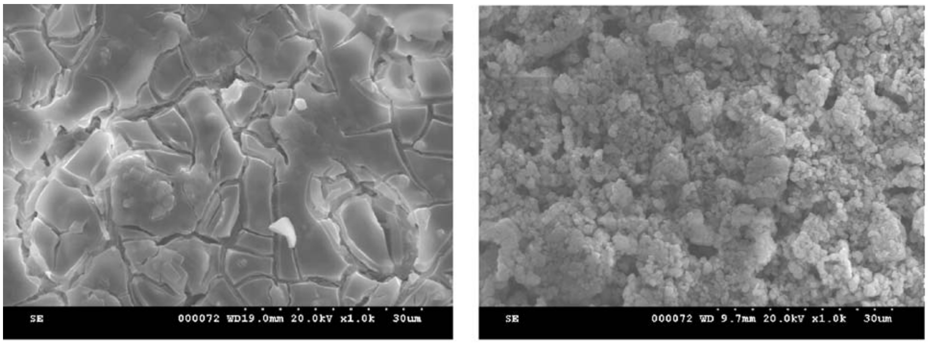


(a) Au/Al_2O_3/M(DP) (b) Pt/Al_2O_3/M(IMP)

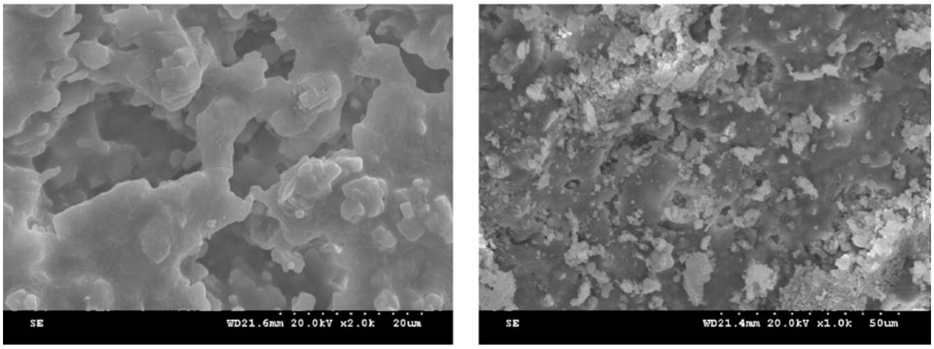


(c) Au/SiO_2/M(IMP) (d) Pt/SiO_2/M(IMP)

Fig. 2. TEM images of: (a) gold and (b) platinum-coated monolith catalysts.



(a) Al_2O_3/M (b) $HM//Pt/Al_2O_3/M$



(c) SiO_2/M (d) $HM//Pt/SiO_2/M$

Fig. 3. SEM images of: (a) Al_2O_3/M; (b) $HM//Pt/Al_2O_3/M$; (c) SiO_2/M; (d) $HM//Pt/SiO_2$ (×1000).

Fig. 5 shows the variation of NOx and propene conversion with reaction temperature over $Au/Al_2O_3/M$ and $HM/Au/Al_2O_3/M$ catalysts. The conversion of $Au/Al_2O_3/M$ catalyst at 400 °C was ca. 55%. However, the monolith catalyst coated with H-mordenite as the upper layer on $Au/Al_2O_3/M$ was greatly increased to 70% even at same temperature. Concentration of propene was rapidly reduced with increasing the reaction temperature, and completely oxidized at 450 °C. As a result, the maximum activity of $HM/Au/Al_2O_3/M$ catalyst was higher than $Au/Al_2O_3/M$ catalyst because of the upper layer of H-mordenite on $Au/Al_2O_3/M$.

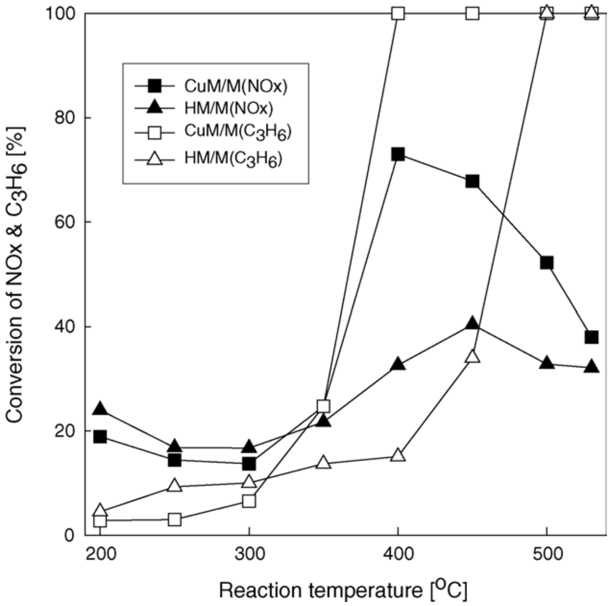


Fig. 4. Effect of reaction temperature on conversion of NO and C_3H_6 over HM/M, CuM/M catalysts.

