

REFERENCES

1. Chauvel, A., and Lefebvre, G. Petrochemical process, Technical and economic characteristics: 2. Major oxygenated chlorinated and nitrated derivatives. Houston: Gulf Publishing Company, 1989.
2. Bosch, H., and Janssen, F. Catalytic reduction of nitric oxides: A review on the fundamentals and technology. Catal. Today 2 (1988): 369-521.
3. Williams, I. Environmental Chemistry: A modular approach. Chichester: John Wiley & Sons, 2001.
4. De Nevers, N. Air pollution control engineering. New York: McGraw-Hill, 1995.
5. Cooper, C. D., and Alley, F. C. Air pollution control: A design approach. Illinois: Waveland Press, 1994.
6. Armor, J. N. Environmental catalysis. Appl. Catal. B 1 (1992): 221-256.
7. Cohn, G., Steele, D., and Andersen, H. U.S. Patent 2,975,025, 1961.
8. Heck, R. M., and Farrauto, R. J. Catalytic air pollution control: Commercial technology. New York: Van Nostrand Reinhold, 1995.
9. Wei, J. Catalysis for motor vehicle emissions. Adv. Catal. 24 (1975): 57-129.
10. Iwamoto, M., Yokoo, S., Sakai, K., and Kagawa, S. Catalytic decomposition of nitric oxide over copper(II)-exchanged Y-type zeolites. J. Chem. Soc., Faraday Trans. 1 77 (1981): 1629-1638.
11. Shelef, M. Selective catalytic reduction of NO_x with N-free reductants. Chem. Rev. 95 (1995): 209-225.
12. Li, Y., and Hall, W. K. Catalytic decomposition of nitric oxide over Cu-zeolites. J. Catal. 129 (1991): 202-215.
13. Inui, T., Iwamoto, S., Kojo, S., and Yoshida, T. Decomposition of nitric oxide on metallosilicates under a large excess oxygen condition with coexistence of a low concentration of cetane. Catal. Lett. 13 (1992): 87-94.
14. Iwamoto, M., Furukawa, H., Mine, Y., Uemura, F., Mikuriya, S., and Kagawa, S. Copper(II) Ion-exchanged ZSM-5 zeolites as highly active catalysts for direct and continuous decomposition of nitrogen monoxide. J. Chem. Soc., Chem. Commun. (1986): 1272-1273.

15. Sato, S., Yu-u, Y., Yahiro, H., Mizuno, N., and Iwamoto, M. Cu-ZSM-5 zeolite as highly active catalyst for removal of nitrogen monoxide from emission of diesel engines. Appl. Catal. 70 (1991): L1-L5.
16. D'Itri, J. L., and Sachtler, W. M. H. Reduction of NO over impregnated Cu/ZSM-5 in the presence of O₂. Catal. Lett. 15 (1992): 289-295.
17. Held, W., Konig, A., Richter, T., and Puppe, L. Catalytic NO_x reduction in net oxidizing exhaust gas. SAE 900496, 1990.
18. Iwamoto, M. Decomposition of NO on copper ion-exchanged zeolite catalysts. Proceeding of Meeting of Catalytic Technology for Removal of Nitrogen Monoxide. Tokyo (1990): 17-22.
19. Montreuil, C. N., and Shelef, M. Selective reduction of nitric oxide over Cu-ZSM-5 zeolite by water-soluble oxygen-containing organic compounds. Appl. Catal. B 1 (1992): L1-L8.
20. Ansell, G. P., Diwell, A. F., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, A. P. Mechanism of the lean NO_x reaction over Cu/ZSM-5. Appl. Catal. B 2 (1993): 81-100.
21. Centi, G., Perathoner, S., and Dall'Olio, L. Modification of the surface reactivity of Cu-MFI during chemisorption and transformation of the reagents in the selective reduction of NO with propane and O₂. Appl. Catal. B 7 (1996): 359-377.
22. Smits, R. H. H., and Iwasawa, Y. Reaction mechanisms for the reduction of nitric oxide by hydrocarbons on Cu-ZSM-5 and related catalysts. Appl. Catal. B 6 (1995): L201-L207.
23. Yahiro, H., and Iwamoto, M. Copper ion-exchanged zeolite catalysts in deNO_x reaction. Appl. Catal. A 222 (2001): 163-181.
24. Gaudin, C., Duprez, D., Mabilon, G., and Prigent, M. Effect of pretreatments in various atmospheres on the transient DeNO_x activity of a Cu-MFI catalyst. J. Catal. 160 (1996): 10-18.
25. Quincoces, C. E., Kikot, A., Basaldella, E. I., and Gonzalez, M. G. Effect of hydrothermal treatment on Cu-ZSM-5 catalyst in the selective reduction of NO. Ind. Eng. Chem. Res. 38 (1999): 4236-4240.
26. Guyon, M., Le Chanu, V., Gilot, P., Kessler, H., and Prado, G. Experimental study of the formation and the reaction of an intermediate during the lean NO_x reaction over Cu-ZSM-5. Appl. Catal. B 8 (1996): 183-196.

27. Adelman, B. J., Beutel, T., Lei, G. D., and Sachtler, W. M. H. On the mechanism of selective NO_x reduction with alkanes over Cu/ZSM-5. Appl. Catal. B 11 (1996): L1-L9.
28. Hwang, I. C., Kim, D. H., and Woo, S. I. The existence of dual Cu site involved in the selective catalytic reduction of NO with propene on Cu/ZSM-5. Catal. Lett. 42 (1996): 177-184.
29. Li, Y., and Armor, J. N. Catalytic reduction of nitrogen oxides with methane in the presence of excess oxygen. Appl. Catal. B 1 (1992): L31-L40.
30. Yogo, K., Ihara, M., Terasaki, I., and Kikuchi, E. Selective catalytic reduction of nitric oxide by ethene on gallium ion-exchanged ZSM-5 under oxygen-rich conditions. Appl. Catal. B 2 (1993): L1-L5.
31. Abreu, C. T., Ribeiro, M. F., Henriques, C., Ribeiro, F. R., and Delahay, G. Deactivation of CuMFI catalysts under NO selective catalytic reduction by propene: Influence of zeolite form, Si/Al ratio and copper content. Catal. Lett. 43 (1997): 31-36.
32. Iwamoto, M. Heterogeneous catalysis for removal of NO in excess oxygen progress in 1994. Catal. Today 29 (1996): 29-35.
33. Poignant, F., Saussey, J., Lavalley, J. C., and Mabilon, G. NH₃ formation during the reduction of nitrogen monoxide by propane on H-Cu-ZSM-5 in excess oxygen. J. Chem. Soc., Chem. Commun. (1995): 89-90.
34. Halasz, I., and Brenner, A. Selectivity-determining role of C₃H₈/NO ratio in the reduction of nitric oxide by propane in presence of oxygen over ZSM-5 zeolites. Catal. Lett. 51 (1998): 195-206.
35. Chajar, Z., Primet, M., Praliaud, H., Chevrier, M., Gauthier, C., and Mathis, F. Nitrogen dioxide effect in the reduction of nitric oxide by propane in oxidizing atmosphere. Catal. Lett. 28 (1994): 33-40.
36. Vassallo, J., Miro, E., and Petunchi, J. On the role of gas-phase reactions in the mechanism of the selective reduction of NO_x. Appl. Catal. B 7 (1995): 65-78.
37. Hamada, H., Kintaichi, Y., Sasaki, M., and Ito, T. Selective reduction of nitrogen monoxide with propane over alumina and HZSM-5 zeolite: Effect of oxygen and nitrogen dioxide intermediate. Appl. Catal. 70 (1991): L15-L20.

38. Cant, N. W., and Cowan, A. D. The mechanism of nitrogen oxides reduction by hydrocarbons and in other systems. Catal. Today 35 (1997): 89-95.
39. Li, Y., and Armor, J. N. The effect of SO₂ on the catalytic performance of Co-ZSM-5 and Co-ferrierite for the selective reduction of NO by CH₄ in the presence of O₂. Appl. Catal. B 5 (1995): L257-L270.
40. Inui, T., Yoshida, S., Saigo, K., and Iwamoto, S. On-site supply of active reductants for NO conversion through reforming reactions of hydrocarbons. Catal. Today 35 (1997): 171-175.
41. Seyedeyn-Azad, F., and Zhang, D. K. Selective catalytic reduction of nitric oxide over Cu and Co ion-exchanged ZSM-5 zeolite: the effect of SiO₂/Al₂O₃ ratio and cation loading. Catal. Today 68 (2001): 161-171.
42. Ren, L. L., Zhang, T., Liang, D. B., Xu, C. H., Tang, J. W., and Lin, L. W. Effect of addition of Zn on the catalytic activity of a Co/HZSM-5 catalyst for the SCR of NO_x with CH₄. Appl. Catal. B 35 (2002): 317-321.
43. Shi, C., Cheng, M. J., Qu, Z. P., Yang, X. F., and Bao, X. H. On the selectively catalytic reduction of NO_x with methane over Ag-ZSM-5 catalysts. Appl. Catal. B 36 (2002): 173-182.
44. Tapanee, D., Piyasan, P., and Inui, T. Enhancement of activity for NO removal of MFI-type H-Co-silicate by high-temperature pretreatment. Catal. Lett. 61 (1999): 77-82.
45. Kagawa, K., Ichikawa, Y., Iwamoto, S., and Inui, T. Elimination of NO on Co ion-exchanged Co center dot Al bimetallosilicate catalyst under excess oxygen condition. Micropor. Mesopor. Mat. 25 (1998): 15-23.
46. Kagawa, K., Kon, S., Iwamoto, S., and Inui, T. Enhancement of NO-elimination activity of Co-silicate catalyst by high-temperature calcination in steam-containing air. Catal. Lett. 52 (1998): 139-144.
47. Inui, T., Iwamoto, S., Kon, S., Sakimon, T., and Kagawa, K. Evidently advantageous features of metallosilicates as the catalysts for elimination of NO in the exhaust gases containing a large excess of O₂ and H₂O. Catal. Today 38 (1997): 169-174.
48. Inui, T., Iwamoto, S., Kojo, S., Shimizu, S., and Hirabayashi, T. Removal of nitric oxide on metallosilicate catalysts. Catal. Today 22 (1994): 41-57.
49. Auroux, A., Sprinceana, D., and Gervasini, A. Support effects on de-NO_x catalytic properties of supported tin oxides. J. Catal. 195 (2000): 140-150.

50. Burch, R., Halpin, E., and Sullivan, J. A. A comparison of the selective catalytic reduction of NO_x over Al_2O_3 and sulphated Al_2O_3 using CH_3OH and C_3H_8 as reductants. Appl. Catal. B 17 (1998): 115-129.
51. Obuchi, A., Wogerbauer, C., Koppel, R., and Baiker, A. Reactivity of nitrogen containing organic intermediates in the selective catalytic reduction of NO_x with organic compounds: A model study with tert-butyl substituted nitrogen compounds. Appl. Catal. B 19 (1998): 9-22.
52. Subramanian, S., Kudla, R. J., Chun, W., and Chattha, M. S. Removal of nitric-oxide by its reduction with hydrocarbons over alumina under lean conditions. Ind. Eng. Chem. Res. 32 (1993): 1805-1810.
53. Shimizu, K., Kawabata, H., Satsuma, A., and Hattori, T. Role of acetate and nitrates in the selective catalytic reduction of NO by propene over alumina catalyst as investigated by FTIR. J. Phys. Chem. B 103 (1999): 5240-5245.
54. Kintaichi, Y., Hamada, H., Tabata, M., Sasaki, M., and Ito, T. Selective reduction of nitrogen oxides with hydrocarbons over solid acid catalysts in oxygen-rich atmospheres. Catal. Lett. 6 (1990): 239-244.
55. Meunier, F. C., Breen, J. P., Zuzaniuk, V., Olsson, M., and Ross, J. R. H. Mechanistic aspects of the selective reduction of NO by propene over alumina and silver-alumina catalysts. J. Catal. 187 (1999): 493-505.
56. Teraoka, Y., Harada, T., Iwasaki, T., Ikeda, T., and Kagawa, S. Selective reduction of nitrogen monoxide with hydrocarbons over SnO_2 catalyst. Chem. Lett. (1993): 773-776.
57. Tabata, M., Tsuchida, H., Miyamoto, K., Yoshinari, T., Yamazaki, H., Hamada, H., Kintaichi, Y., Sasaki, M., and Ito, T. Reduction of NO_x in diesel exhaust with methanol over alumina catalyst. Appl. Catal. B 6 (1995): 169-183.
58. Hamada, H., Kintaichi, Y., Yoshinari, T., Tabata, M., Sasaki, M., and Ito, T. Performance of solid acid type catalysts for the selective reduction of nitrogen-oxides by hydrocarbons and alcohols. Catal. Today 17 (1993): 111-119.
59. Haneda, M., Bion, N., Daturi, M., Saussey, J., Lavalley, J. C., Duprez, D., and Hamada, H. In situ Fourier transform infrared study of the selective reduction of NO with propene over $\text{Ga}_2\text{O}_3\text{-Al}_2\text{O}_3$. J. Catal. 206 (2002): 114-124.

60. Shimizu, K., Satsuma, A., and Hattori, T. Selective catalytic reduction of NO by hydrocarbons on Ga₂O₃/Al₂O₃ catalysts. Appl. Catal. B 16 (1998): 319-326.
61. Haneda, M., Kintaichi, Y., and Hamada, H. Enhanced activity of metal oxide-doped Ga₂O₃-Al₂O₃ for NO reduction by propene. Catal. Today 54 (1999): 391-400.
62. Okimura, Y., Yokoi, H., Ohbayashi, K., Shimizu, K., Satsuma, A., and Hattori, T. Selective catalytic reduction of nitrogen oxides with hydrocarbons over Zn-Al-Ga complex oxides. Catal. Lett. 52 (1998): 157-161.
63. Wei, J. Y., Ma, J., Zhu, Y. X., Cai, X. H., and Xie, Y. C. Sn_xTi_{1-x}O₂ solid solution catalysts for nitrogen oxide selective catalytic reduction by propene in presence of oxygen. Chinese J. Chem. 19 (2001): 1063-1069.
64. Buciuman, F. C., Joubert, E., Menezo, J. C., and Barbier, J. Catalytic properties of La_{0.8}A_{0.2}MnO₃ (A = Sr, Ba, K, Cs) and LaMn_{0.8}B_{0.2}O₃ (B = Ni, Zn, Cu) perovskites: Part 2 Reduction of nitrogen oxides in the presence of oxygen. Appl. Catal. B 35 (2001): 149-156.
65. Harada, T., Teraoka, Y., and Kagawa, S. Perovskite-type oxides as catalysts for selective reduction of nitric oxide by ethylene. Appl. Surf. Sci. 121 (1997): 505-508.
66. Hansen, K. K., Skou, E. M., Christensen, H., and Turek, T. Perovskites as catalysts for the selective catalytic reduction of nitric oxide with propene: Relationship between solid state properties and catalytic activity. J. Catal. 199 (2001): 132-140.
67. Wei, M. D., Teraoka, Y., and Kawaga, S. Catalytic property of A(2)(II)B(II)B(VI)O(6) double perovskites (B-VI = Mo, W) for the reduction of nitric oxide with propane in the presence of oxygen. Mater. Res. Bull. 35 (2000): 521-530.
68. Hong, S. S., Lee, G. D., Park, J. W., Park, D. W., Cho, K. M., and Oh, K. J. Catalytic reduction of NO over perovskite-type catalysts. Korean J. Chem. Eng. 14 (1997): 491-497.
69. Carniti, P., Gervasini, A., Modica, V. H., and Ravasio, N. Catalytic selective reduction of NO with ethylene over a series of copper catalysts on amorphous silicas. Appl. Catal. B 28 (2000): 175-185.

70. Kim, T. W., Song, M. W., Koh, H. L., and Kim, K. L. Surface properties and reactivity of Cu/ γ -Al₂O₃ catalysts for NO reduction by C₃H₆: Influences of calcination temperatures and additives. Appl. Catal. A 210 (2001): 35-44.
71. Ozawa, M., Toda, H., Kato, O., and Suzuki, S. Solid-state thermal behavior of copper-modified alumina toward lean-burn exhaust NO removal catalyst. Appl. Catal. B 8 (1996): 123-140.
72. Yan, J. Y., Kung, H. H., Sachtler, W. M. H., and Kung, M. C. Synergistic effect in lean NO_x reduction by CH₄ over Co/Al₂O₃ and H-zeolite catalysts. J. Catal. 175 (1998): 294-301.
73. Bethke, K. A., Li, C., Kung, M. C., Yang, B., and Kung, H. H. The role of NO₂ in the reduction of NO by hydrocarbon over Cu-ZrO₂ and Cu-ZSM-5 catalysts. Catal. Lett. 31 (1995): 287-299.
74. Bethke, K. A., Kung, M. C., Yang, B., Shah, M., Alt, D., Li, C., and Kung, H. H. Metal-oxide catalysts for lean NO_x reduction. Catal. Today 26 (1995): 169-183.
75. Meunier, F. C., Zuzaniuk, V., Breen, J. P., Olsson, M., and Ross, J. R. H. Mechanistic differences in the selective reduction of NO by propene over cobalt- and silver-promoted alumina catalysts: kinetic and in situ DRIFTS study. Catal. Today 59 (2000): 287-304.
76. Radtke, F., Koepfel, R. A., Minardi, E. G., and Baiker, A. Catalytic reduction of nitrogen oxides by olefins in the presence of oxygen over copper/alumina: Influence of copper loading and formation of byproducts. J. Catal. 167 (1997): 127-141.
77. Hernandez-Huesca, R., Santamaria-Gonzalez, J., Braos-Garcia, P., Maireles-Torres, P., Rodriguez-Castellon, E., and Jimenez-Lopez, A. Selective catalytic reduction of NO by propane on copper containing alumina pillared alpha-zirconium phosphates. Appl. Catal. B 29 (2001): 1-11.
78. Pasel, J., Speer, V., Albrecht, C., Richter, F., and Papp, H. Metal doped sulfated ZrO₂ as catalyst for the selective catalytic reduction (SCR) of NO with propane. Appl. Catal. B 25 (2000): 105-113.
79. Zuzaniuk, V., Meunier, F. C., and Ross, J. R. H. Differences in the reactivity of organo-nitro and nitrito compounds over Al₂O₃-based catalysts active for the selective reduction of NO_x. J. Catal. 202 (2001): 340-353.

80. Chi, Y., and Chuang, S. S. C. The effect of oxygen concentration on the reduction of NO with propylene over CuO/ γ -Al₂O₃. Catal. Today 62 (2000): 303-318.
81. Chi, Y. W., and Chuang, S. S. C. Infrared study of NO adsorption and reduction with C₃H₆ in the presence of O₂ over CuO/Al₂O₃. J. Catal. 190 (2000): 75-91.
82. Chen, L. Y., Horiuchi, T., Osaki, T., and Mori, T. Catalytic selective reduction of NO with propylene over Cu-Al₂O₃ catalysts: Influence of catalyst preparation method. Appl. Catal. B 23 (1999): 259-269.
83. Shimizu, K., Maeshima, H., Satsuma, A., and Hattori, T. Transition metal-aluminate catalysts for NO reduction by C₃H₆. Appl. Catal. B 18 (1998): 163-170.
84. Masuda, K., Tsujimura, K., Shinoda, K., and Kato, T. Silver-promoted catalyst for removal of nitrogen oxides from emission of diesel engines. Appl. Catal. B 8 (1996): 33-40.
85. Ohtsuka, H. The selective catalytic reduction of nitrogen oxides by methane on noble metal-loaded sulfated zirconia. Appl. Catal. B 33 (2001): 325-333.
86. Giroir, F. A., Denton, P., Boreave, A., Praliaud, H., and Primet, M. The role of support acidity in the selective catalytic reduction of NO by C₃H₆ under lean-burn conditions. Top. Catal. 16/17 (2001): 237-241.
87. Schiesser, W., Vinek, H., and Jentys, A. Oxidation state of platinum clusters during the reduction of NO_x with propene and propane. Catal. Lett. 73 (2001): 67-72.
88. Sullivan, J. A., Burch, R., and Shestov, A. A. Transient techniques in the study of lean-NO_x reduction over supported Pt catalysts. Chem. Eng. Res. Des. 78 (2000): 947-953.
89. Takami, A., Takemoto, T., Iwakuni, H., Yamada, K., Shigetsu, M., and Komatsu, K. Zeolite-supported precious metal catalysts for NO_x reduction in lean burn engine exhaust. Catal. Today 35 (1997): 75-81.
90. Ueda, A., Oshima, T., and Haruta, M. Reduction of nitrogen monoxide with propene in the presence of oxygen and moisture over gold supported on metal oxides. Appl. Catal. B 12 (1997): 81-93.
91. Wogerbauer, C., Maciejewski, M., and Baiker, A. Structure sensitivity of NO reduction over iridium catalysts in HC-SCR. J. Catal. 205 (2002): 157-167.