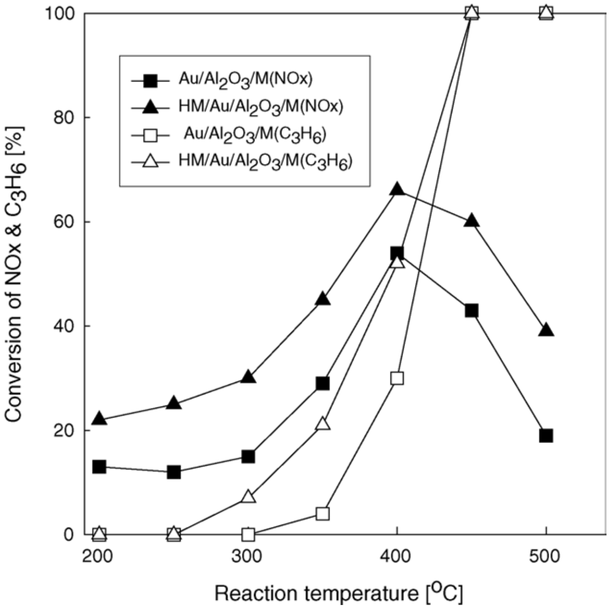


Fig. 5. Effect of reaction temperature on conversion of NO and C_3H_6 over $Au/Al_2O_3/M$ and $HM/Au/Al_2O_3/M$ catalysts.

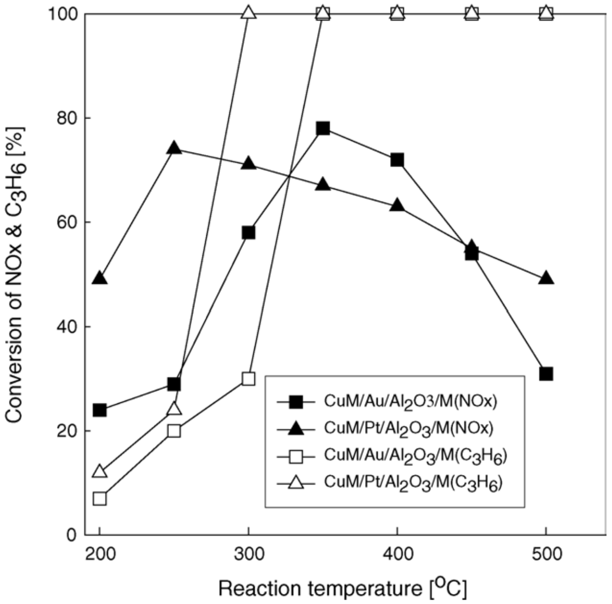


Fig. 6. Effect of reaction temperature on conversion of NO and C_3H_6 over CuM//Au/Al_2O_3/M and CuM//Pt/Al_2O_3/M catalysts.

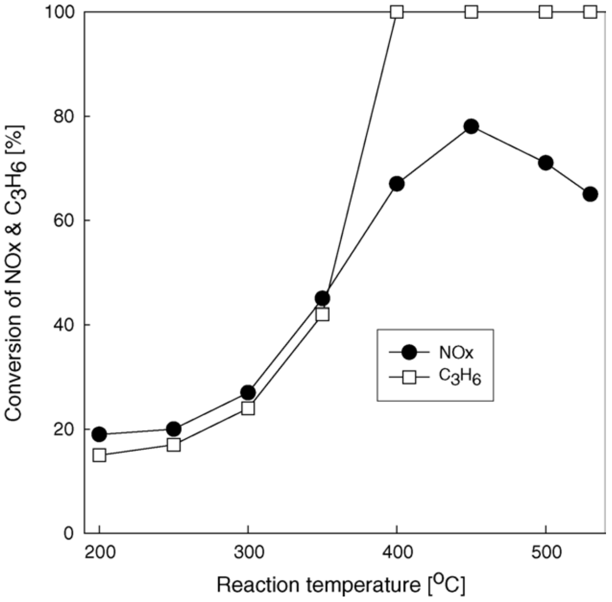


Fig. 8. Effect of reaction temperature on conversion of NO and C_3H_6 over CuZSM-5//Au/Al_2O_3/M catalyst.

Fig. 6 shows the variation of NOx and propene conversion with reaction temperature over CuM//Au/Al_2O_3/M and CuM//Pt/Al_2O_3/M, respectively. When CuM was substituted for HM of the upper layer, conversion of NOx was more increased. The maximum activity on CuM//Au/Al_2O_3/M was obtained at ca. 350 °C that was shifted to lower temperature. Also, temperature window was remarkably broadened comparing with that of Au/Al_2O_3/M catalyst. Moreover, removal performance of NOx was enhanced when gold of lower layer was substituted for platinum. The conversion of NOx is rapidly decreased with decreasing concentration of propene from reaction temperature of 250 °C, and propene was completely oxidized at 300 °C. The maximum activity on CuM//Pt/Al_2O_3/M was obtained at 250 °C. The temperature window of this catalyst was more broadened than that of CuM//Au/Al_2O_3/M catalyst and shifted to lower temperature, but the conversion was lower. These results implied that the double wash-coat catalyst was very effective for the SCR of NOx with propene.

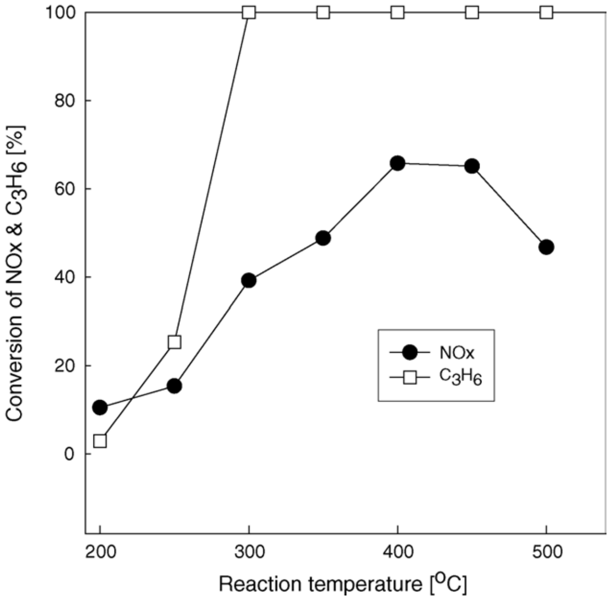


Fig. 7. Effect of reaction temperature on conversion of NO and C_3H_6 over CuM//Pt/SiO_2/M catalyst.

Fig. 7 shows the variation of NOx and propene conversion with reaction temperature over CuM//Pt/SiO_2/M catalyst. The support of lower layer in this catalyst was SiO_2 as a substitute of Al_2O_3. The maximum activity of CuM//Pt/SiO_2/M catalyst was higher than that of Pt/SiO_2/M catalyst without upper layer, but much poor than that of CuM//Pt/SiO_2/M catalyst. In other words, maximum conversion was obtained at 400 °C, and temperature window was shifted to higher temperature. It was known that Al_2O_3 was proper as the support of noble metal in lower layer.

Fig. 8 shows the variation of NOx and propene conversion with reaction temperature over CuZSM-5//Au/Al_2O_3/M catalysts. The concentration of NOx was rapidly decreased with the decrease of propene from reaction temperature of 250 °C, and the maximum activity on CuZSM-5//Au/Al_2O_3/M was obtained at 450 °C. The conversion of NOx was similar to that of CuM//Au/Al_2O_3/M catalyst. The removal performance of this catalyst was better than HZSM-5//Au/Al_2O_3/M.

3.3. Temperature-programmed desorption

Fig. 9 shows TPD spectra of NO and propene for Pt/SiO_2/M and CuM//Pt/SiO_2/M catalysts. In NO response, basic pattern on CuM//Pt/SiO_2/M was same as that on Pt/SiO_2/M, but unique small peak between 250 and 300 °C appeared on