92. Nawdali, M., Iojoiu, E., Gelin, P., Praliaud, H., and Primet, M. Influence of the pre-treatment on the structure and reactivity of Ir/ γ -Al₂O₃ catalysts in the selective reduction of nitric oxide by propene. Appl. Catal. A 220 (2001): 129-139.
93. Son, I. H., Kim, M. C., Koh, H. L., and Kim, K. L. On the promotion of Ag/ γ -Al₂O₃ by Cs for the SCR of NO by C₃H₆. Catal. Lett. 75 (2001): 191-197.
94. Bamwenda, G. R., Obuchi, A., Ogata, A., and Mizuno, K. An FTIR study of the species adsorbed on a Rh/Al₂O₃ catalyst in the selective reduction of NO by propylene. Chem. Lett. (1994): 2109-2112.
95. Keshavaraja, A., She, X., and Flytzani-Stephanopoulos, M. Selective catalytic reduction of NO with methane over Ag-alumina catalysts. Appl. Catal. B 27 (2000): L1-L9.
96. Acke, F., and Skoglundh, M. Comparison between ammonia and propene as the reducing agent in the selective catalytic reduction of NO under lean conditions over Pt black. Appl. Catal. B 20 (1999): 133-144.
97. Huang, H. Y., Long, R. Q., and Yang, R. T. A highly sulfur resistant Pt-Rh/TiO₂/Al₂O₃ storage catalyst for NO_x reduction under lean-rich cycles. Appl. Catal. B 33 (2001): 127-136.
98. Wogerbauer, C., Maciejewski, M., Schubert, M. M., and Baiker, A. Effect of sodium on the catalytic properties of iridium black in the selective reduction of NO_x by propene under lean-burn conditions. Catal. Lett. 74 (2001): 1-7.
99. Iwamoto, M., and Hamada, H. Removal of nitrogen monoxide from exhaust gases through novel catalytic processes. Catal. Today 10 (1991): 57-71.
100. Martinez, A., Gomez, S. A., and Fuentes, G. A. Deactivation of Cu-ZSM-5 during selective catalytic reduction of NO by propane under wet conditions. Catalyst deactivation: Stud. Surf. Sci. Catal. 111 (1997): 225-230.
101. Gomez, S. A., Campero, A., Martinez-Hernandez, A., and Fuentes, G. A. Changes in Cu²⁺ environment upon wet deactivation of Cu-ZSM-5 deNO_x catalysts Appl. Catal. A 197 (2000): 157-164.
102. Ciambelli, P., Corbo, P., and Migliardini, F. Potentialities and limitations of lean de-NO_x catalysts in reducing automotive exhaust emissions. Catal. Today 59 (2000): 279-286.

103. Ciambelli, P., Corbo, P., Gambino, M., Migliardini, F., Minelli, G., Moretti, G., and Porta, P. The effect of preparation and steaming on the catalytic properties of Cu- and Co-ZSM-5 in lean NO_x reduction. Zeolites: A refined tool for designing catalytic sites: Stud. Surf. Sci. Catal. 97 (1995): 295-302.
104. Yan, J. Y., Lei, G. D., Sachtler, W. M. H., and Kung, H. H. Deactivation of Cu/ZSM-5 catalysts for lean NO_x reduction: Characterization of changes of Cu state and zeolite support. J. Catal. 161 (1996): 43-54.
105. Chen, H. Y., and Sachtler, W. M. H. Activity and durability of Fe/ZSM-5 catalysts for lean burn NO_x reduction in the presence of water vapor. Catal. Today 42 (1998): 73-83.
106. Chajar, Z., Denton, P., de Bernard, F. B., Primet, M., and Praliaud, H. Influence of silver on the catalytic activity of Cu-ZSM-5 for NO SCR by propane: Effect of the presence of water and hydrothermal agings. Catal. Lett. 55 (1998): 217-222.
107. Ishihara, T., Kagawa, M., Hadama, F., and Takita, Y. Copper ion-exchanged SAPO-34 as a thermostable catalyst for selective reduction of NO with C₃H₆. J. Catal. 169 (1997): 93-102.
108. Ishihara, T., Kagawa, M., Hadama, F., Nishiguchi, H., Ito, M., and Takita, Y. Thermostable molecular sieves, silicoaluminophosphate (SAPO)-34, for the removal of NO_x with C₃H₆ in the coexistence of O₂, H₂O, and SO₂. Ind. Eng. Chem. Res. 36 (1997): 17-22.
109. Prasertthram, P., Phatanasri, S., Rungsimanop, J., and Kanchanawanichkun, P. Effect of Pd on the stability improvement of Cu/H-MFI for NO removal under hydrothermal pretreatment conditions. J. Mol. Catal. A 169 (2001): 113-126.
110. Tanabe, T., Iijima, T., Koiwai, A., Mizuno, J., Yokota, K., and Isogai, A. ESR study of the deactivation of Cu-ZSM-5 in a net oxidizing atmosphere. Appl. Catal. B 6 (1995): 145-153.
111. Engelhardt, G., and Michel, D. High-resolution solid-state NMR of silicates and zeolites. Chichester: John Wiley & Sons, 1987.
112. Obuchi, A., Ohi, A., Nakamura, M., Ogata, A., Mizuno, K. and Ohuchi, H. Performance of platinum-group metal catalysts for the selective reduction of nitrogen oxides by hydrocarbons. Appl. Catal. B 2 (1993): 71-80.

113. Zhang, G., Yamaguchi, T., Kawakami, H. and Suzuki, T. Selective reduction of nitric oxide over platinum catalysts in the presence of sulfur dioxide and excess oxygen. Appl. Catal. B 1 (1992): L15-L20.
114. Farrauto, R. J., and Bartholomew, C. H. Fundamentals of industrial catalytic processes. London: Blackie Academic and Professional, 1997.
115. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M. Transition metal-promoted silica and alumina catalysts for the selective reduction of nitrogen monoxide with propane. Appl. Catal. 75 (1991): L1-L8.
116. Burch R., Millington, P. J., and Walker, A. P. Mechanism of the selective reduction of nitrogen monoxide on platinum-based catalysts in the presence of excess oxygen. Appl. Catal. B 4 (1994): 65-94.
117. Bourges, P., Lunati, S., and Mabilon, G. N₂O and NO₂ formation during NO reduction on precious metal catalysts. Catalysis and automotive pollution control IV: Stud. Surf. Sci. Catal. 116 (1998): 213-222.
118. Sasaki, M., Hamada, H., Kintaichi, Y., and Ito, T. Role of oxygen in selective reduction of nitrogen monoxide by propane over zeolite and alumina-based catalysts. Catal. Lett. 15 (1992): 297-304.
119. Roberts, K. L., and Amiridis, M. D. Kinetic investigation of the selective catalytic reduction of nitric oxide by propylene over Pt/Al₂O₃. Ind. Eng. Chem. Res. 36 (1997): 3528-3532.
120. Captain, D. K., Roberts, K. L., and Amiridis, M. D. The selective catalytic reduction of nitric oxide by propylene over Pt/SiO₂. Catal. Today 42 (1998): 93-100.
121. Tanaka, T., Okuhara, T., and Misono, M. Intermediacy of organic nitro and nitrite surface species in selective reduction of nitrogen monoxide by propene in the presence of excess oxygen over silica-supported platinum. Appl. Catal. B 4 (1994): L1-L9.
122. 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 (1995): 311-323.
123. Okuhara, T., Hasada, Y., and Misono, M. In situ diffuse reflectance IR of catalytic reduction of nitrogen oxides by propene in the presence of oxygen over silica-supported platinum. Catal. Today 35 (1997): 83-88.

124. Xin, M., Hwang, I. C., and Woo, S. I. In situ FTIR study of the selective catalytic reduction of NO on Pt/ZSM-5. Catal. Today 38 (1997): 187-192.
125. Xin, M., Hwang, I. C., and Woo, S. I. FTIR studies of the reduction of nitric oxide by propene on Pt/ZSM-5 in the presence of oxygen. J. Phys. Chem. B 101 (1997): 9005-9009.
126. Captain, D. K., and Amiridis, M. D. In situ FTIR studies of the selective catalytic reduction of NO by C₃H₆ over Pt/Al₂O₃. J. Catal. 184 (1999): 377-389.
127. Captain, D. K., and Amiridis, M. D. NO reduction by propylene over Pt/SiO₂: An in situ FTIR study. J. Catal. 194 (2000): 222-232.
128. Rottländer, C., Andorf, R., Plog, C., Krutzsch, B., and Baerns, M. Selective NO reduction by propane and propene over a Pt/ZSM-5 catalyst: A transient study of the reaction mechanism. Appl. Catal. B 11 (1996): 49-63.
129. Lacombe, S., Hoebink, J. H. B. J., and Marin, G. B. Platinum catalyzed reduction of nitric oxide by n-butane in the presence of oxygen: Role of the hydrocarbon. Appl. Catal. B 12 (1997): 207-224.
130. Eckhoff, S., Hesse, D., van den Tillaart, J. A. A., Leyrer, J., and Lox, E. S. Mechanistic investigation on the selective reduction of NO with propene in the presence of oxygen over supported platinum. Catalysis and automotive pollution control IV: Stud. Surf. Sci. Catal. 116 (1998): 223-231.
131. Burch, R., Shestov, A. A., and Sullivan, J. A. A transient kinetic study of the mechanism of the NO/C₃H₆/O₂ reaction over Pt-SiO₂ catalysts: Part 2 Steady-state isotopic transient kinetic analysis. J. Catal. 182 (1999): 497-506.
132. Ansell, G. P., Bennett, P. S., Cox, J. P., Frost, J. C., Gray, P. G., Jones, A. -M., Rajaram, R. R., Walker, A. P., Litorell, M., and Smedler, G. The development of a model capable of prediction diesel lean NO_x catalyst performance under transient conditions. Appl. Catal. B 10 (1996): 183-201.
133. Burch, R., and Watling, T. C. Kinetics of the reduction of NO by C₃H₆ and C₃H₈ over Pt based catalysts under lean-burn conditions. Catalysis and automotive pollution control IV: Stud. Surf. Sci. Catal. 116 (1998): 223-231.
134. Burch, R., Sullivan, J. A., and Watling, T. C. Mechanistic considerations for the reduction of NO_x over Pt/Al₂O₃ and Al₂O₃ catalysts under lean-burn conditions. Catal. Today 42 (1998): 13-23.

135. Engler, B. H., Leyrer, J., Lox, E. S., and Ostgathe, K. Catalytic reduction of nitrogen oxides in diesel exhaust gas. Catalysis and automotive pollution control III: Stud. Surf. Sci. Catal. 96 (1995): 529-547.
136. Burch, R., and Watling, T. C. The difference between alkanes and alkenes in the reduction of NO by hydrocarbons over Pt catalysts under lean-burn conditions. Catal. Lett. 43 (1997): 19-23.
137. Burch, R., Fornasiero, P., and Watling, T. C. Kinetics and mechanism of the reduction of NO by n-octane over Pt/Al₂O₃ under lean-burn conditions. J. Catal. 176 (1998): 204-214.
138. Acke, F., and Skoglundh, M. Differences in reduction mechanisms for the selective reduction of NO under oxygen excess over Pt based catalysts using propane or propene as the reducing agent. Appl. Catal. B 22 (1999): L1-L3.
139. Burch, R., and Watling, T. C. The effect of promoters on Pt/Al₂O₃ catalysts for the reduction of NO by C₃H₆ under lean-burn conditions. Appl. Catal. B 11 (1997): 207-216.
140. Efthimiadis, E. A., Lionda, G. D., Christoforou, S. C., and Vasalos, I. A. The effect of CH₄, H₂O and SO₂ on the NO reduction with C₃H₆. Catal. Today 40 (1998): 15-26.
141. Sumiya, S., Saito, M., He, H., Feng, Q., Takezawa, N., and Yoshida, K. Reduction of lean NO_x by ethanol over Ag/Al₂O₃ catalysts in the presence of H₂O and SO₂. Catal. Lett. 50 (1998): 87-91.
142. Abe, A., Aoyama, N., Sumiya, S., Kakuta, N., and Yoshida, K. Effect of SO₂ on NO_x reduction by ethanol over Ag/Al₂O₃ catalyst. Catal. Lett. 51 (1998): 5-9.
143. Fritz, A., and Pitchon, V. The current state of research on automotive lean NO_x catalysis. Appl. Catal. B 13 (1997): 1-25.
144. Naito, S., and Tanimoto, M. The role of oxygen in the reduction of NO with propene over Rh/Al₂O₃ in oxidizing atmosphere. Chem. Lett. (1993): 1935-1938.
145. Hamada, H. Selective reduction of NO by hydrocarbons and oxygenated hydrocarbons over metal oxide catalysts. Catal. Today 22 (1994): 21-40.
146. Burch, R., and Millington, P. J. Selective reduction of NO_x by hydrocarbons in excess oxygen by alumina- and silica-supported catalysts. Catal. Today 29 (1996): 37-42.

147. Bamwenda, G. R., Obuchi, A., Ogata, A., Oi, J., Kushiyama, S., and Mizuno, K. The role of the metal during NO₂ reduction by C₃H₆ over alumina and silica-supported catalysts. J. Mol. Catal. A 126 (1997): 151-159.
148. Nikolopoulos, A. A., Stergioula, E. S., Efthimiadis, E. A., and Vasalos I. A. Selective catalytic reduction of NO by propene in excess oxygen on Pt- and Rh-supported alumina catalysts. Catal. Today 54 (1999): 439-450.
149. Toubeli, A., Efthimiadis, E. A., and Vasalos, I. A. NO reduction by C₃H₆ in excess oxygen over fresh and sulfated Pt- and Rh-based catalysts. Catal. Lett. 69 (2000): 157-164.
150. Nawdali, M., Praliaud, H., and Primet, M. SCR of NO over Ir/Al₂O₃ catalysts: Importance of the activation procedure and influence of the dispersion. Topics Catal. 16/17 (2001): 199-204.
151. Nakatsuji, T., and Komppa, V. Structural evolution of highly active Ir-based catalysts for the selective reduction of NO with reductants in oxidizing conditions. Topics Catal. 16/17 (2001): 217-223.
152. Obuchi, A., Ogata, A., Takahashi, H., Oi, J., Bamwenda, G. R., and Mizuno, K. Selective reduction of nitrogen oxides with various organic substances on precious metal catalysts under a high GHSV condition. Catal. Today 29 (1996): 103-107.
153. Burch, R., and Ottery, D. The selective reduction of nitrogen oxides by higher hydrocarbons on Pt catalysts under lean-burn conditions. Appl. Catal. B 13 (1997): 105-111.
154. Perez-Ramirez, J., Garcia-Cortes, J. M., Illan-Gomez, M. J., Kapteijn, F., Moulijn, J. A., and de Lecea, C. S. M. Reduction of NO by propene over Pt, Pd and Rh-based ZSM-5 under lean-burn conditions. React. Kin. Catal. Lett. 69 (2000): 385-392.
155. Burch, R., and Watling, T. C. Kinetics and mechanism of the reduction of NO by C₃H₈ over Pt/Al₂O₃ under lean-burn conditions. J. Catal. 169 (1997): 45-54.
156. Acke, F., Westerberg, B., Eriksson, L., Johansson, S., Skoglundh, M., Fridell, E., and Smedler, G. Influence of the platinum-support interaction on the direct reduction of NO_x under lean conditions. Catalysis and automotive pollution control IV: Stud. Surf. Sci. Catal. 116 (1998): 285-294.

157. Garcia-Cortes, J. M., Perez-Ramirez, J., Illan-Gomez, M. J., Kapteijn, F., Moulijn, J. A., and de Lecea, C. S. M. Comparative study of Pt-based catalysts on different supports in the low-temperature de-NO_x-SCR with propene Appl. Catal. B 30 (2001): 399-408.
158. González-Velasco, J. R., Botas, J. A., Ferret, R., and Gutiérrez-Ortiz, M. A. Comparative three-way behaviour of Pt, Pd and Rh single and combined phases in a full gas mixture with oscillating feedstream. Catalysis and automotive pollution control IV: Stud. Surf. Sci. Catal. 116 (1998): 73-82.
159. Inaba, M., Kintaichi, Y., and Hamada, H. Cooperative effect of platinum and alumina for the selective reduction of nitrogen monoxide with propane. Catal. Lett. 36 (1996): 223-227.
160. Burch, R. Low NO_x options in catalytic combustion and emission control. Catal. Today 35 (1997): 27-36.
161. Burch, R., and Ottery, D. Selective catalytic reduction of NO_x by hydrocarbons on Pt/Al₂O₃ catalysts at low temperatures without the formation of N₂O. Appl. Catal. B 9 (1996): L19-L24.
162. Kameoka, S., Ukisu, Y., and Miyadera, T. Selective catalytic reduction of NO_x with CH₃OH, C₂H₅OH and C₃H₆ in the presence of O₂ over Ag/Al₂O₃ catalyst: Role of surface nitrate species. Phys. Chem. Chem. Phys. 2 (2000): 367-372.
163. Zhu, T. L., Hao, J. M., and Li, W. B. Enhancing effect of SO₂ on selective catalytic reduction of NO by methanol over Ag/Al₂O₃. Chem. Lett. (2000): 478-479.
164. Cowan, A. D., Dumpelmann, R., and Cant, N. W. The rate-determining step in the selective reduction of nitric oxide by methane over a Co/ZSM-5 catalyst in the presence of oxygen. J. Catal. 151 (1995): 356-363.
165. Lobree, L. J., Aylor, A. W., Reimer, J. A., and Bell, A. T. Role of cyanide species in the reduction of NO by CH₄ over Co-ZSM-5. J. Catal. 169 (1997): 188-193.
166. Sun, T., Fokema, M. D., and Ying, J. Y. Mechanistic study of NO reduction with methane over Co²⁺ modified ZSM-5 catalysts. Catal. Today 33 (1997): 251-261.

167. Chang, Y. F., Sanjurjo, A., McCarty, J. G., Krishnan, G., Woods, B., and Wachsman, E. Microwave-assisted NO reduction by methane over Co-ZSM-5 zeolites. Catal. Lett. 57 (1999): 187-191.
168. Pinaeva, L. G., Sadovskaya, E. M., Suknev, A. P., Goncharov, V. B., Sadykov, V. A., Balzhinimaev, B. S., Decamp, T., and Mirodatos, C. On the oxygen effect in nitric oxide reduction by methane over Co/ZSM-5. Chem. Eng. Sci. 54 (1999): 4327-4335.
169. Ansell, G. P., Golunski, S. E., Hayes, J. W., Walker, A. P., Burch, R., and Millington, P. J. The mechanism of the lean NO_x reaction over Pt-based catalysts. Catalysis and automotive pollution control III: Stud. Surf. Sci. Catal. 96 (1995): 577-590.
170. Burch, R., and Millington, P. J. Selective reduction of nitrogen oxides by hydrocarbons under lean-burn conditions using supported platinum group metal catalysts. Catal. Today 26 (1996): 185-206.
171. Jayat, F., Lembacher, C., Schubert, U., and Martens, J. A. Catalytic NO_x reduction in lean burn exhaust over Pt/silica catalysts with controlled Pt particle size. Appl. Catal. B 21 (1999): 221-226.
172. Lee, J. -H., and Kung, H. H. Effect of Pt dispersion on the reduction of NO by propene over alumina-supported Pt catalysts under lean-burn conditions. Catal. Lett. 51 (1998): 1-4.
173. Denton, P., Giroir-Fendler, A., Praliaud, H., and Primet, M. Role of the nature of the support (alumina or silica), of the support porosity, and of the Pt dispersion in the selective reduction of NO by C₃H₆ under lean-burn conditions. J. Catal. 189 (2000): 410-420.
174. Van den Tillaart, J. A. A., Leyrer, J., Eckhoff, S., and Lox, E. S. Effect of support oxide and noble metal precursor on the activity of automotive diesel catalysts. Appl. Catal. B 10 (1996): 53-68.
175. Doumeki, R., Hatano, M., Kinoshita, H., Yamashita, E., Hirano, M., Fukuoka, A., and Komiya, S. Effect of Pt precursors on N₂/N₂O selectivity for selective reduction of NO by hydrocarbon on supported Pt catalysts. Chem. Lett. (1999): 515-516.
176. Xue, E., Seshan, K., and Ross, J. R. H. Roles of supports, Pt loading and Pt dispersion in the oxidation of NO to NO₂ and SO₂ to SO₃. Appl. Catal. B 11 (1996): 65-79.