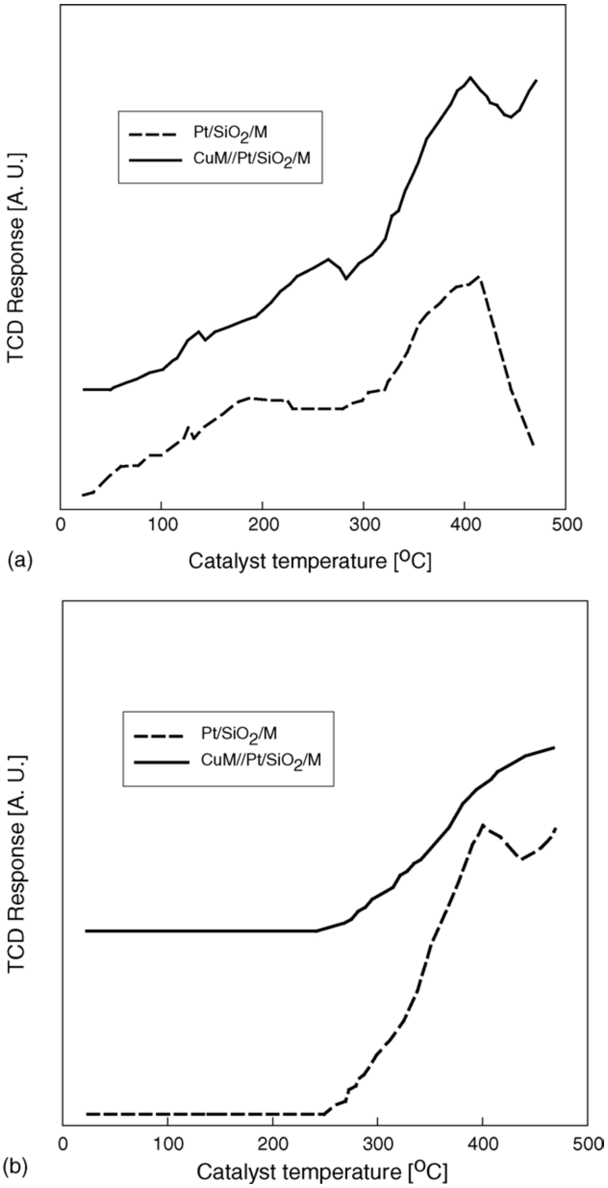


Fig. 9. TPD spectra of NO and C_3H_6 over Pt/SiO_2/M and CuM//Pt/SiO_2/M catalysts.

CuM//Pt/SiO_2/M. This small peak may be due to NO adsorbed on CuM. It was so considered that NO corresponding to basic pattern might permeate to the lower layer even though CuM was present on upper layer.

A large amount of propene can be adsorbed onto the lower layer. Desorption peak obtained from Pt/SiO_2/M increased faster from catalysts temperature of about 250 °C, but that obtained from CuM//Pt/SiO_2/M increased slowly. And amount of propene desorbed from Pt/SiO_2/M is much more than that from CuM//Pt/SiO_2/M. In other words, CuM as upper layer inhibited the adsorption of propene onto the lower layer. It was, therefore, considered that CuM of CuM//Pt/SiO_2/M prevented the propene from entering onto Pt/SiO_2 layer, and the adsorbed propene react easily with NO_2 departing from lower layer.

3.4. Mechanism

Fig. 10 shows conceivable reaction mechanism for double wash-coat catalysts on basis of the above results. The role of zeolite in upper layer was to permeate NO and oxygen selectively. Propene was mainly adsorbed on zeolite in upper layer. The adsorbed propene reacts rapidly with NO_2, which was formed by NO + O_2 reaction in lower layer. The upper layer was considered to be a membrane that has substantially different permeability and adsorption capacity to the various reactants and products.

4. Conclusions

Catalytic performance of double wash-coated monolith catalysts was examined for SCR of NOx with C_3H_6. In this study, Au (or Pt) supported on Al_2O_3 (or SiO_2) was applied to the lower layer of double wash-coated monolith catalyst, and the upper layer was zeolite (H-mordenite, Cu-mordenite, HZSM-5, CuZSM-5). The double wash-coated catalysts were more active than the catalyst with only zeolite or without the upper layer. Temperature window of CuM//Pt/Al_2O_3/M was broadened and shifted towards lower temperature. It was known that two-functional monolith catalyst was effective in controlling NOx in exhaust gas by SCR with hydrocarbons.

Acknowledgement

This research was supported by the Program for the Training of Graduate Students in Regional Innovation, which was conducted by the Ministry of Commerce, Industry and Energy of the Korean Government.

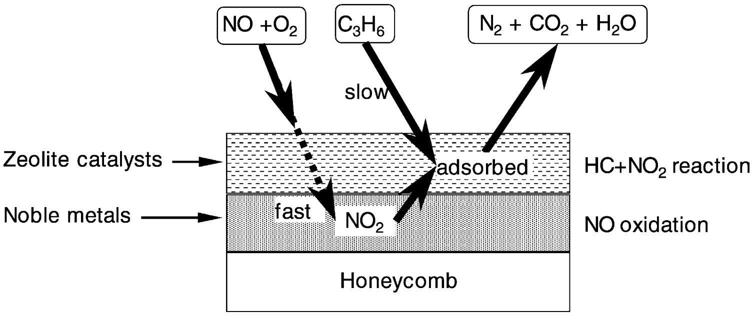


Fig. 10. Conceivable mechanism for SCR with propene on double wash-coat catalysts.

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