177. Iwamoto, M., Yahiro, H., Shin, H. K., Watanabe, M., Guo, J. W., Konno, M., Chikahisa, T., and Murayama, T. Performance and durability of Pt-MFI zeolite catalyst for selective reduction of nitrogen monoxide in actual diesel engine exhaust. Appl. Catal. B 5 (1994): L1-L6.
178. Shin, H. K., Hirabayashi, H., Yahiro, H., Watanabe, M., and Iwamoto, M. Selective catalytic reduction of NO by ethene in excess oxygen over platinum ion-exchanged MFI zeolites. Catal. Today 26 (1995): 13-21.
179. Cho, B. K., and Yie, J. E. Nitric oxide reduction by ethylene over Pt-ZSM-5 under lean conditions: Steady-state activity. Appl. Catal. B 10 (1996): 263-280.
180. Obuchi, A., Kaneko, I., Oi, J., Ohi, A., Ogata, A., Bamwenda, G. R., and Kushiyama, S. A practical scale evaluation of catalysts for the selective reduction of NO_x with organic substances using a diesel exhaust. Appl. Catal. B 15 (1998): 37-47.
181. Amiridis, M. D., Roberts, K. L., and Pereira, C. J. The selective catalytic reduction of NO by propylene over Pt supported on dealuminated Y zeolite. Appl. Catal. B 14 (1997): 203-209.
182. Pérez-Ramírez, J., García-Cortés, J. M., Kapteijn, F., Mul, G., Moulijn, J. A., and de Lecea C. S. M. Characterization and performance of Pt-USY ion the SCR of NO_x with hydrocarbons under lean-burn conditions. Appl. Catal. B 29 (2001): 285-298.
183. Long, R. Q., and Yang, R. T. Pt/MCM-41 catalyst for selective catalytic reduction of nitric oxide with hydrocarbons in the presence of excess oxygen. Catal. Lett. 52 (1998): 91-96.
184. Jentys, A., Schiesser, W., and Vinek, H. Catalytic activity of Pt and tungstophosphoric acid supported on MCM-41 for the reduction of NO_x in the presence of water vapor. Catal. Today 59 (2000): 313-321.
185. Schiesser, W., Vinek, H., and Jentys, A. Surface species during catalytic reduction of NO by propene studied by in situ IR-spectroscopy over Pt supported on mesoporous Al₂O₃ with MCM-41 type structure. Appl. Catal. B 33 (2001): 263-274.

186. Dumpelmann, R., Cant, N. W., and Trimm, D. L. Enhancement of the reaction of nitric oxide and carbon monoxide by hydrogen and water over platinum and rhodium-containing catalysts. Catalysis and automotive pollution control III: Stud. Surf. Sci. Catal. 96 (1995): 123-135.
187. Haj, K. O., Schneider, S., Maire, G., Zyade, S., Ziyad, M., and Garin, F. Influence of alumina-supported M-Pt catalysts in DeNO_x reactions with M = Pd or Ir or Ru. Topics Catal. 16/17 (2001): 205-208.
188. Bensaddik, A., Mouaddib, N., Krawczyk, M., Pitchon, V., Garin, F., and Maire, G. Promoting effect of zinc in DeNO_x reaction over Pt/Al₂O₃. Catalysis and automotive pollution control IV: Stud. Surf. Sci. Catal. 116 (1998): 265-274.
189. Garin, F., Girard, P., Ringler, S., Maire, G., and Davias, N. Mechanistic studies of NO_x reduction reactions under oxidative atmosphere on alumina supported 1 wt% Pt and 1 wt% Pt-0.5 wt% Zn catalysts (Part I). Appl. Catal. B 20 (1999): 205-218.
190. Ringler, S., Girard, P., Maire, G., Hilaire, S., Roussy, G., and Garin, F. Mechanistic studies of NO_x reduction reactions under oxidative atmosphere on alumina supported 0.2 wt% platinum catalyst treated under microwave (Part II). Appl. Catal. B 20 (1999): 219-233.
191. Tanaka, T., Yokota, K., Isomura, N., Doi, H., and Sugiura, M. Effect of the addition of Mo and Na to Pt catalysts on the selective reduction of NO. Appl. Catal. B 16 (1998): 199-208.
192. Krantz, K., Ozturk, S., and Senkan, S. Application of combinatorial catalysis to the selective reduction of NO by C₃H₆. Catal. Today 62 (2000): 281-289.
193. Seker, E., and Gulari, E. Improved N₂ selectivity for platinum on alumina prepared by sol-gel technique in the reduction of NO_x by propene. J. Catal. 179 (1998): 339-342.
194. Seker, E., and Gulari, E. Activity and N₂ selectivity of sol-gel prepared Pt/alumina catalysts for selective NO_x reduction. J. Catal. 194 (2000): 4-13.
195. Iwamoto, M., Hernandez, A. M., and Zengyo, T. Oxidation of NO to NO₂ on a Pt-MFI zeolite and subsequent reduction of NO_x by C₂H₄ on an In-MFI zeolite: A novel de-NO_x strategy in excess oxygen. Chem. Commun. (1997): 37-38.

196. Iwamoto, M., Zengyo, T., Hernandez, A. M., and Araki, H. Intermediate addition of reductant between an oxidation and a reduction catalyst for highly selective reduction of NO in excess oxygen. Appl. Catal. B 17 (1998): 259-266.
197. Iwamoto, M., Zengyo, T., and Hernandez, A. M. Highly selective reduction of NO in excess oxygen through the intermediate addition of reductant between oxidation and reduction catalysts. Res. Chem. Intermed. 24 (1998): 115-122.
198. Misono, M. Catalytic reduction of nitrogen oxides by bifunctional catalysts: A possible breakthrough for high performance lean DeNO_x catalysts. Cattech4 2 (1998): 183-196.
199. Obuchi, A., Kaneko, I., Uchisawa, J., Ohi, A., Ogata, A., Bamwenda, G. R., and Kushiyama, S. The effect of layering of functionally different catalysts for the selective reduction of NO_x with hydrocarbons. Appl. Catal. B 19 (1998): 127-135.
200. Lunati, S., Bourges, P., and Mabilon, G. NO elimination by ethene on a pre-coked alumina supported platinum catalyst in the presence of excess oxygen. 2nd World Congress on Environmental Catalysis. Miami (1998): 364-365.
201. Matsuoka, K., Orikasa, H., Itoh, Y., Chambrion, P., and Tomita, A. Reaction of NO with soot over Pt-loaded catalyst in the presence of oxygen. Appl. Catal. B 26 (2000): 89-99.
202. García-Cortés, J. M., Illán-Gómez, M. J., Solano, A. L., and de Lecea, C. S. M. Low temperature selective catalytic reduction of NO_x with C₃H₆ under lean-burn conditions on activated carbon-supported platinum. Appl. Catal. B 25 (2000): 39-48.
203. Burch, R., and Watling, T. C. Adsorbate-assisted NO decomposition in NO reduction by C₃H₆ over Pt/Al₂O₃ catalysts under lean-burn conditions. Catal. Lett. 37 (1996): 51-55.
204. Burch, R., and Sullivan, J. A. A transient kinetic study of the mechanism of the NO/C₃H₆/O₂ reaction over Pt-SiO₂ catalysts: Part 1 Non-steady-state transient switching experiments. J. Catal. 182 (1999): 489-496.
205. Anderson, J. R., and Pratt, K. C. Introduction to characterization and testing of catalysts. Australia: Academic Press Australia, 1985.

206. Querini, C. A., and Fung, S. C. Temperature-programmed oxidation technique: Kinetics of coke-O₂ reaction on supported metal catalysts. Appl. Catal. A 117 (1994): 53-74.
207. Larsson, M., Hultén, M., Blekkan, E. A., and Andersson, B. The effect of reaction conditions and time on stream on the coke formed during propane dehydrogenation. J. Catal. 164 (1996): 44-53.
208. Snape, C. E., McGhee, B. J., Martin, S. C., and Andresen, J. M. Structural characterisation of catalytic coke by solid-state ¹³C-NMR spectroscopy. Catal. Today 37 (1997): 285-293.
209. Pieck, C. L., Jablonski, E. L., Parera, J. M., Frety, R., and Lefebvre, F. Characterization of residual coke during burning. Ind. Eng. Chem. Res. 31 (1992): 1017-1021.
210. Barbier, J. Coking of reforming catalysts. Catalyst deactivation: Stud. Surf. Sci. Catal. 34 (1987): 1-18.
211. Nortier, P., Fourre, P., Saad, A. B. M., Saur, O., and Lavalley, J. C. Effects of crystallinity and morphology on the surface properties of alumina. Appl. Catal. 61 (1990): 141-160.
212. Barzetti, T., Selli, E., Moscotti, D., and Forni, L. Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts. J. Chem. Soc. Faraday Trans. 92 (1996): 1401-1407.
213. Magnacca, G., and Morterra, C. A case study: Surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species. Catal. Today 27 (1996): 497-532.
214. Konsolakis, M., and Yentekakis, I. V. Strong promotional effects of Li, K, Rb and Cs on the Pt-catalysed reduction of NO by propene. Appl. Catal. B 29 (2001): 103-113.
215. Xin, M., Hwang, I. C., Kim, D. H., Cho, S. I., and Woo, S. I. The effect of the preparation conditions of Pt/ZSM-5 upon its activity and selectivity for the reduction of nitric oxide. Appl. Catal. B 21 (1999): 183-190.
216. Barias, O. A., Holmen, A., and Blekkan, E. A. Propane dehydrogenation over supported Pt and Pt-Sn catalysts: Catalyst preparation, characterization, and activity measurements. J. Catal. 158 (1996): 1-12.

217. Aylor, A. W., Lobree, L. J., Reimer, J. A., and Bell, A. T. An infrared study of NO reduction by CH₄ over Co-ZSM-5. 11th international congress on catalysis-40th anniversary: Stud. Surf. Sci. Catal. 101 (1996): 661-670.
218. Goryashenko, S. S., Park, Y. K., Kim, D. S., and Park, S. E. Mechanistic study of the SCR of NO with propylene over Co/ZSM-5 using in-situ FT-IR. Res. Chem. Intermed. 24 (1998): 933-951.
219. Lombardo, E. A., Sill, G. A., d'Itri, J. L., and Hall, W. K. The possible role of nitromethane in the SCR of NO_x with CH₄ over M-ZSM5 (M = Co, H, Fe, Cu). J. Catal. 173 (1998): 440-449.
220. Panit, A. Removal mechanism of intermediates in selective catalytic reduction of nitrogenmonoxide with propylene in the presence of excess oxygen over cobalt ion-exchanged MFI catalyst. Master's Thesis, Department of Chemical Engineering, Graduate School, Chulalongkorn University, 2000.
221. Isarangura Na Ayutthaya, S. Roles of NO_x on the formation and the removal of an intermediate of the NO_x reduction by hydrocarbons on zeolite catalysts. Master's Thesis, Department of Chemical Engineering, Graduate School, Chulalongkorn University, 2000.
222. Burch, R., and Watling, T. C. The effect of sulphur on the reduction of NO by C₃H₆ and C₃H₈ over Pt/Al₂O₃ under lean-burn conditions. Appl. Catal. B 17 (1998): 131-139.



APPENDICES

ศูนย์วิทยทรัพยากร
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APPENDIX A

SPECIFICATION OF ALUMINA SUPPORT (Al₂O₃) TYPE NKH-3

Table A.1 Chemical composition of alumina support type NKH-3

Chemical Composition	Weight percent
Al ₂ O ₃	60-70
SiO ₂	30-35
Fe ₂ O ₃	0.3-0.5
TiO ₂	0.5-0.7
CaO	0.1-0.2
MgO	0.2-0.4
Na ₂ O	0.3-0.4
K ₂ O	0.2-0.3
ZrO ₂ + HfO ₂	0.03-0.04

Table A.2 Physical properties of alumina support type NKH-3

Physical properties	
Bulk Density (g/ml)	1.3-1.5
Apparent Specific Gravity	3.1-3.3
Packing Density (lb/ft ³)	20-25
Pore Volume (ml/g)	1.0-1.3
Surface Area (m ² /g)	340-350

APPENDIX B

CALIBRATION CURVES

The thermal conductivity detectors (TCD) independently connected with two gas chromatographs (SHIMADZU GC-8ATP and SHIMADZU GC-8AIT) were used to analyze the concentration of the sampling gases in the catalytic activity test and an experimental set for studying the nature of surface species. The calibration curves of oxygen, nitrogen and carbon monoxide are obtained from TCD of GC 8ATP whereas those of oxygen, methane, carbon dioxide, nitrous oxide, propene, propane and sulfur dioxide are obtained from TCD of GC 8AIT. It is noted that the operating condition of gas chromatograph for making the calibration curves is maintained to be similar to that for testing the reaction. These calibration curves are given in Figures B.1-B.10.



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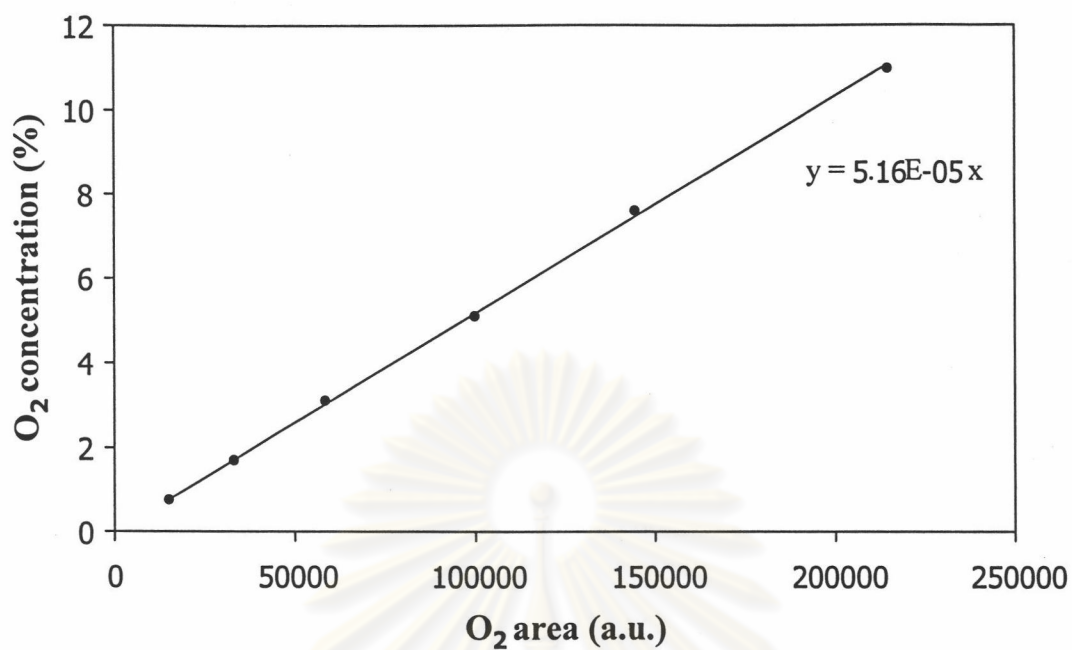


Figure B.1 The calibration curve of oxygen from TCD of GC 8ATP

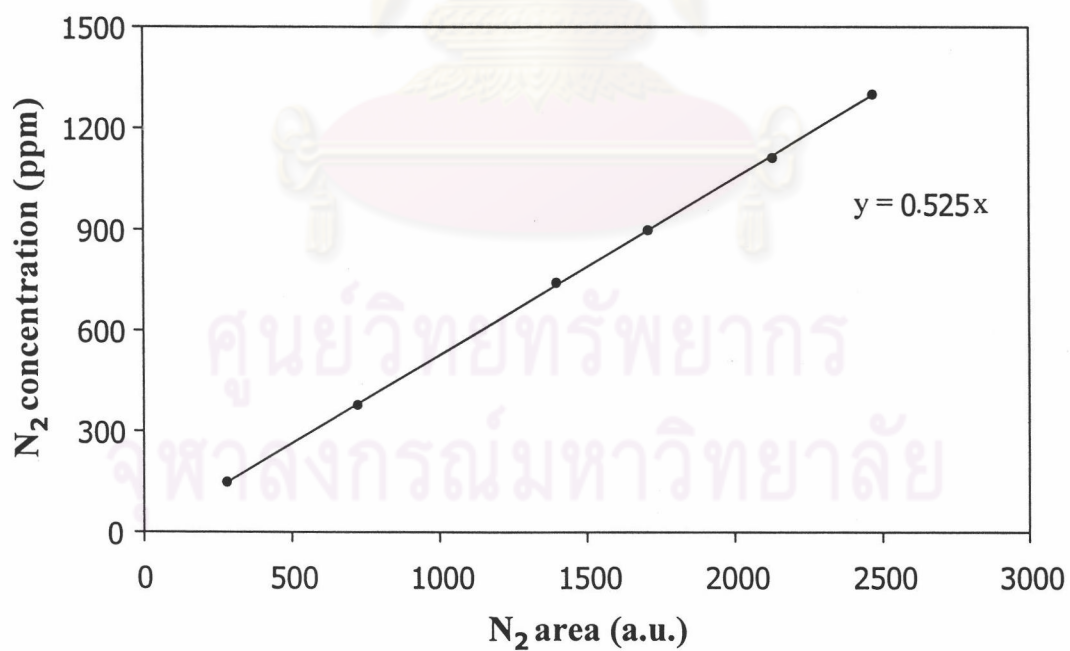


Figure B.2 The calibration curve of nitrogen

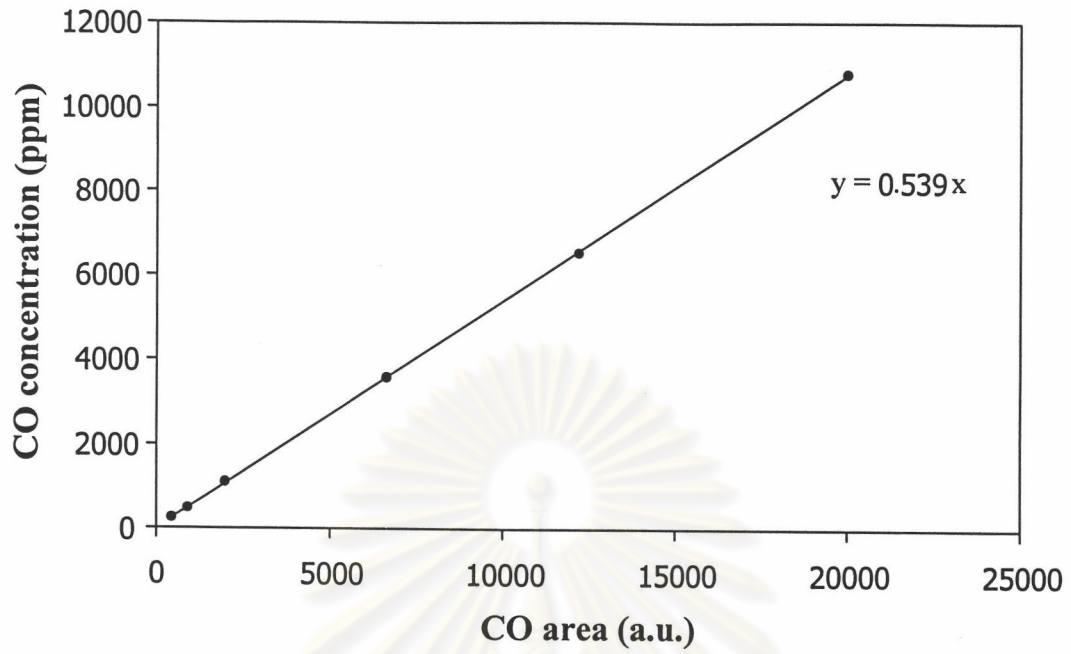


Figure B.3 The calibration curve of carbon monoxide

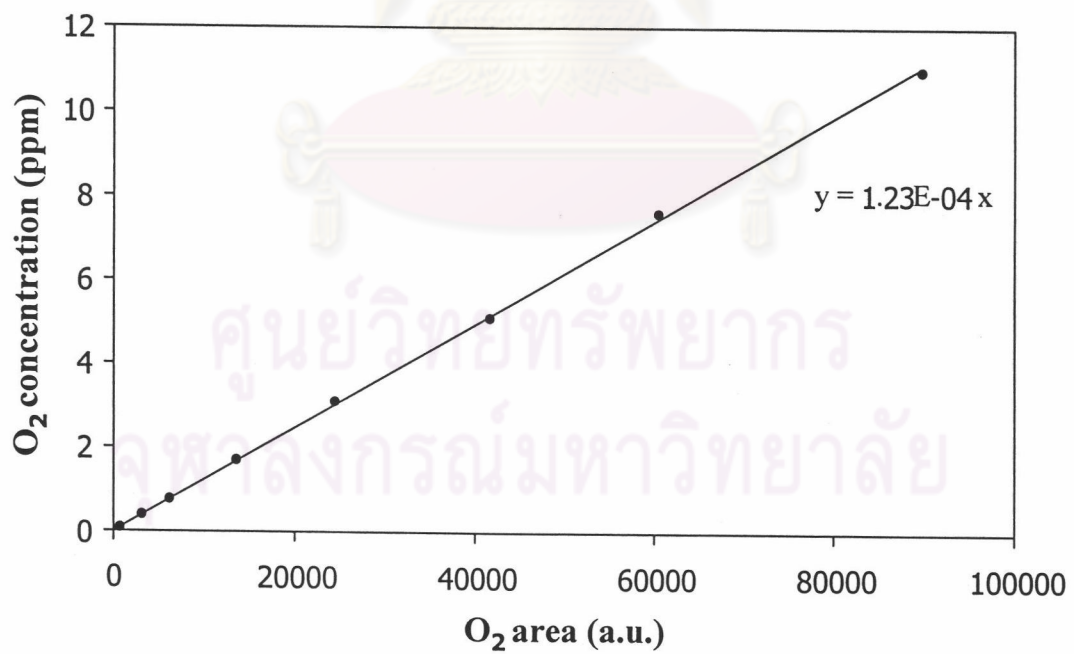


Figure B.4 The calibration curve of oxygen from TCD of GC 8AIT

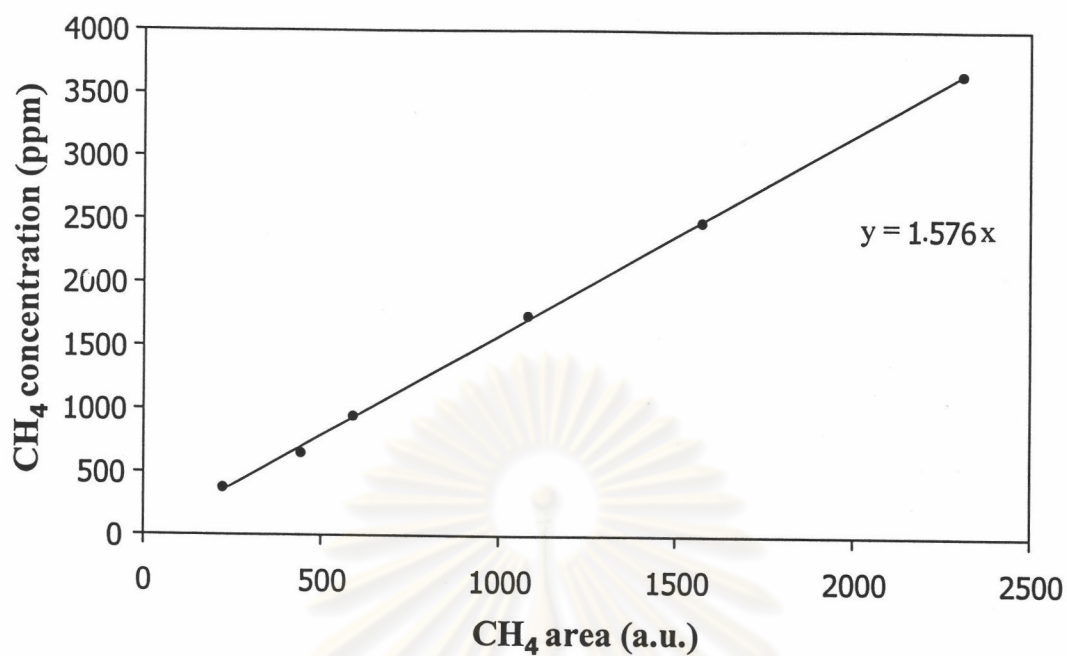


Figure B.5 The calibration curve of methane

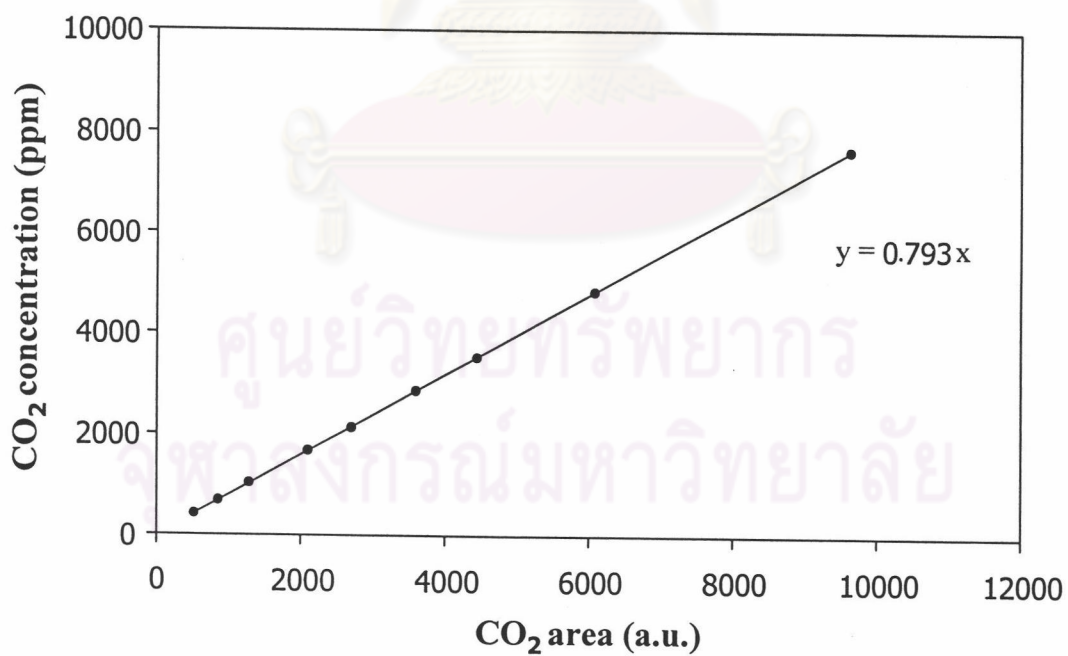


Figure B.6 The calibration curve of carbon dioxide

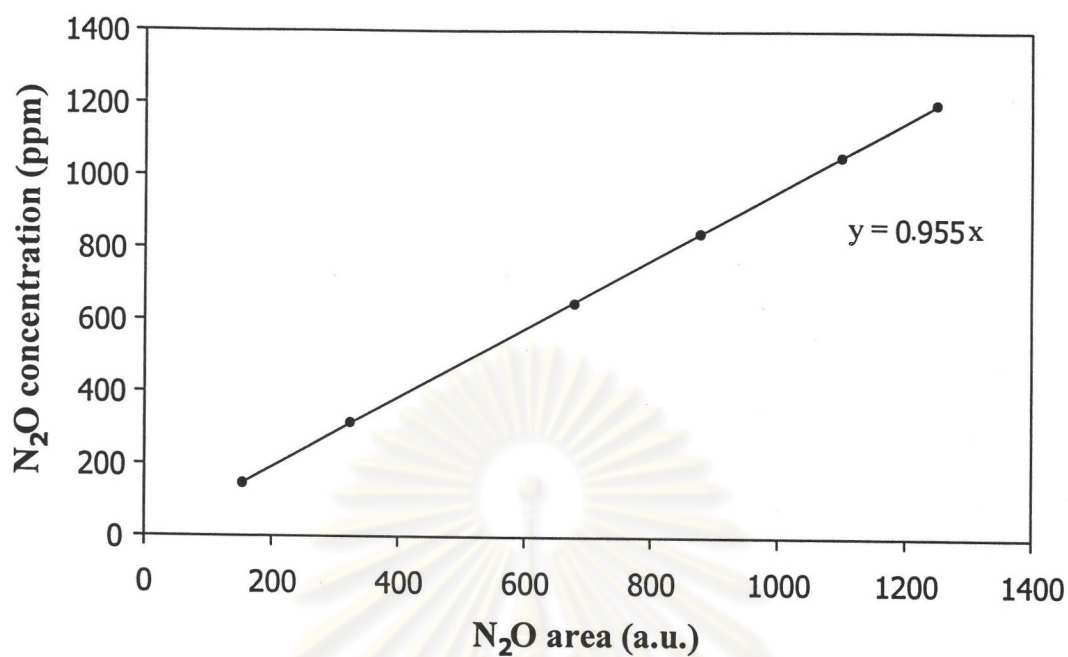


Figure B.7 The calibration curve of nitrous oxide

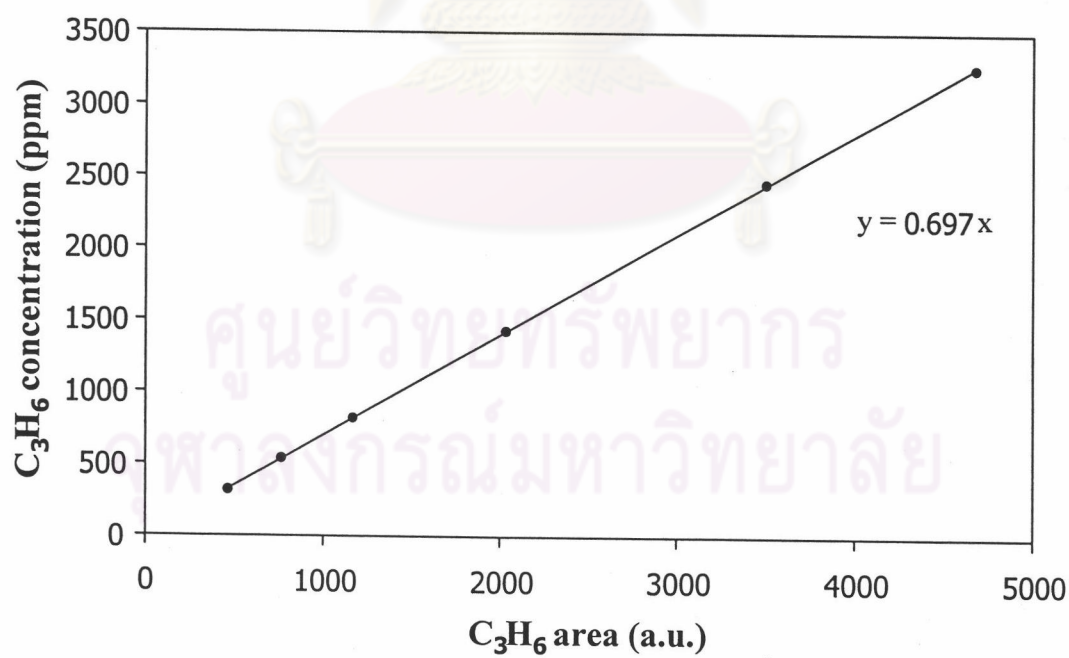


Figure B.8 The calibration curve of propene

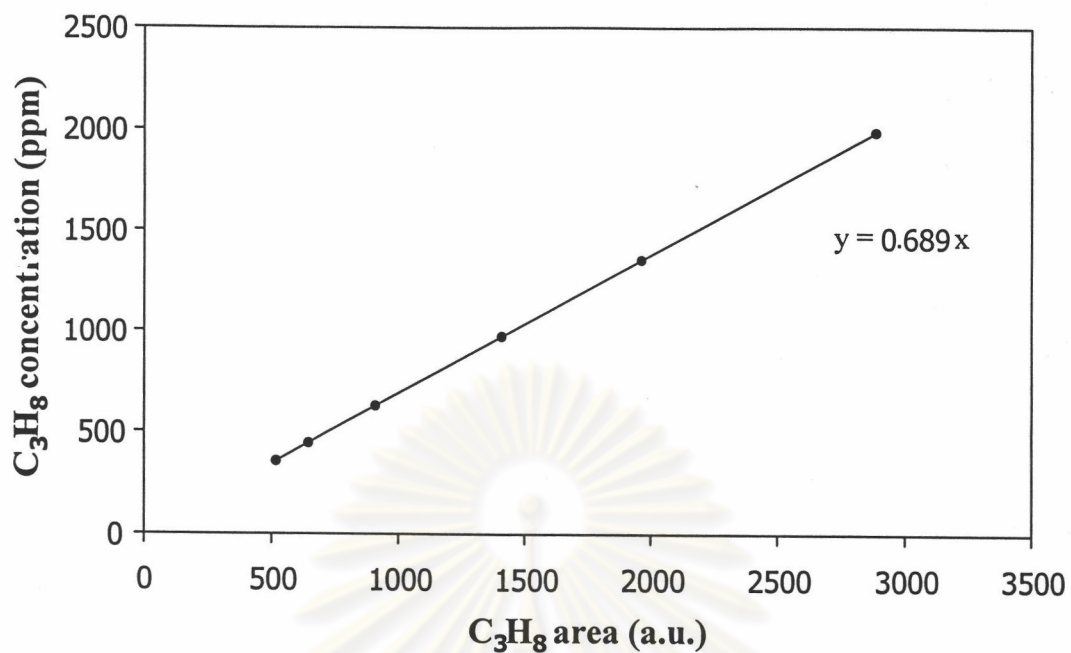


Figure B.9 The calibration curve of propane

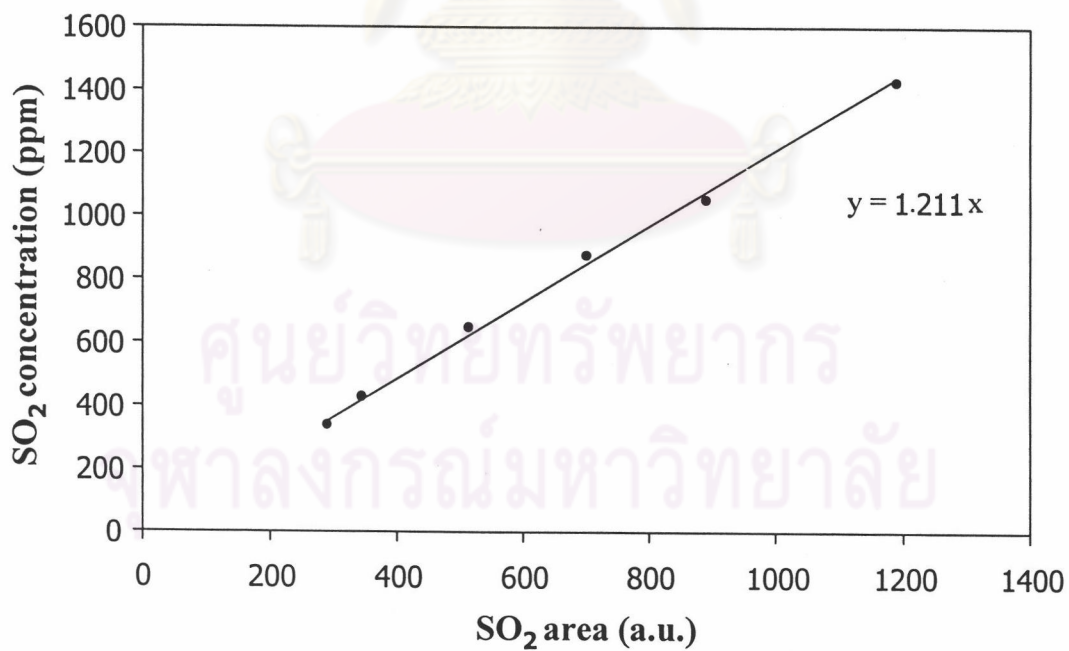


Figure B.10 The calibration curve of sulfur dioxide

APPENDIX C

SAMPLES OF CALCULATION

C.1 Calculation of Catalyst Preparation

The sample calculation shown below is for 1 wt% Pt – 2 wt% M/Al₂O₃ (M = Li, Cr, Fe, Ni, Ga, Co, Sn or W). The hydrochloric acid is only added to the impregnation solution by 5%wt of the alumina support in case of the use of Sn as the second metal. The alumina support weight used for all preparations is 2 g.

If X g of the alumina support is used, so each 100 g of the catalyst is composed of

Platinum	1	g
Second metal (M)	2	g
Alumina support	X	g
Then	$1 + 2 + X = 100$	g
	$X = 97$	g

In case of 1 wt% Pt – 2 wt% Sn/Al₂O₃ catalyst, if X g of the alumina support is used, so each 100 g of this catalyst is composed of

Platinum	1	g
Tin	2	g
Hydrochloric acid	$0.05 \times X$	g
Alumina support	X	g
Then	$1 + 2 + 0.05 \times X = 100$	g
	$X = 92.38$	g

The platinum and the second metals are obtained from the different metal precursors; therefore, the real metal contents in each metal precursor are shown in Table B.1. It is remarked that the stock solution of chloroplatinic acid hexahydrate has the concentration of 1 g in 25 ml of water and concentration as well as density of hydrochloric acid solution is 37%v/v and 1.19 g/ml, respectively.

Table C.1 The actual metal contents in various metal precursors used in this work

Metal	MW of metal	Metal precursor	MW of metal precursor	Purity (%)	Metal Content (%)
Pt	195.080	H ₂ PtCl ₆ ·6H ₂ O	517.90	98.5	37.10
Li	6.941	LiNO ₃	68.94	95.0	9.56
Cr	51.996	Cr(NO ₃) ₃ ·9H ₂ O	400.15	97.0	12.60
Fe	55.847	Fe(NO ₃) ₃ ·9H ₂ O	404.02	99.0	13.68
Ni	58.690	Ni(NO ₃) ₂ ·6H ₂ O	290.81	99.0	19.98
Ga	69.720	Ga(NO ₃) ₃	255.70	100.0	27.27
Co	58.933	Co(CH ₃ COO) ₂ ·4H ₂ O	249.08	99.0	23.42
Sn	118.710	SnCl ₂ ·2H ₂ O	225.63	97.0	51.03
W	183.850	(NH ₄) ₁₀ H ₂ (W ₂ O ₇) ₆	3060.59	99.0	71.36

The calculation procedure of the amount of each ingredient for the required composition of 1 wt% Pt – 2 wt% M/Al₂O₃ catalyst is shown in an example of 1 wt% Pt – 2 wt% Sn/Al₂O₃ catalyst as follows:

For 2 g of the alumina support used:

$$\begin{aligned}
 1. \text{ Platinum required} &= (1 \times 2) / 92.38 && \text{g} \\
 &= 2.165 \times 10^{-2} && \text{g}
 \end{aligned}$$

$$\begin{aligned}
 \text{Chloroplatinic acid hexahydrate required} &= 2.165 \times 10^{-2} \times 100 \times 25 / 37.10 && \text{ml} \\
 &= 1.459 && \text{ml}
 \end{aligned}$$

$$\begin{aligned}
 2. \text{ Tin required} &= 2 \times 2 / 92.38 && \text{g} \\
 &= 4.33 \times 10^{-2} && \text{g}
 \end{aligned}$$

$$\begin{aligned}
 \text{Stannous chloride dihydrate required} &= 4.33 \times 10^{-2} \times 100 / 51.03 && \text{g} \\
 &= 0.0849 && \text{g}
 \end{aligned}$$

3. Hydrochloric acid and solution required

$$= 2 \times 0.05 \quad \text{g}$$

$$= 0.1 \quad \text{g}$$

The amount of hydrochloric acid by volume

$$= 0.1 / (1.19 \times 0.37) \quad \text{ml}$$

$$= 0.227 \quad \text{ml}$$

As the pore volume of the alumina support is 1 ml/g, the total volume of impregnating solution that must be used is 2 ml by the requirement of dry impregnation method. The de-ionized water is added until the volume of impregnating solution is 2 ml as equal to the volume of the alumina pore volume.

For the other catalysts, the calculation procedure is similar to that of 1 wt% Pt – 2 wt% Sn/Al₂O₃ catalyst, except no addition of Hydrochloric acid.

C.2 Calculation of Specific Surface Area

From Brunauer-Emmett-Teller (BET) equation

$$\frac{p}{n(1-p)} = \frac{1}{n_m C} + \frac{(C-1)p}{n_m C} \quad (\text{C.1})$$

Where, p = Relative partial pressure of adsorbed gas, P/P_0

P_0 = Saturated vapor pressure of adsorbed gas in the condensed state at the experimental temperature, atm

P = Equilibrium vapor pressure of adsorbed gas, atm

n = Gas adsorbed at pressure P , ml. at the NTP/g of sample

n_m = Gas adsorbed at monolayer, ml. at the NTP/g of sample

C = $\text{Exp} [(H_C - H_1)/RT]$

H_C = Heat of condensation of adsorbed gas on all other layers

H_1 = Heat of adsorption into the first layer

Assume $C \rightarrow \infty$, then

$$\frac{p}{n(1-p)} = \frac{p}{n_m}$$

$$n_m = n(1-p) \quad (\text{C.2})$$

The surface area, S , of the catalyst is given by

$$S = S_b \times n_m \quad (\text{C.3})$$

From the gas law

$$\frac{P_b V}{T_b} = \frac{P_t V}{T_t} \quad (\text{C.4})$$

Where, P_b = Pressure at 0°C

P_t = Pressure at $t^\circ\text{C}$

T_b = Temperature at $0^\circ\text{C} = 273.15 \text{ K}$

T_t = Temperature at $t^\circ\text{C} = 273.15 + t \text{ K}$

V = Constant volume

Then, $P_b = (273.15 / T_t) \times P_t = 1 \text{ atm}$

Partial pressure

$$P = \frac{[\text{Flow of } (\text{He} + \text{N}_2) - \text{Flow of He}]}{\text{Flow of } (\text{He} + \text{N}_2)} \quad (\text{C.5})$$

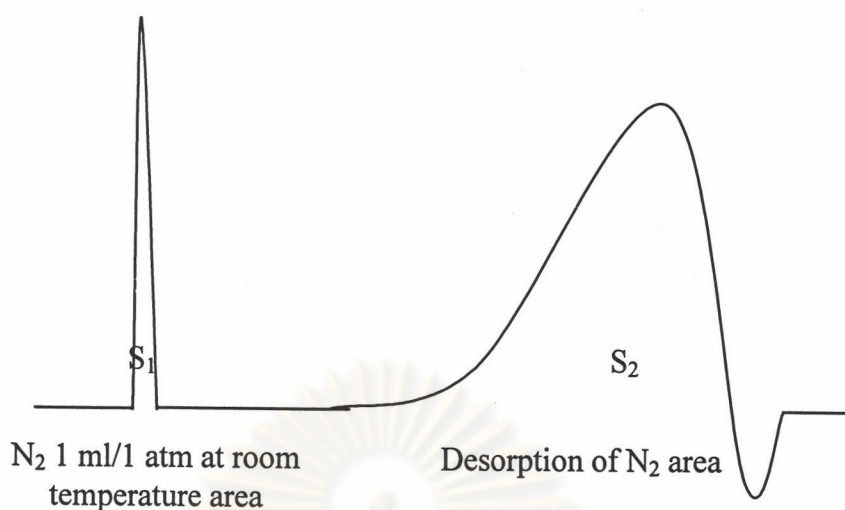
$$= 0.3 \text{ atm}$$

For nitrogen gas, the saturated vapor pressure equals to

$$P_0 = 1.1 \text{ atm}$$

then, $p = P/P_0 = 0.3/1.1 = 0.2727$

To measure the volume of nitrogen adsorbed, n



$$n = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \text{ ml. /g of catalyst} \quad (\text{C.6})$$

Where, S_1 = N_2 1 ml/1 atm at room temperature area

S_2 = Desorption of N_2 area

W = Sample weight, g

T = Room temperature, K

Therefore,

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times (1-p)$$

$$n_m = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \quad (\text{C.7})$$

Whereas, the surface area of nitrogen gas from literature equal to

$$S_b = 4.373 \text{ m}^2/\text{ml of nitrogen gas}$$

Then,

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 0.7272 \times 4.343$$

$$S = \frac{S_2}{S_1} \times \frac{1}{W} \times \frac{273.15}{T} \times 3.1582 \text{ m}^2/\text{g} \quad (\text{C.8})$$

C.3 Calculation of Metal Active Sites

To calculate the metal active sites of the catalyst measured by CO adsorption technique at room temperature, the following procedure is shown:

Let the weight of catalyst used	= W	g
Integral area of CO peak after adsorption	= A	unit
Integral area of 50 μ l of standard CO peak	= B	unit
Amounts of CO adsorbed on catalyst	= B-A	unit
Volume of CO adsorbed on catalyst	= [(B-A)/B] \times 50	μ l
Volume of 1 mole of CO at 30°C	= 24.86 \times 10 ⁶	μ l
Mole of CO adsorbed on catalyst	= [(B-A)/B][50/24.86 \times 10 ⁶]	mole
Molecule of CO adsorbed on catalyst	= [2.01 \times 10 ⁻⁶][(B-A)/B][6.02 \times 10 ²³]	molecules
Metal active sites	= 1.21 \times 10 ¹⁸ [(B-A)/B][1/W]	molecules of CO/g of catalyst

In addition, the platinum dispersion, which is the ratio between the apparent platinum molecules observed from the measurement of CO adsorption and the actual platinum molecules obtained from the measurement of atomic absorption spectroscopy, can also be calculated.

Example of the calculation of metal active sites and metal dispersion is shown as follows:

For 1 wt% Pt/Al₂O₃ catalyst,

The weight of catalyst used	= 0.1	g
Integral area of CO peak after 1 st adsorption	= 72	unit
Integral area of CO peak after 2 nd adsorption	= 84	unit
Integral area of CO peak after 3 rd adsorption	= 2269	unit
Integral area of 50 μ l of standard CO peak	= 2734	unit
Amounts of CO adsorbed on catalyst	= (3 \times 2734)-72-84-2269	
	= 5777	unit

$$\begin{aligned}
 \text{Volume of CO adsorbed on catalyst} &= [5777/2734] \times 50 \\
 &= 105.65 \quad \mu\text{l} \\
 \text{Volume of 1 mole of CO at } 30^\circ\text{C} &= 24.86 \times 10^6 \quad \mu\text{l} \\
 \text{Mole of CO adsorbed on catalyst} &= [105.65/24.86 \times 10^6] \\
 &= 4.25 \times 10^{-6} \quad \text{mole} \\
 \text{Molecule of CO adsorbed on catalyst} &= [4.25 \times 10^{-6}] \times [6.02 \times 10^{23}] \quad \text{molecules}
 \end{aligned}$$

Therefore,

$$\begin{aligned}
 \text{Metal active sites} &= 2.55 \times 10^{18} / 0.1 \\
 &= 2.55 \times 10^{19} \quad \text{molecules of CO/g of catalyst}
 \end{aligned}$$

$$\text{The actual percentage of platinum loading} = 1 \quad \text{wt\%}$$

$$\begin{aligned}
 \text{The actual platinum molecules} &= 0.01 \times 6.02 \times 10^{23} / 195.08 / 0.1 \\
 &= 3.09 \times 10^{19} \quad \text{molecules/g of catalyst}
 \end{aligned}$$

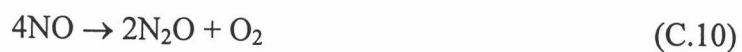
Therefore,

$$\begin{aligned}
 \text{The platinum dispersion} &= 2.55 \times 10^{19} \times 100 / 3.09 \times 10^{19} \\
 &= 83 \quad \%
 \end{aligned}$$

C.4 Calculation of NO and HC Conversions

In the catalytic activity test, the NO reduction and HC oxidation are evaluated in form of the conversions of NO and HC, respectively. Due to the lack of an instrument for directly detecting NO_x, NO conversion is calculated from N₂ and N₂O products analyzed by gas chromatographs. The following procedure is shown below:

The absolute NO conversion to N₂ and N₂O can be expressed as the reactions (C.9) and (C.10).



Therefore,

$$\text{NO conversion to N}_2 \text{ (\%)} = (2[\text{N}_2]_{\text{out}}/[\text{NO}]_{\text{in}}) \times 100 \quad (\text{C.11})$$

$$\text{NO conversion to N}_2\text{O (\%)} = (2[\text{N}_2\text{O}]_{\text{out}}/[\text{NO}]_{\text{in}}) \times 100 \quad (\text{C.12})$$

Where,

$$[\text{NO}]_{\text{in}} = \text{NO concentration in feed stream} \quad (\text{ppm})$$

$$[\text{N}_2]_{\text{out}} = \text{N}_2 \text{ concentration in product stream} \quad (\text{ppm})$$

$$[\text{N}_2\text{O}]_{\text{out}} = \text{N}_2\text{O concentration in product stream} \quad (\text{ppm})$$

From the calibration curves (Figures B.2 and B.7),

$$[\text{N}_2]_{\text{out}} = 0.525 \times [\text{Area}(\text{N}_2)] \quad (\text{C.13})$$

$$[\text{N}_2\text{O}]_{\text{out}} = 0.955 \times [\text{Area}(\text{N}_2\text{O})] \quad (\text{C.14})$$

Where,

$$[\text{Area}(\text{N}_2)] = \text{Area of N}_2 \text{ peak from integrator plot on GC 8ATP}$$

$$[\text{Area}(\text{N}_2\text{O})] = \text{Area of N}_2\text{O peak from integrator plot on GC 8AIT}$$

If the NO concentration in feed stream is equal to 1000 ppm (only used in this work),

$$\text{NO conversion to N}_2 \text{ (\%)} = 0.105 \times [\text{Area}(\text{N}_2)] \quad (\text{C.15})$$

$$\text{NO conversion to N}_2\text{O (\%)} = 0.191 \times [\text{Area}(\text{N}_2\text{O})] \quad (\text{C.16})$$

The HC conversion is calculated as follows:

$$\text{HC conversion (\%)} = 100 \times ([\text{HC}]_{\text{in}} - [\text{HC}]_{\text{out}}) / [\text{HC}]_{\text{in}} \quad (\text{C.17})$$

Where,

$$[\text{HC}]_{\text{in}} = \text{HC concentration in feed stream} \quad (\text{ppm})$$

$$[\text{HC}]_{\text{out}} = \text{HC concentration in product stream} \quad (\text{ppm})$$

If HC = C₃H₆, from the calibration curves (Figure E.8),

$$[\text{C}_3\text{H}_6]_{\text{in}} = 0.697 \times [\text{Area}(\text{C}_3\text{H}_6)]_{\text{in}} \quad (\text{C.18})$$

$$[\text{C}_3\text{H}_6]_{\text{out}} = 0.697 \times [\text{Area}(\text{C}_3\text{H}_6)]_{\text{out}} \quad (\text{C.19})$$

Where,

$$[\text{Area}(\text{C}_3\text{H}_6)]_{\text{in}} = \text{Area of C}_3\text{H}_6 \text{ peak in feed from integrator plot on GC 8AIT}$$

$$[\text{Area}(\text{C}_3\text{H}_6)]_{\text{out}} = \text{Area of C}_3\text{H}_6 \text{ peak in product from integrator plot on GC 8AIT}$$

If the C_3H_6 concentration in feed stream is equal to 1000 ppm,

$$\text{HC conversion (\%)} = 100 \times ([\text{Area}(C_3H_6)]_{\text{in}} - [\text{Area}(C_3H_6)]_{\text{out}}) / [\text{Area}(C_3H_6)]_{\text{in}} \quad (\text{C.20})$$

Example,

$$[\text{Area}(N_2)] = 100$$

$$[\text{Area}(N_2O)] = 85$$

If the NO concentration in feed stream is equal to 1000 ppm (only used in this work),

$$\text{NO conversion to } N_2 (\%) = 0.105 \times 100 = 10.5$$

$$\text{NO conversion to } N_2O (\%) = 0.191 \times 85 = 16.2$$

Where,

$$[\text{Area}(C_3H_6)]_{\text{in}} = 1534$$

$$[\text{Area}(C_3H_6)]_{\text{out}} = 1128$$

If the C_3H_6 concentration in feed stream is equal to 1000 ppm,

$$\text{HC conversion (\%)} = 100 \times (1534 - 1128) / 1534 = 26.5$$

C.5 Calculation of the Amount of Surface Species

The amount of carbon in surface species on the catalyst surface obtained from the TPD step in an experimental set of three continuous steps is used to represent the amount of surface species. Hence, the amount of total surface species and particular surface species are calculated.

The concentration of CO_2 in Y-axis is initially converted as the molar flow rate of CO_2 by the assumption of ideal gas behavior as follows:

$$F_{CO_2} = C_{CO_2} \times v = [y_{CO_2} \times P] \times v / [R \times T] \quad (\text{C.21})$$

Where,

F_{CO_2} = Molar flow rate of CO_2 (mole/min)

C_{CO_2} = Concentration of CO_2 (mole)

v = Total volumetric flow rate (liter/min)

y_{CO_2} = mole fraction of CO_2

P = Total pressure (atm)

R = Gas constant = 0.08206 (atm·liter/mole·K)

T = Absolute temperature (K)

Subsequently, the temperature in X-axis is converted as time through the heating rate of TPD step. The relationship between the molar flow rate and time is graphically obtained. Then the area under this curve gives the value of total CO_2 mole released from the catalyst surface. Finally, this value is converted to mass of carbon. The same method for CH_4 and CO curve is obtained and the summation of mass of carbon from CO_2 , CH_4 and CO becomes the total amount of carbon in surface species.

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APPENDIX D

LIST OF PUBLICATIONS

D.1 International Paper

1. Piyasan Prasertthdam, Choowong Chaisuk, Apiwat Panit, and Kriangsak Kraiwattanawong, "Some aspects about the nature of surface species on Pt-based and MFI-based catalysts for the selective catalytic reduction of NO by propene under lean-burn condition", Applied Catalysis B: Environmental, to be published.

2. Piyasan Prasertthdam, Choowong Chaisuk, and Pornsawan Kanchanawanichkun, "Comparative study of coke deposition on catalysts in reactions with and without oxygen", Research on Chemical Intermediates, 24(5), 605-612 (1998).

D.2 International Conference

1. Piyasan Prasertthdam and Choowong Chaisuk, "Role of NO on propene and NO conversion over Pt/Al₂O₃ catalyst under lean-burn condition at low temperature", 2nd World Congress on Environmental Catalysis 1998, Miami Beach, Florida, U.S.A., Nov. 15-20, 1998, 402.

2. Piyasan Prasertthdam and Choowong Chaisuk, "The effect of NO on coke formation over Pt catalyst in NO reduction by propene under lean-burn condition", Proceedings of region symposium on Chemical Engineering 1998, Manila, Philippines, Oct. 14-16, 1998, 146.

3. Piyasan Prasertthdam and Choowong Chaisuk, "Comparative study of coke deposition on Pt catalysts in reactions with and without oxygen", 15th Canadian Symposium on Catalysis 1998, Quebec, Canada, May 17-20, 1998, 44.

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Some aspects about the nature of surface species on Pt-based and MFI-based catalysts for the selective catalytic reduction of NO by propene under lean-burn condition

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Received 30 November 2001; received in revised form 1 March 2002; accepted 4 March 2002

Abstract

The nature of surface species for the selective catalytic reduction of NO by propene under lean-burn condition is relatively investigated on Pt/Al₂O₃ and Co-ZSM-5 catalysts. An experimental set of three continuous steps including adsorption, temperature programmed desorption (TPD) and temperature programmed oxidation (TPO) is performed to observe the particular behavior of surface species on both catalysts. The surface species on Pt/Al₂O₃ are almost totally released during TPD step, whereas those on Co-ZSM-5 are necessarily removed by the oxidizing gas on TPO step. It is suggested that the different nature of surface species on both catalysts should possibly play an important role on the reaction mechanism pathway. For Co-ZSM-5 catalyst, the surface species, which are formed by the interaction of NO, propene and oxygen, are distinctly assigned as the intermediate species in the NO reduction mechanism. On the other hand, for Pt/Al₂O₃ catalyst, the observation of several surface species and the investigation about their reactivities indicate that several reaction mechanisms are simultaneously proceeded at the same operating condition. © 2002 Published by Elsevier Science B.V.

Keywords: Pt/Al₂O₃; Co-ZSM-5; SCR of NO by propene; Lean-burn condition; Surface species; Reaction mechanism

1. Introduction

Nitrogen oxides (NO_x) are emitted primarily both from stationary and automotive sources and contribute largely to a variety of environmental problems such as the formation of acid rain and the resultant acidification of aquatic systems, the photochemical reaction in the stratosphere destroying the ozone in the atmosphere and the harmful impact for the respiratory sys-

tem of human being [1]. To alleviate these problems, the emission of nitrogen oxides is seriously controlled. There are two major conventional catalytic technologies for the abatement of the emission of nitrogen oxides into the atmosphere. One is the selective catalytic reduction using ammonia as a reductant (NH₃-SCR) [2]. However, there are many problems associated with this process including ammonia slip, equipment corrosion, as well as danger in transportation and storage of ammonia. Hence, this technology can be conveniently used for only stationary sources such as power plants. The second technology is the three-way catalyst (TWC) that is highly efficient in the simultaneous

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47 removal of carbon monoxide, hydrocarbons and nitro-
48 gen oxides [3]. However, it requires an exhaust gas
49 composition operating very close to the stoichiometric
50 point. Thus, the emissions from diesel and lean-burn
51 gasoline engines are not effectively controlled on this
52 catalyst. From these reasons, neither of the above two
53 catalytic technologies is applicable for the emissions
54 from both mobile sources and stationary sources con-
55 taining oxygen excess [4].

56 The most attractive approach for the removal of
57 NO_x is the catalytic decomposition of NO [5]. This
58 method is feasible because no reducing agent is re-
59 quired. Thermodynamically, NO can decompose to
60 dinitrogen under 800 °C but, kinetically, it remains sta-
61 ble in the absence of catalyst [6]. However, no suit-
62 able catalyst with a significant activity in real exhaust
63 gases has been identified [7]. It is widely accepted that
64 the poisoning of the catalyst surface by oxygen atom
65 from the exhaust gas or from the decomposition itself
66 is the main problem. Hence, the only way to reduce
67 NO_x emission in lean exhaust gases is the injection of
68 reducing agents into the exhaust gas stream [8,9].

69 In 1986, the outstanding activity for the catalytic
70 decomposition of NO on Cu-ZSM-5 compared to the
71 earlier known catalysts was reported by Iwamoto et al.
72 [10]. This finding was remarkable but its catalytic ac-
73 tivity dropped sharply with a decrease in the NO con-
74 centration and this catalyst suffered from severe deac-
75 tivation in the presence of oxygen or sulfur oxides. It
76 was later demonstrated that Cu-ZSM-5 showed a sig-
77 nificant activity when it was used for a real lean-burn
78 engine; moreover, the rate of reaction increased in the
79 presence of oxygen. It was shown that the reaction
80 taking place in this case was not the decomposition
81 of NO but the reduction of NO by hydrocarbons con-
82 tained in the emission gases. In 1990, Held et al. [11]
83 and Iwamoto [12], independently proposed that the
84 reduction of NO over Cu-ZSM-5 could be greatly en-
85 hanced in an excess of oxygen by the presence of
86 small amounts of hydrocarbon. Following this discov-
87 ery, many catalysts such as various kinds of solid acids
88 and bases, including ZSM-5 loaded with metal ions,
89 were demonstrated to be active catalysts for this reac-
90 tion [13]. Generally, this reaction is the so-called se-
91 lective catalytic reduction by hydrocarbon (HC-SCR).

92 Catalysts reported for this reaction so far can be
93 classified into zeolites, metal oxides and noble met-
94 als. Various zeolites have a promising activity at high

95 temperature; however, there are major problems with
96 these catalysts both in terms of thermal stability [14]
97 and sensitivity to water [15]. On the other hand, metal
98 oxides and noble metals are not adequate for the very
99 demanding challenge of providing high activity and
100 good selectivity but their activities are little diminished
101 by sulfur oxides or water [16,17]. Hence, the develop-
102 ment and design of SCR catalysts have been continu-
103 ously investigated to overcome these limitations. Al-
104 though there are many literatures reported to the suc-
105 cess for testing this reaction on several catalysts, the
106 outstanding knowledge about the reaction mechanisms
107 and the active intermediate species is still ambiguous.

108 Generally, two main different mechanisms have
109 been reported in the literatures, i.e. the NO decom-
110 position mechanism [18–21] and the NO reduction
111 mechanism [22–27]. The first mechanism has mainly
112 been mentioned for the noble metal group catalysts,
113 especially platinum-based catalysts. In this case, the
114 hydrocarbons are contributed to remove the surface
115 oxygen poisoning the active sites, while nitrogen
116 product is dominantly formed via NO dissociation.
117 Hence, the complex surface species such as organic
118 nitro species are distinctly neglected and either N
119 atom or NO molecule is addressed as the interme-
120 diate species for this mechanism [20]. On the other
121 hand, the NO reduction mechanism is widely pro-
122 posed to explain with various catalysts, especially
123 zeolite group catalysts. Although its pathway may
124 be different in details, the same significant concept
125 is the complex surface species playing an important
126 role for producing nitrogen. For example, the hy-
127 drocarbons react with oxygen to partially oxidized
128 hydrocarbons, which are reactive by nitrogen dioxide
129 to form nitrogen [23]. Additionally, the hydrocar-
130 bons may first react with nitrogen dioxide produced
131 by NO oxidation to organic nitro species leading to
132 the formation of nitrogen [27]. Thus, there are many
133 types of surface species, e.g. organic nitro compound
134 [27,28], isocyanate species [29–31] and oxygenated
135 organic complex [32], independently assigned as the
136 intermediate species for this mechanism. However,
137 the influencing parameters, e.g. types of catalyst [1],
138 reaction conditions [30] and types of reductant [33],
139 should be carefully taken into account for considering
140 in details about the reaction mechanism as well.

141 Typically, propene is used to be a model reductant
142 gas to explain the reaction mechanism on various cat-

143 alysts. Among the catalysts tested for the selective
144 catalytic reduction of NO by propene, Pt/Al₂O₃ has
145 extensively been studied in order to increase its cat-
146 alytic activity and selectivity. However, the high rates
147 of nitrous oxide formation and the narrow temperature
148 window of the catalytic performance are crucial prob-
149 lems for application practice [34]. Nevertheless, mech-
150 anism studies from many literatures suggest that the
151 selective catalytic reduction of NO by propene on this
152 catalyst has not been clarified to take place through the
153 NO decomposition or the NO reduction mechanism
154 [34]. Consequently, an exact role of the catalytic sur-
155 face species has not particularly been addressed to be
156 the intermediate species or the spectator species upon
157 such reaction. In case of Pt/Al₂O₃, the differences in
158 mechanism studies, from a group of zeolite catalysts,
159 have been raised because the reaction on zeolites is
160 distinctly proceeded via the NO reduction mechanism.
161 To understand a role of the catalytic surface species
162 for this reaction better, Co-ZSM-5 catalyst is cho-
163 sen to represent a group of zeolites for comparing to
164 Pt/Al₂O₃ catalyst. Co-ZSM-5 is an attractive catalyst
165 because its activity for the selective catalytic reduc-
166 tion of NO by methane is very high, compared to other
167 ion-exchanged ZSM-5 catalysts. Although the intro-
168 duction of the other hydrocarbons instead of methane
169 has not much been studied, the previous works have
170 been unanimous that the proposed mechanism for the
171 selective catalytic reduction of NO by various hydro-
172 carbons over Co-ZSM-5 is the same pathway [35–46].
173 It contains two main steps, i.e. the hydrocarbon activa-
174 tion leading to the N-containing intermediate species
175 and the conversion of these species to final products.

176 From the earlier introduction, attempt to investigate
177 the role of surface species on the reaction mechanism
178 of the selective catalytic reduction of NO by propene is
179 made over two catalysts, i.e. Co-ZSM-5 and Pt/Al₂O₃.
180 In this work, the surface species are indirectly studied
181 as described in the next section.

182 2. Experimental

183 2.1. Catalyst preparation

184 A 1 wt.% Co-ZSM-5 catalyst was prepared by the
185 ion-exchange of Na-ZSM-5 having Si/Al molar ra-
186 tio of 25 (ALSI-PENTA Zeolithe GmbH, Alustr.50,

92421 Schwabach, Germany) with 0.01 M aqueous
187 solution of cobalt(II) acetate at 80 °C for 24 h under
188 continuous stirring. After the ion-exchange process,
189 the sample was thoroughly washed with deionized wa-
190 ter for 3–5 times to remove some ions using a cen-
191 trifuge separator, dried at 110 °C overnight and cal-
192 cined in air at 540 °C for 3.5 h. 193

A 1 wt.% Pt/Al₂O₃ catalyst was prepared by incipient
194 wetness impregnation method. The alumina
195 support used in this study was obtained from Sumi-
196 tomo Aluminum Smelting (type NKH-3) and the metal
197 salt precursor was chloroplatinic acid hexahydrate
198 (H₂PtCl₆·6H₂O) obtained from Wako Pure Chemical
199 Industries. After impregnation, the sample was dried at
200 110 °C overnight and calcined in air at 500 °C for 3 h. 201

202 2.2. Catalytic evaluation

The aim for this catalytic test is to investigate the
203 nature of surface species for the selective catalytic re-
204 duction of NO by propene on both Co-ZSM-5 and
205 Pt/Al₂O₃ catalysts. All experiments were conducted
206 by using a quartz tubular downflow reactor with 0.6 cm
207 inside diameter. The effluent gases were analyzed by
208 a gas chromatograph (SHIMADZU GC 8A) equipped
209 with molecular sieve 5 Å column for separating oxy-
210 gen, nitrogen and carbon monoxide and porapak QS
211 column for separating carbon dioxide, nitrous oxide
212 and hydrocarbons. Prior to the catalyst test, 0.2 g of
213 Co-ZSM-5 was pretreated in helium at 500 °C for
214 1 h, whereas 0.1 g of Pt/Al₂O₃ was reduced in hydro-
215 gen flow at 500 °C for 1 h and subsequently treated
216 under 10% oxygen in helium at 500 °C for 1 h. An
217 experimental set of three continuous steps was per-
218 formed, i.e. first-adsorption step for producing the sur-
219 face species, second-temperature programmed desorp-
220 tion (TPD) step for removing the weakly adsorbed sur-
221 face species and third-temperature programmed oxida-
222 tion (TPO) step for testing the reactivity of the re-
223 maining deposits to the oxidizing gas. During the first
224 step, the sample was exposed to the selected reactant
225 gas mixture containing 0–1000 ppm NO, 0–2000 ppm
226 propene and 0–10% oxygen diluted in helium at a
227 given temperature until saturation. The TPD experi-
228 ment on the second step was subsequently carried out
229 from 100 to 800 °C under helium flow. Afterwards,
230 the removal of deposits was performed by heating the
231 sample from 100 to 800 °C under various oxidizing
232

233 gases, i.e. 1000 ppm NO, 1% O₂ and the gas mixture
234 of 1000 ppm NO and 1% O₂.

235 3. Results and discussion

236 3.1. Co-ZSM-5 catalyst

237 3.1.1. The catalytic behavior for time on stream 238 experiment

239 First, the catalytic behavior for the selective catalytic
240 reduction of NO by propene on Co-ZSM-5 was
241 studied by considering the time on stream experiment.
242 The gas mixture used in this experiment contained
243 1000 ppm NO, 2000 ppm propene and 10% oxygen
244 diluted in helium. Fig. 1 shows the nitrogen product
245 concentration from the reactor outlet in this experimental
246 set. At the beginning step, the gas mixture was
247 immediately introduced into the system at 550 °C.
248 It was obviously seen that the nitrogen concentration
249 detected from reactor outlet gradually decreased
250 at the initial time (0–30 min), and then reached
251 a constant value. After 150 min, the gas mixture was
252 subsequently switched off and the sample was cooled
253 down from 550 to 400 °C under helium flow. Next,
254 the gas mixture was again switched into the reactor
255 at this temperature (400 °C). It was observed that the
256 nitrogen concentration diminished as a function of time
257 after introducing the gas mixture. Interestingly, the
258 nitrogen concentration was close to 0 value within 1 h.
259 After that, the gas mixture was switched off and the

260 reaction temperature was raised to 550 °C under helium
261 atmosphere. Like the previous step, the gas mixture
262 was again introduced to the reactor at this temperature
263 (550 °C). It was clearly found that the initial nitrogen
264 concentration at 550 °C in the second test was much
265 higher than that in the first test and then it
266 dramatically decreased with time. Finally, the nitrogen
267 concentration reached to a constant value, which
268 was approximately equal to the nitrogen concentration
269 in the first test. Presumably, NO conversion to nitrogen
270 at 550 °C reached the steady value at this stage.
271 It was believed that the decrease of nitrogen concentration
272 at both temperatures was due to the deposits. It was
273 expected that the negligible effect of deposits was
274 existed at the high temperature (550 °C). On the
275 other hand, it was speculated that these deposits may
276 hardly be removed at lower temperature; therefore,
277 the nitrogen production was significantly suppressed
278 at 400 °C. These results were corresponding with the
279 work reported by Chen et al. [47] who observed the
280 decrease of NO conversion at 300 °C as a function of
281 time on stream for the selective catalytic reduction by
282 *iso*-butane and *n*-butane over Fe-ZSM-5. Additionally,
283 they suggested that the deactivation was accounted for
284 the formation of active deposits, which significantly
285 blocked the accessible sites for NO adsorption. Thus,
286 the reaction, which was catalyzed by the iron sites,
287 will be hindered [43]. Comparing the initial NO conversion
288 at 550 °C between the first test and the second one,
289 it was obvious that the second test gave much more
290 NO conversion than the first one. There were two

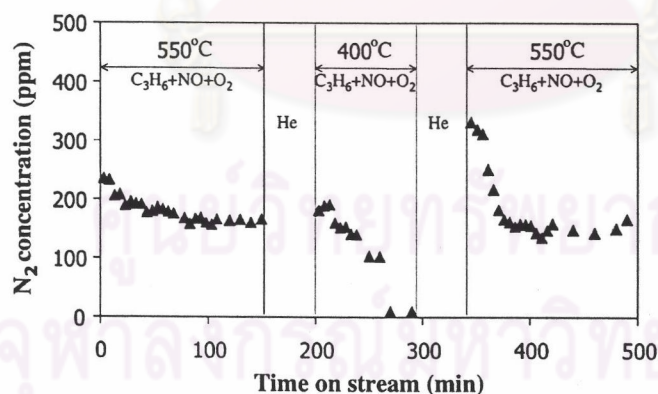


Fig. 1. The nitrogen concentration from the reactor outlet as a function of time on stream for the selective catalytic reduction of NO by propene on Co-ZSM-5 at 400 and 550 °C. The gas reactant composition 1000 ppm NO, 2000 ppm C₃H₆ and 5% O₂, GHSV = 2000 h⁻¹.

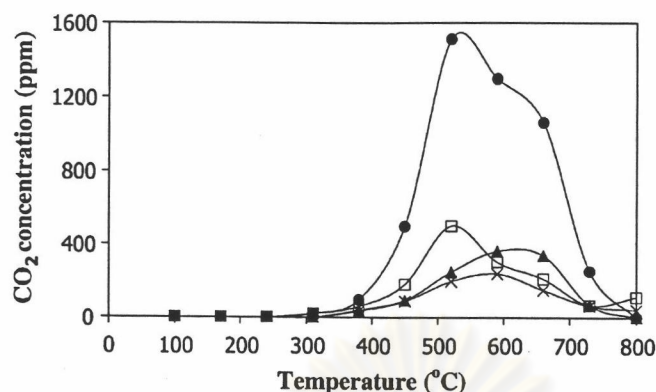


Fig. 2. The carbon dioxide concentration released during TPO by O₂ on Co-ZSM-5 after dosing various adsorbed gas mixtures at 100 °C: (x) 2000 ppm C₃H₆, (□) 2000 ppm C₃H₆ + 1000 ppm NO, (▲) 2000 ppm C₃H₆ + 5% O₂, (●) 2000 ppm C₃H₆ + 1000 ppm NO + 5% O₂.

291 possible explanations for this observation. First, the
 292 deposits, kinds of intermediate species, can react with
 293 the reactant gases to produce nitrogen product. In the
 294 other case, the deposits can decompose themselves to
 295 nitrogen product when the reaction temperature was
 296 high enough. Furthermore, the latter case was in ac-
 297 cordance with the report by Walker [37] who men-
 298 tioned that the carbonaceous deposits merely acted as
 299 reductant for impinging on NO or NO₂. However, it
 300 can be concluded from these results that the deposits
 301 should be reversible, viz. the NO reduction activity
 302 could be recovered when the reaction temperature was
 303 high enough that these deposits could be removed.

304 3.1.2. The formation of intermediate species

305 From the earlier introduction, it was suggested that
 306 the formation of intermediate species should play
 307 an important role on the NO reduction mechanism.
 308 These intermediate species may be produced by vari-
 309 ous ways, for example, the only hydrocarbons being
 310 the active carbonaceous species [48], the hydrocar-
 311 bons reacting with oxygen leading to the production
 312 of partially oxidized hydrocarbon species [23], and
 313 etc. This part showed the formation of intermediate
 314 species on Co-ZSM-5 by varying the adsorbed gas
 315 mixture in absorption step. The procedure for testing
 316 was described in Section 2.

317 Four sets of gas mixture (C₃H₆, C₃H₆+NO, C₃H₆+
 318 O₂ and C₃H₆ + NO + O₂) were used as a testing gas
 319 in the adsorption step. Co-ZSM-5 was dosed by each
 320 gas set at 100 °C until the saturation. After that, TPD

321 and TPO by only oxygen steps were continuously pro-
 322 ceeded to investigate the characteristic of the surface
 323 species. It was noted that the surface species were en-
 324 tirely removed on TPO step, while no species was re-
 325 leased during TPD step. TPO spectra of Co-ZSM-5
 326 catalyst dosed by the adsorbed gas mixture are il-
 327 lustrated in Figs. 2 and 3. It was observed that car-
 328 bon dioxide and nitrogen were only two types of the
 329 product gases emitted from reactor on TPO experi-
 330 ments. Hence, the amounts of such gases should refer
 331 to the total amount of the deposits on catalyst sur-
 332 face. Fig. 2 obviously shows that the amount of car-
 333 bon dioxide from C₃H₆ + NO + O₂ experiment set
 334 was much more than that from the other three sys-
 335 tems. This result implied that the most possibility for
 336 the formation step of intermediate species was the co-
 337 operation of the three reactant gas species, i.e. NO,
 338 propene and oxygen. The nitrogen removed during
 339 TPO step could also support this explanation as il-
 340 lustrated in Fig. 3. It was clearly seen that nitrogen
 341 would be emerged from only C₃H₆ + NO + O₂ sys-
 342 tem. Therefore, it can be concluded that the interme-
 343 diate species for the selective catalytic reduction of
 344 NO by propene on Co-ZSM-5 catalyst were neces-
 345 sarily formed by the interaction of NO, propene and
 346 oxygen.

347 Chang and McCarty [44] found that co-adsorption
 348 of NO and oxygen led to a substantial increase in
 349 the amount of NO_x adsorbed on the catalysts irre-
 350 spective of cation type or degree of metal loading.
 351 Similar behavior over Co-ZSM-5 catalyst that NO

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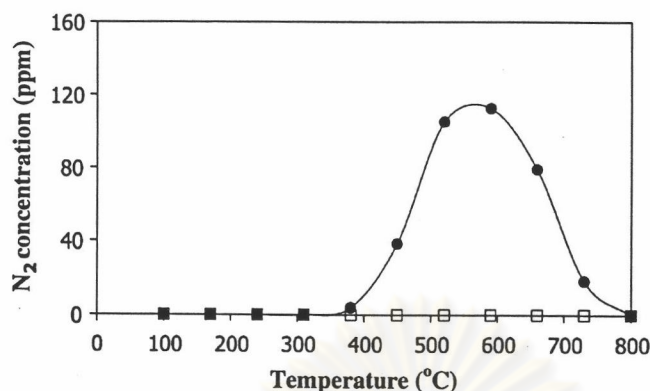


Fig. 3. The nitrogen concentration released during TPO by O₂ on Co-ZSM-5 after dosing various adsorbed gas mixtures at 100 °C: (□) 2000 ppm C₃H₆ + 1000 ppm NO, (●) 2000 ppm C₃H₆ + 1000 ppm NO + 5% O₂.

352 was hardly adsorbed at the reaction temperatures was
 353 also reported, but the interaction between NO and Co
 354 cations was greatly enhanced in the presence of oxy-
 355 gen [39]. In addition, Pinaeva et al. [45] suggested
 356 that Co ion located at the interface of Co clusters and
 357 zeolites was found to react with NO in the presence
 358 of oxygen to form anchored NO₂ delta+ species stabi-
 359 lized on Co-ZSM-5 under the reaction conditions.
 360 Therefore, it can be proposed from these results that
 361 the initial step for the selective catalytic reduction of
 362 NO by propene in the presence of oxygen excess on
 363 Co-ZSM-5 catalyst was the adsorption of NO_y species
 364 formed by the interaction of NO and oxygen. These
 365 species will subsequently interact with propene and

form nitrogen-containing deposits, which should be
 the intermediate species of such reaction; however, the
 formation of intermediate species may mainly depend
 on types of hydrocarbon reductant as well.

3.1.3. The removal of intermediate species

In order to study the image of the removal of in-
 termediate species for the selective catalytic reduction
 of NO by propene in the presence of oxygen excess
 over Co-ZSM-5, TPO experiment step was independ-
 ently conducted by varying oxidizing gases (NO, O₂
 and NO + O₂). In this part, Co-ZSM-5 catalyst was
 exposed by only gas mixture of C₃H₆ + NO + O₂ at
 100 °C. Figs. 4 and 5 show the concentrations of car-

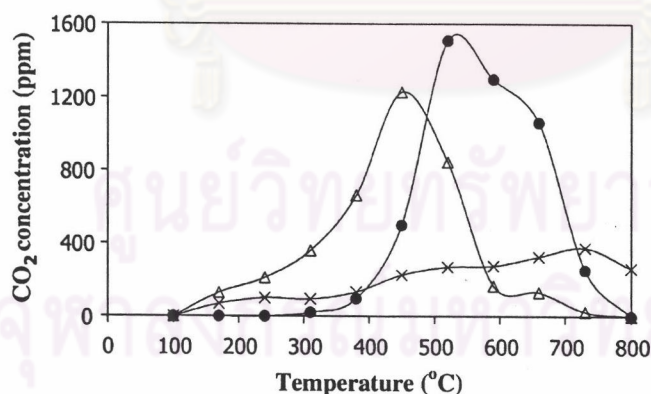


Fig. 4. The carbon dioxide concentration released during TPO by varying oxidizing gases on Co-ZSM-5 after dosing 2000 ppm C₃H₆ + 1000 ppm NO + 5% O₂ at 100 °C: (x) 1000 ppm NO, (●) 1% O₂, (Δ) 1000 ppm NO + 1% O₂.

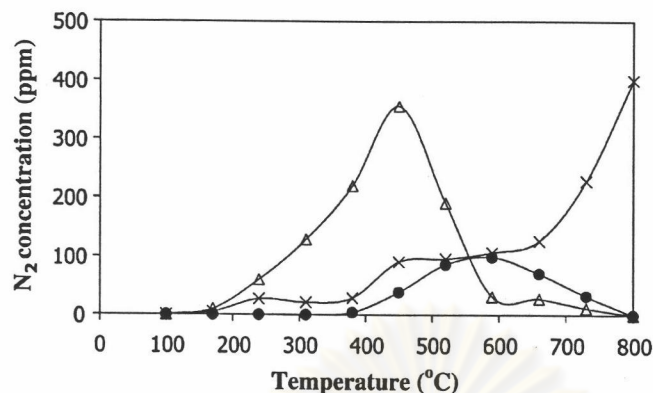


Fig. 5. The nitrogen concentration released during TPO by varying oxidizing gases on Co-ZSM-5 after dosing 2000 ppm C_3H_6 + 1000 ppm NO + 5% O_2 at 100°C: (x) 1000 ppm NO, (●) 1% O_2 , (Δ) 1000 ppm NO + 1% O_2 .

379 bon dioxide and nitrogen on TPO step, respectively.
 380 As seen in Fig. 4, a small amount of carbon dioxide
 381 was emerged by using only NO as the oxidizing gas.
 382 When the oxidizing gas became either only oxygen or
 383 a gas mixture of NO and oxygen, a large amount of
 384 carbon dioxide was distinctly obtained. These results
 385 implied that the removal of intermediate species was
 386 effectively occurred in the presence of oxygen. Inter-
 387 estingly, when a gas mixture of NO and oxygen was
 388 used instead of only oxygen, the intermediate species
 389 could be removed at lower temperature region. There-
 390 fore, it can be concluded that the cooperation of NO
 391 and oxygen possibly accelerated the removal of inter-
 392 mediate species.

393 Although the amount of carbon dioxide emerged
 394 during TPO step by only oxygen or a gas mixture of
 395 NO and oxygen was not much different, the nitrogen
 396 concentration for both cases was remarkably differ-
 397 ent as illustrated in Fig. 5. TPO step by a gas mixture
 398 of NO and oxygen showed that the amount of nitro-
 399 gen product was largely released at lower tempera-
 400 ture. This result implied that the increase of nitrogen
 401 product could be attributed to nitrogen atom in NO
 402 feed, which can interact with the remaining intermedi-
 403 ate species and produce nitrogen. Hence, the obtained
 404 nitrogen product was generated from nitrogen atoms
 405 both in the intermediate species and in the oxidizing
 406 gases. This was in agreement with the literature re-
 407 ported by Chen et al. [43]. From their results obtained
 408 by the isotopic labeling technique on Fe-ZSM-5, it

409 was found that one nitrogen atom in every nitrogen
 410 product came from the deposits, while the other came
 411 from the gas phase nitrogen dioxide.

412 In addition, TPO step performed by using NO as
 413 the oxidizing gas significantly provided the nitrogen
 414 product at high temperature as also shown in Fig. 5.
 415 However, such nitrogen should not be produced by the
 416 deposits since there was no carbon dioxide detected at
 417 the same temperature as seen in Fig. 4. It was believed
 418 that this nitrogen could be produced through the NO
 419 decomposition, which favored at very high tempera-
 420 ture under the absence of oxygen. This result was cor-
 421 responding with the work by Wang et al. [46] who ob-
 422 served that NO was reduced in oxygen-free feed over
 423 Co-ZSM-5 at high temperature. From their results, it
 424 was suggested that NO could be reduced on Co^{2+} ion
 425 without nitrogen dioxide formation.

3.2. Pt/Al_2O_3 catalyst

3.2.1. The catalytic behavior for temperature programmed reaction

426
 427 Fig. 6 shows the temperature programmed reac-
 428 tion profiles of Pt/Al_2O_3 catalyst for $C_3H_6 + O_2$ and
 429 $C_3H_6 + NO + O_2$ systems. It was clearly observed that
 430 the C_3H_6 light-off temperature for $C_3H_6 + O_2$ sys-
 431 tem was lower than that for $C_3H_6 + NO + O_2$ system.
 432 This result was corresponding with the references sug-
 433 gested that at low temperatures NO blocked the active
 434 sites responsible for propene oxidation [49,50]. Con-
 435
 436

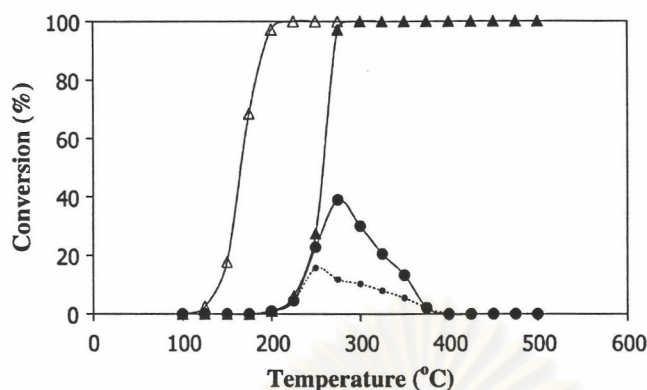


Fig. 6. The temperature programmed reaction profiles of Pt/Al₂O₃ for C₃H₆ + O₂ and C₃H₆ + NO + O₂ systems; the gas reactant composition 1000 ppm C₃H₆ and 5% O₂ for C₃H₆ + O₂ system: (Δ) C₃H₆ conversion, and 1000 ppm NO, 1000 ppm C₃H₆; 5% O₂ for C₃H₆ + NO + O₂ system: (▲) C₃H₆ conversion, (●) NO conversion, (---) NO conversion to N₂, GHSV = 60000 h⁻¹ for both.

437 sidering the C₃H₆ + NO + O₂ system, the onset of
 438 NO reduction and the peak in the NO conversion were
 439 closely related to the oxidation of propene. Conversion
 440 of propene and of NO both began at the same temper-
 441 ature and raised together until NO reduction reached a
 442 maximum value at approximately similar temperature
 443 where the propene oxidation was complete. This coinci-
 444 dence of propene and NO conversions was a general
 445 phenomenon within lean-NO_x catalysis [20].

446 3.2.2. The nature of surface species

447 For the inhibition of propene activation by NO ob-
 448 tained from temperature programmed reaction results,

449 it was interesting to study the influence of NO on the
 450 formation of surface species over Pt/Al₂O₃ catalyst.
 451 The characterization of surface species was investi-
 452 gated by an experimental set containing three contin-
 453 uous steps, i.e. adsorption, TPD and TPO by only oxy-
 454 gen. Two sets of gas mixture (C₃H₆ + O₂ and C₃H₆ +
 455 NO + O₂) were first used in adsorption step at 100 °C
 456 to produce the surface species. Fig. 7 depicts the rele-
 457 vant traces of outlet gases obtained on TPD step after
 458 dosing each gas mixture on Pt/Al₂O₃. The main outlet
 459 gases for C₃H₆+NO+O₂ system were carbon dioxide
 460 and nitrogen, while only carbon dioxide was released
 461 when there was no NO in the adsorbed gas mixture.

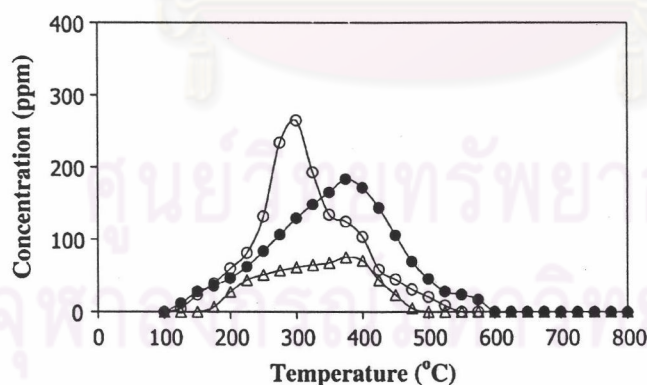


Fig. 7. The TPD profiles of Pt/Al₂O₃ after dosing 1000 ppm C₃H₆ + 5% O₂ at 100 °C: (●) carbon dioxide; 1000 ppm C₃H₆ + 1000 ppm NO + 5% O₂ at 100 °C: (○) carbon dioxide, (Δ) nitrogen.

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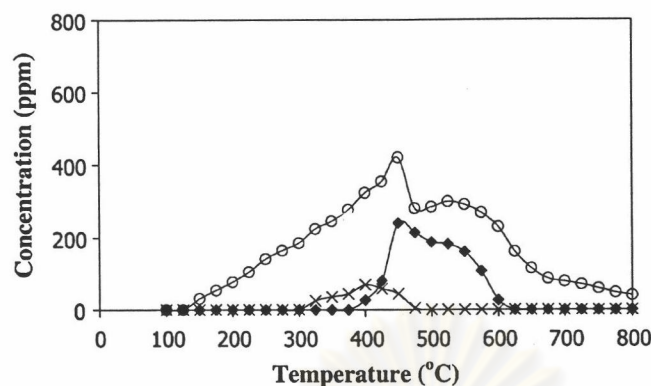


Fig. 8. The TPD profiles of Pt/Al₂O₃ after dosing 1000 ppm C₃H₆ + 5% O₂ at 150 °C: (○) carbon dioxide, (×) methane, (◆) carbon monoxide.

462 It was significantly noticed that no species was detected during TPO step. For C₃H₆+O₂ system, a sharp
 463 peak of carbon dioxide appeared at 375 °C whereas
 464 for C₃H₆ + NO + O₂ system, it was shifted to lower
 465 temperature (at approximately 300 °C) with a shoulder
 466 at ca. 375 °C. It was noted that the amount of carbon
 467 dioxide released from both systems was equivalent.
 468 Taking close consideration, it was seen that there were
 469 two peaks in C₃H₆+NO+O₂ system after deconvolu-
 470 tion, i.e. at 300 and 375 °C. In addition, the deconvolu-
 471 tion of nitrogen profile obtained from C₃H₆+NO+O₂
 472 system showed a peak at 375 °C and a broad peak at
 473 low temperature range (200–350 °C). From these re-
 474 sults, it was inclined that the presence of NO in the
 475 adsorbed gas mixture induced N-containing surface
 476 species at 300 °C. According to the report of Xin et al.
 477 [51], nitro and nitrito organic compounds were abso-
 478 lutely detected by DRIFTS after addition of a mixture
 479 of C₃H₆ + NO + O₂ onto Pt-ZSM-5 at 100 °C. The
 480 coincident position of carbon dioxide peak at 375 °C
 481 in both systems and the appearance of nitrogen peak
 482 at the same temperature for C₃H₆ + NO + O₂ system
 483 may imply two aspects. First, these carbon dioxide
 484 peaks at 375 °C represented to the same type of sur-
 485 face species whereas nitrogen peak was occurred due
 486 to the decomposition of adsorbed NO. Second, types
 487 of surface species for two systems were different but
 488 their partial structures may be similar.

490 However, the nature of surface species could be cer-
 491 tainly changed under the reaction condition. Okuhara

492 et al. [27] found that for the reaction of C₃H₆ +
 493 NO₂ + O₂ on Pt/SiO₂, the organic nitro and nitrite
 494 compounds appeared at low temperature whereas the
 495 organic carbonyl species and isocyanate species oc-
 496 curred at higher temperature. Therefore, the surface
 497 species over Pt/Al₂O₃ were also observed after dosing
 498 the gas mixture of C₃H₆ + O₂ and C₃H₆ + NO + O₂ at
 499 each reaction temperature of 150 and 225 °C, respec-
 500 tively. At a given temperature, propene conversion of
 501 each system was equally ca. 20%. Figs. 8 and 9 illus-
 502 trate the traces of outlet gases during TPD step con-
 503 taining carbon dioxide, methane, and carbon mono-
 504 xide for C₃H₆ + O₂ system and the additional nitrogen
 505 and nitrous oxide for C₃H₆ + NO + O₂ system. It was
 506 significantly remarked that most of surface species
 507 were released during TPD step whereas the amount of
 508 outlet gases by TPO step was extremely small. This
 509 suggested that the surface species could easily decom-
 510 pose themselves on Pt/Al₂O₃, unlike Co-ZSM-5, and
 511 the formation and removal of surface species were
 512 therefore clearly not the controlling steps for the se-
 513 lective catalytic reduction of NO by propene on this
 514 catalyst.

515 In case of C₃H₆ + O₂ system, as seen in Fig. 8, the
 516 carbon dioxide profile showed two main peaks at 450
 517 and 525 °C. There was a little amount of methane at a
 518 temperature range 300–475 °C. It was interesting that
 519 for the carbon monoxide trace, its peak and shoulder
 520 were located to be coincident with the carbon diox-
 521 ide peak at 450 and 525 °C, respectively. In case of

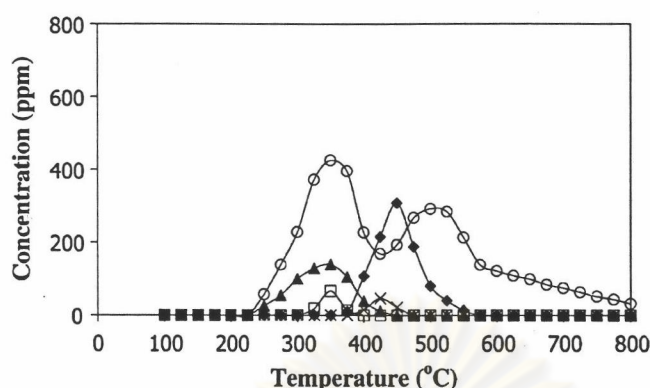


Fig. 9. The TPD profiles of Pt/Al₂O₃ after dosing 1000 ppm C₃H₆ + 1000 ppm NO + 5% O₂ at 225 °C: (○) carbon dioxide, (×) methane, (◆) carbon monoxide, (▲) nitrogen, (□) nitrous oxide.

522 C₃H₆ + NO + O₂ system as shown in Fig. 9, there
 523 were two carbon dioxide peaks in TPD profile, while
 524 the other gases gave only one peak. Nitrogen and ni-
 525 trous oxide peaks existed at low temperature whereas
 526 methane and carbon monoxide peaks were located at
 527 higher temperature. The deconvolution of these TPD
 528 profiles indicated that there were at least three types
 529 of surface species occurred on the catalyst surface.
 530 They were addressed as C_xH_yO_zN_w, (C_iH_jO_k)_{LT},
 531 and (C_lH_mO_n)_{HT} species decomposing themselves
 532 at low temperature region (200–400 °C), at moder-
 533 ate one (350–550 °C) and at high one (400–800 °C),
 534 respectively. The existence of these surface species
 535 was in agreement with the observation by IR techni-
 536 que in several references [31,52–54]. For example,
 537 Captain and Amiridis [31] noticed cyanide, iso-
 538 cyanate, acetate, and formate species on Pt/Al₂O₃ in
 539 C₃H₆ + NO + O₂ system by the use of in situ Fourier
 540 transform infrared spectroscopy and also found that
 541 only isocyanate species disappeared by flushing with
 542 helium at 250 °C. In addition, only isocyanate and
 543 acetate species were observed when increasing the
 544 reaction temperature at 350 °C and again only the
 545 intensity of isocyanate peak was essentially affected
 546 after the reactor was flushed with helium.

547 Considering the feature of surface species obtained
 548 by dosing the gas mixture of C₃H₆ + O₂ at 150 °C,
 549 the position of both carbon dioxide peaks was defi-
 550 nitely coincident with that of two TPD peaks as-
 551 signed as (C_iH_jO_k)_{LT}, and (C_lH_mO_n)_{HT} species in

C₃H₆ + NO + O₂ system. From this result, it was be-
 552 lieved that NO assisted the production of the particu-
 553 lar surface species assigned as C_xH_yO_zN_w species
 554 whereas two types of partially oxidized hydrocarbons,
 555 (C_iH_jO_k)_{LT}, and (C_lH_mO_n)_{HT} species, were certainly
 556 generated in both C₃H₆ + O₂ and C₃H₆ + NO + O₂
 557 systems. 558

3.2.3. The reactivity of surface species 559

In fact, the obtained surface species may possibly
 560 play a role to be either the intermediate species or
 561 the spectator species depending on the reaction condi-
 562 tion as reported in some literatures. Tanaka et al.
 563 [52] proposed that nitro, nitrite and carbonyl surface
 564 species were key reaction intermediates for the selec-
 565 tive catalytic reduction of NO by propene on Pt/SiO₂
 566 at 120 °C. While Xin et al. [53] suggested that nitro,
 567 nitrito and isocyanate species were not the catalytic
 568 active intermediates for the selective catalytic reac-
 569 tion of NO by propene on Pt-ZSM-5 at 250 °C. On
 570 the other hand, Captain and Amiridis [31] concluded
 571 that carboxylates, nitrates and cyanide species were
 572 probably the spectator byproducts of the selective cat-
 573 alytic reduction of NO by propene on Pt/Al₂O₃ at
 574 250 °C, whereas the surface isocyanate species could
 575 be a potential reaction intermediate in such reaction.
 576 With the above-mentioned reason, the reactivity of
 577 C_xH_yO_zN_w, (C_iH_jO_k)_{LT}, and (C_lH_mO_n)_{HT} species
 578 with the oxidizing reactant gas in the reaction temper-
 579 ature range was studied. The reactivity test was con-
 580

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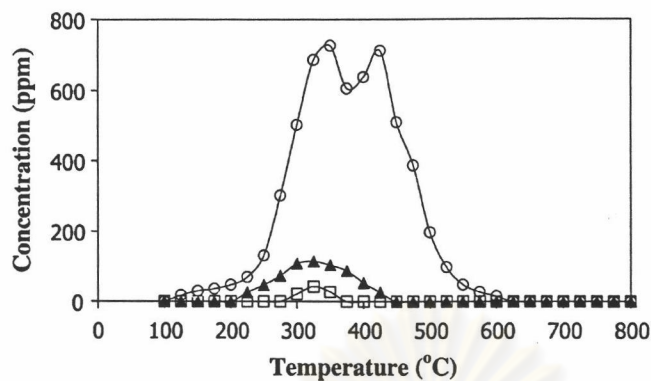


Fig. 10. The TPO profiles of Pt/Al₂O₃ by using 1% O₂ as the oxidizing gas after dosing 1000 ppm C₃H₆ + 1000 ppm NO + 5% O₂ at 225 °C: (○) carbon dioxide, (▲) nitrogen, (□) nitrous oxide.

581 ducted by using TPO technique after the production
582 of surface species through dosing a gas mixture of
583 C₃H₆ + NO + O₂ on Pt/Al₂O₃ at 225 °C. The oxidiz-
584 ing gases were varied as 1000 ppm NO, 1% O₂ and the
585 gas mixture of 1000 ppm NO and 1% O₂. It was noted
586 that the TPD step was negligible in this reactivity test.

587 Figs. 10–12 illustrate the concentrations of carbon
588 dioxide, nitrogen and nitrous oxide during TPO exper-
589 iment by using NO, O₂ and NO + O₂ as the oxidizing
590 gas, respectively. It was noted that neither methane nor
591 carbon monoxide was detected when each oxidizing
592 gas was used for removing the surface species. It was
593 also found that the position of carbon dioxide peak
594 addressed as C_xH_yO_zN_w species was unaffected with

595 changing oxidizing gas (NO, O₂ or NO + O₂). Further-
596 more, the nitrous oxide peak was not shifted under either
597 O₂ or NO + O₂ atmosphere. The observation of nitro-
598 gen peak at 350 °C was rather difficult under NO or
599 NO + O₂ atmosphere because nitrogen atoms in the ox-
600 idizing gas could possibly interact with other surface
601 species to produce nitrogen. However, the introduction
602 of only O₂ during TPO experiment did not influence
603 the position of nitrogen peak. These results revealed
604 that C_xH_yO_zN_w species could decompose themselves
605 under the oxidizing gas at the same temperature at
606 which they decomposed under helium flow. Therefore,
607 it was pronounced that neither NO nor O₂ was
608 involved in the decomposition of C_xH_yO_zN_w species at

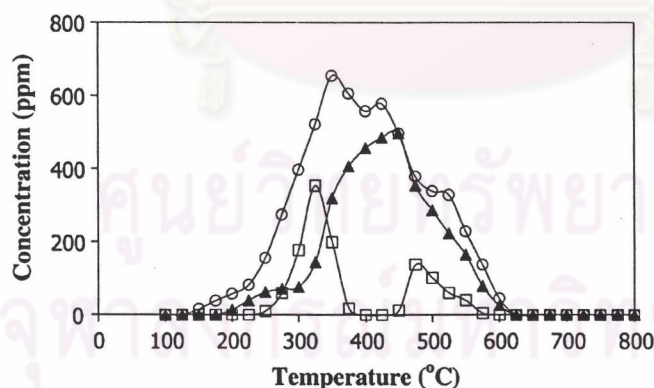


Fig. 11. The TPO profiles of Pt/Al₂O₃ by using 1000 ppm NO as the oxidizing gas after dosing 1000 ppm C₃H₆ + 1000 ppm NO + 5% O₂ at 225 °C: (○) carbon dioxide, (▲) nitrogen, (□) nitrous oxide.

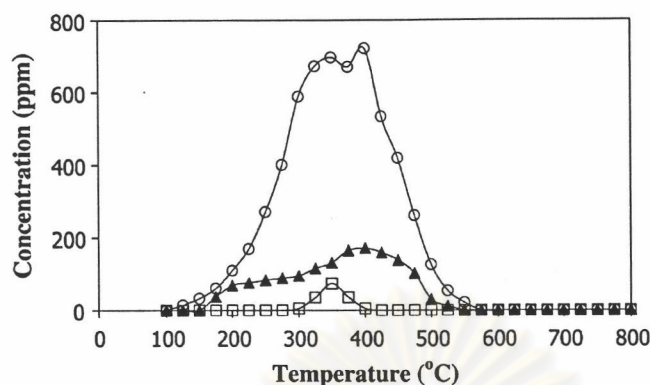


Fig. 12. The TPO profiles of Pt/Al₂O₃ by using 1000 ppm NO + 1% O₂ as the oxidizing gas after dosing 1000 ppm C₃H₆ + 1000 ppm NO + 5% O₂ at 225 °C: (○) carbon dioxide, (▲) nitrogen, (□) nitrous oxide.

609 any temperature. This was also in agreement with the
610 work by Captain and Amiridis [31] who reported that
611 the surface cyanide on Pt/Al₂O₃ was not reacting in
612 NO, NO₂, O₂ and NO + O₂ environments at 250 °C.

613 A larger amount of carbon dioxide released at
614 low temperature and the disappearance of the carbon
615 dioxide peak at high temperature (525 °C) in
616 the presence of O₂ or NO + O₂ as the oxidizing gas
617 indicated that the surface species decomposing at
618 high temperature, (C_lH_mO_n)_{HT} species, were easily
619 removed by these oxidizing gases. However, the existence
620 of carbon dioxide peak at 525 °C in case that
621 only NO was used as the oxidizing gas showed that
622 O₂ was a more potential oxidizing gas than NO to be
623 reactive with (C_lH_mO_n)_{HT} species. This corresponds
624 with the work by Tanaka et al. [52] who suggested
625 that on Pt/SiO₂ the carbonyl species reacted rapidly
626 with NO₂ and O₂ at 120 °C, while these species
627 were inactive to NO. Considering the reactivity of
628 (C_iH_jO_k)_{LT} species to the different oxidizing gas, the
629 relatively small shift to lower temperature of the peak
630 of (C_iH_jO_k)_{LT} species for all oxidizing gases manifested
631 that these species were slightly reactive with
632 NO, O₂ and NO + O₂. The reactivity of (C_lH_mO_n)_{HT}
633 species to either O₂ or NO + O₂ and the shift to lower
634 temperature of a (C_iH_jO_k)_{LT} species peak were also
635 observed in C₃H₆ + O₂ system but they were not seen
636 here. These results supported the above suggestion
637 that (C_iH_jO_k)_{LT} and (C_lH_mO_n)_{HT} species were not
638 only produced in C₃H₆ + NO + O₂ system but also
639 generated in C₃H₆ + O₂ system.

3.3. The role of surface species on the reaction mechanism for the selective catalytic reduction of NO by propene on Co-ZSM-5 and Pt/Al₂O₃ catalysts

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643 For Co-ZSM-5 catalyst, many literatures concluded
644 that the reaction mechanism involved the adsorbed nitrogen
645 dioxide reacting with hydrocarbon to produce
646 the intermediate species on Co ion [35,36,38–43,55].
647 These intermediate species were subsequently oxidized
648 by nitrogen dioxide to form nitrogen product.
649 From the results described in Section 3.1.2, it was suggested
650 that the coexistence of three reactants (C₃H₆ +
651 NO + O₂) enhanced the formation of deposits. It was
652 also believed that these deposits obtained during TPO
653 step became the intermediate species for the selective
654 catalytic reduction of NO by propene on Co-ZSM-5.
655 Goryashenko et al. [41] mentioned that the gas phase
656 nitrogen dioxide was not involved directly in the selective
657 catalytic reduction of NO. The formation of
658 nitrogen dioxide adsorbed on cobalt cations was also
659 observed by Sun et al. [39]. Hence, it was possible
660 that the intermediate species was formed through the
661 interaction of propene and the adsorbed NO_y complex
662 species, which were originated from the adsorbed nitrogen
663 dioxide.

664 The nitrogen production should depend on the removal
665 of intermediate species discussed in Section
666 3.1.3. The removal of intermediate species favorably
667 occurred in the presence of oxygen; nevertheless, it
668 was extremely enhanced by the coexistence of NO and
669 oxygen. The nitrogen product was produced by nitro-

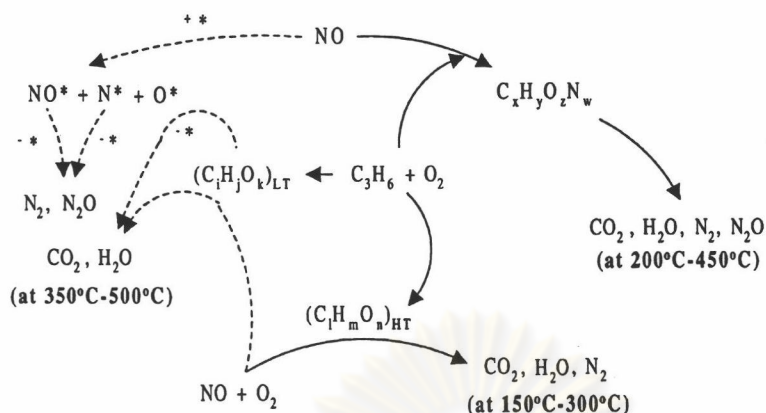
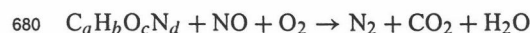
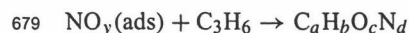
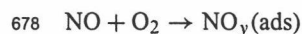


Fig. 13. A proposed reaction mechanism scheme for the selective catalytic reduction of NO by propene under lean-burn condition over Pt/Al₂O₃ ((* is given as the vacancy Pt sites).

670 gen atom from both intermediate species and NO reactant feed. It was concluded that the coexistence of
671 NO and oxygen was necessary for the removal of intermediate species, which was corresponding with the
672 literatures [35,36,38–43,55]. Hence, the mechanism for the selective catalytic reduction of NO by propene
673 under oxygen excess on Co-ZSM-5 was proposed as follows:
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681 For Pt/Al₂O₃ catalyst, although there were two
682 different mechanisms, most researchers proposed that the selective catalytic reduction of NO by propene occurred only on Pt sites for both mechanisms [56–58].
683 From the results described in Section 3.2, the observation of three types of surface species indicated the complication in formation of surface species. Each
684 surface species played an independently different role on the overall reaction mechanism. However,
685 the weak adsorption of surface species resulted in the formation and removal of surface species being
686 not the controlling steps for such reaction. It was postulated that there were at least three pathways in the overall reaction mechanism depending on the
687 reaction temperature range. At low temperature range (150–300 °C), the NO reduction mechanism was
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697 mainly observed. (C_lH_mO_n)_{HT} species on the catalyst surface easily reacted with either nitrogen dioxide
698 or oxygen to produce nitrogen and carbon dioxide. The decomposition of C_xH_yO_zN_w species occurred
699 at moderate temperature range (200–450 °C). It was significantly remarked that the decomposition of
700 C_xH_yO_zN_w species was an only mechanism pathway attributed to produce nitrous oxide product. At high
701 temperature range (350–500 °C), nitrogen dioxide and oxygen slightly assisted to remove (C_iH_jO_k)_{LT}
702 species. However, the nitrogen production was still unclear. Two aspects should presumably explain this
703 behavior. In the first case, NO could adsorb and decompose to nitrogen on vacant sites, which were occurred
704 by the removal of (C_iH_jO_k)_{LT} species. In the second case, nitrogen product was generated by the
705 reaction between nitrogen dioxide and (C_iH_jO_k)_{LT} species. Hence, the mechanism for the selective catalytic
706 reduction of NO by propene under oxygen excess on Pt/Al₂O₃ was proposed as shown in Fig. 13.
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717 4. Conclusions

718 The different nature of surface species on Co-ZSM-5 and Pt/Al₂O₃ catalyst may possibly play an important
719 role on the reaction mechanism pathway for the selective catalytic reduction of NO by propene under
720 lean-burn condition. The strong adsorption of surface species on Co-ZSM-5 shows that these surface
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724 species become the intermediate species and their for-
 725 mation and removal directly relate to the controlling
 726 step in the reaction mechanism. On the other hand,
 727 the weak adsorption of surface species on Pt/Al₂O₃
 728 indicates the complication of the reaction mechanism
 729 pathway. The reaction should possibly via several co-
 730 operative mechanisms at the same reaction condition.
 731 Hence, it is difficult to control the required reaction
 732 mechanism over this catalyst. These are dependent
 733 on various parameters, e.g. the reaction temperature,
 734 type of reductant, the reactant concentration, etc.

735 Acknowledgements

736 The authors would like to thank Thailand Research
 737 Fund (TRF) and National Science and Technology De-
 738 velopment Agency (NSTDA) for the financial support
 739 of this project.

740 References

- 741 [1] A. Fritz, V. Pitchon, *Appl. Catal. B* 13 (1997) 1.
 742 [2] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B* 18
 743 (1998) 1.
 744 [3] J. Wei, *Advan. Catal.* 24 (1975) 57.
 745 [4] M. Misono, Y. Hirao, C. Yokoyama, *Catal. Today* 38 (1997)
 746 157.
 747 [5] M. Iwamoto, *Stud. Surf. Sci. Catal.* 54 (1990) 121.
 748 [6] M. Shelef, *Chem. Rev.* 95 (1995) 209.
 749 [7] Y. Teraoka, M. Yoshimatsu, N. Yamazoe, T. Seiyame, *Chem.*
 750 *Lett.* (1984) 893.
 751 [8] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata, *Appl.*
 752 *Catal.* 64 (1990) L1.
 753 [9] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno, M. Iwamoto, *Appl.*
 754 *Catal.* 70 (1991) L1.
 755 [10] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya,
 756 S. Kagawa, *J. Chem. Soc., Chem. Commun.* (1986) 1272.
 757 [11] W. Held, A. Koenig, T. Richter, L. Puppe, SAE Paper 900496
 758 (1990).
 759 [12] M. Iwamoto, in: *Proceedings of the Meeting of Catalyst*
 760 *Technology and Removal of NO*, Tokyo, January 1990, p. 17.
 761 [13] H. Hamada, *Catal. Today* 22 (1994) 21.
 762 [14] T. Tanabe, T. Iijima, A. Koiwai, J. Mizuno, K. Yokota, A.
 763 Isogai, *Appl. Catal. B* 6 (1995) 145.
 764 [15] A. Martinez, S.A. Gomez, G.A. Fuentes, *Stud. Surf. Sci.*
 765 *Catal.* 111 (1997) 225.
 766 [16] G. Zhang, T. Yamaguchi, H. Kawakami, T. Suzuki, *Appl.*
 767 *Catal. B* 1 (1992) L15.
 768 [17] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno, H.
 769 Ohuchi, *Appl. Catal. B* 2 (1993) 71.
 [18] A.V. Kucherov, A.A. Slinkin, S.S. Goryashenko, K.I. 770
 Slovetskaya, *J. Catal.* 118 (1989) 459. 771
 [19] Y. Li, W.K. Hall, *J. Phys. Chem.* 94 (1990) 6145. 772
 [20] R. Burch, P.J. Millington, A.P. Walker, *Appl. Catal. B* 4 773
 (1994) 65. 774
 [21] S. Eckhoff, D. Hesse, J.A.A. van den Tillaart, J. Leyrer, E.S. 775
 Lox, *Stud. Surf. Sci. Catal.* 116 (1997) 223. 776
 [22] Y. Torikai, H. Yahiro, N. Mizuno, M. Iwamoto, *Catal. Lett.* 777
 9 (1991) 91. 778
 [23] M. Sasaki, H. Hamada, Y. Kintaichi, T. Ito, *Catal. Lett.* 15 779
 (1992) 297. 780
 [24] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. 781
 Rajaram, T.J. Truex, A.P. Walker, *Appl. Catal. B* 2 (1993) 81. 782
 [25] M. Shelef, C.N. Montreuil, H.W. Jen, *Catal. Lett.* 26 (1994) 783
 277. 784
 [26] B.H. Engler, J. Leyrer, E.S. Lox, K. Ostgathe, *Stud. Surf.* 785
Sci. Catal. 96 (1995) 529. 786
 [27] T. Okuhara, Y. Hasada, M. Misono, *Catal. Today* 35 (1997) 787
 83. 788
 [28] R.H.H. Smits, Y. Iwasawa, *Appl. Catal. B* 6 (1995) L201. 789
 [29] D.H. Kim, I.C. Hwang, S.I. Woo, *Stud. Surf. Sci. Catal.* 105 790
 (1997) 1557. 791
 [30] D.K. Captain, K.L. Roberts, M.D. Amiridis, *Catal. Today* 42 792
 (1998) 93. 793
 [31] D.K. Captain, M.D. Amiridis, *J. Catal.* 184 (1999) 377. 794
 [32] G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno, J. 795
 Skrzypek, *Appl. Catal. B* 6 (1995) 311. 796
 [33] R. Burch, J.A. Sullivan, T.C. Watling, *Catal. Today* 42 (1998) 797
 13. 798
 [34] R. Burch, P.J. Millington, *Catal. Today* 26 (1995) 185. 799
 [35] Y.J. Li, T.L. Slager, J.N. Armor, *J. Catal.* 150 (1994) 388. 800
 [36] A.D. Cowan, R. Dumpelmann, N.W. Cant, *J. Catal.* 151 801
 (1995) 356. 802
 [37] A.P. Walker, *Catal. Today* 26 (1995) 107. 803
 [38] A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell, *Stud. Surf.* 804
Sci. Catal. 101 (1996) 661. 805
 [39] T. Sun, M.D. Fokema, J.Y. Ying, *Catal. Today* 33 (1997) 251. 806
 [40] M. Misono, *Cattech* 4 2 (1998) 183. 807
 [41] S.S. Goryashenko, Y.K. Park, D.S. Kim, S.E. Park, *Res.* 808
Chem. Intermed. 24 (1998) 933. 809
 [42] E.A. Lombardo, G.A. Sill, J.L. d'Itri, W.K. Hall, *J. Catal.* 810
 173 (1998) 440. 811
 [43] H.Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, *J. Catal.* 180 812
 (1998) 171. 813
 [44] Y.F. Chang, J.G. McCarty, *J. Catal.* 178 (1998) 408. 814
 [45] L.G. Pinaeva, E.M. Sadovskaya, A.P. Suknev, V.B. 815
 Goncharov, V.A. Sadykov, B.S. Balzhinimaev, T. Decamp, C. 816
 Mirodatos, *Chem. Eng. Sci.* 54 (1999) 4327. 817
 [46] X. Wang, H.Y. Chen, W.M.H. Sachtler, *Appl. Catal. B* 26 818
 (2000) L227. 819
 [47] H.Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, *Catal. Today* 820
 54 (1999) 483. 821
 [48] C.J. Bennett, P.S. Bennett, S.E. Golunski, J.W. Hayes, A.P. 822
 Walker, *Appl. Catal. A* 86 (1992) L1. 823
 [49] R. Burch, P.J. Millington, *Catal. Today* 29 (1996) 37. 824
 [50] K.L. Roberts, M.D. Amiridis, *Ind. Eng. Chem. Res.* 36 (1997) 825
 3528. 826

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|-----|---|---|-----|
| 827 | [51] M. Xin, I.C. Hwang, S.I. Woo, <i>J. Phys. Chem. B</i> 101 (1997) | [55] M. Guyon, V. LeChanu, P. Gilot, H. Kessler, G. Prado, <i>Appl. Catal. B</i> 8 (1996) 183. | 835 |
| 828 | 9005. | [56] B.K. Cho, J.E. Yie, <i>Appl. Catal. B</i> 10 (1996) 263. | 836 |
| 829 | [52] T. Tanaka, T. Okuhara, M. Misono, <i>Appl. Catal. B</i> 4 (1994) | [57] C. Rottlander, R. Andorf, C. Plog, B. Krutzsch, M. Baerns, <i>Appl. Catal. B</i> 11 (1996) 49. | 837 |
| 830 | L1. | [58] R. Burch, T.C. Watling, <i>Appl. Catal. B</i> 11 (1997) 207. | 838 |
| 831 | [53] M. Xin, I.C. Hwang, S.I. Woo, <i>Catal. Today</i> 38 (1997) 187. | | 839 |
| 832 | [54] F. Acke, B. Westerberg, L. Eriksson, S. Johansson, M. | | 840 |
| 833 | Skoglundh, E. Fridell, G. Smedler, <i>Stud. Surf. Sci. Catal.</i> 116 | | |
| 834 | (1998) 285. | | |



ศูนย์วิทยทรัพยากร
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VOLUME 24

NUMBER 5 1998

ISSN 0922-6168

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COMPARATIVE STUDY OF COKE DEPOSITION ON CATALYSTS IN REACTIONS WITH AND WITHOUT OXYGEN

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Received 1 December 1997; accepted 27 November 1997

Abstract--Two types of catalysts, i.e. Pt/ γ -Al₂O₃ and Cu/Na-ZSM-5, were used to investigate the catalyst activity and amount of coke formation on the spent catalysts. The reactions of particular interest were the hydrocarbon oxidation and the SCR of NO with and without O₂. Propane and propene were used as the hydrocarbon sources. The reaction conditions were as follows: reaction temperature = 170-500°C, GHSV = 4,000 hr⁻¹, TOS = 2 hr, feed composition depending on each reaction, but the composition of gases were fixed as HC = 3,000 ppm, NO = 1,000 ppm and O₂ = 2.5%, using He balance. It was found that both the case of Pt/ γ -Al₂O₃ and the case of Cu/Na-ZSM-5, propene provided higher conversion and coke deposition than propane in the presence or the absence of O₂ and/or NO. For Pt/ γ -Al₂O₃ catalyst, in case of the absence of oxygen reactions, the propene conversion dropped more rapidly than the propane conversion. Finally the reaction of propene gave a lower percent of hydrocarbon conversion than the reaction of propane. Additionally, propene had a higher percent selectivity of coke formation for the reaction with the absence of oxygen, but propane had a higher percent selectivity of coke formation for the reaction with the presence of oxygen. For Cu/Na-ZSM-5, in the system with absence and presence of oxygen, the addition of oxygen caused a significant change in % coke selectivity. With the presence of NO_x, the percent conversion of both propane and propene decreased and that the % coke selectivity of propane decreased, whereas that of in propene increased.

INTRODUCTION

Coke deposition is an important deactivation mode in the hydrocarbon conversion process. In general, most researchers [1-5] have emphasized only coke formation in reducing atmospheres e.g. dehydrogenation, cracking, reforming etc. Nevertheless, in oxidizing atmospheres, coke deposition can also take place on the catalyst surface. Therefore, in the present work, it is set up to compare the amount of coke formed on Pt/Al₂O₃ and Cu/Na-ZSM-5 catalysts for reactions with the absence and presence of oxygen. The catalytic activity and the amount of coke on the spent Pt/Al₂O₃ and Cu/Na-ZSM-5 catalysts were investigated for reactions with oxygen, i.e. hydrocarbon combustion and reduction of NO_x, and without oxygen, i.e. dehydrogenation or aromatization and reduction of NO_x. Propane and propene were used as the hydrocarbon sources for all four reactions.

EXPERIMENTAL

Pt/Al₂O₃ (0.3 wt.% Pt) catalyst in this study was prepared by a dry impregnation method using H₂PtCl₆ as the salt precursor. The parent Na-ZSM-5 zeolite with Si/Al ratio of 50 was hydrothermally synthesized from gel and decant solution in an autoclave. The structure of ZSM-5 was confirmed by X-ray diffraction (XRD). Cu/Na-ZSM-5 zeolite was prepared by exchanging Cu²⁺ into Na-ZSM-5 sample in the aqueous solution. The catalytic reactions were carried out at atmospheric pressure in a fixed bed reactor. A 0.5 g of catalyst was packed in a quartz tube reactor. In the case of Cu/Na-ZSM-5, before the reaction, the catalyst was heated under He flow from room temperature to 500°C in 1 hr., and held for 1 hr. before being cooled down. In the case of Pt/Al₂O₃, the catalyst was reduced to 500°C for 1 hr using hydrogen as the reductant gas. The 50 cc./min. of mixed gas feed consisting of 100 ppm NO, 3000 ppm hydrocarbon, 2.5% vol. oxygen and He was introduced to the reactor at a space velocity of 4000 hr⁻¹. The temperatures of the reaction with and without oxygen were 170°C and 350°C (in the case of Pt/Al₂O₃) or 500 °C (in the case of Cu/Na-ZSM-5) respectively. The outlet gases were analyzed by SHIMADZU GC-8APT gas chromatograph with MS-5A column for nitrogen, oxygen and carbon monoxide and with SHIMADZU GC-8AIT porapak QS column for carbon dioxide, propane and propene. Coke deposited on the catalysts was characterized by temperature programmed oxidation (TPO). Before starting the TPO, 0.5 g of the spent catalysts was heated to 130°C at 10°C/min. under He atmosphere and held for 3 hr. The heat treatment removed any air and water that was adsorbed on the catalyst. Then the pretreated sample was heated from 50°C to 700°C with a heating rate of 5°C/min. then in a 30 cc./min. stream of 1% O₂ in helium gas. The carbon dioxide formed was determined by SHIMADZU GC-8AIT gas chromatograph using a thermal conductivity detector with parapak QS column. The percentage of carbon in coke can be calculated from TPO curves. CO₂ area is divided by a internal time in which CO₂ flows through the sampling loop (1 cc.). The rate of CO₂ formation is, hence, obtained. The area under the curve of CO₂ formation rate versus time gives the value of total CO₂ formation. Finally, this value is converted to milligram carbon or percentage of carbon by using a calibration curve.

RESULTS AND DISCUSSION

For the Case of Pt/Al₂O₃

The experimental results were shown in Table 1, Figure 1 and Figure 2. In all four reactions, it was observed that the reactions with propene as a reactant gave a larger percent of hydrocarbon conversion in the initial interval of time on stream and also

Table 1
Hydrocarbon conversion, amount of coke and coke selectivity of 0.3% Pt/Al₂O₃.

Reaction	Reactant	Temperature (°C)	% HC conversion (at 5 min.)	% Carbon in coke	% Selectivity of coke formation
HC	Propane	350	59.36	0.17	0.22
	Propene	350	98.88	0.32	0.27
HC+NO	Propane	350	46.17	0.13	0.19
	Propene	350	66.14	0.16	0.34
HC+O ₂	Propane	170	11.71	0.13	1.13
	Propene	170	100.00	0.48	0.29
HC+NO+O ₂	Propane	170	5.59	0.12	1.07
	Propene	170	40.12	0.33	0.54

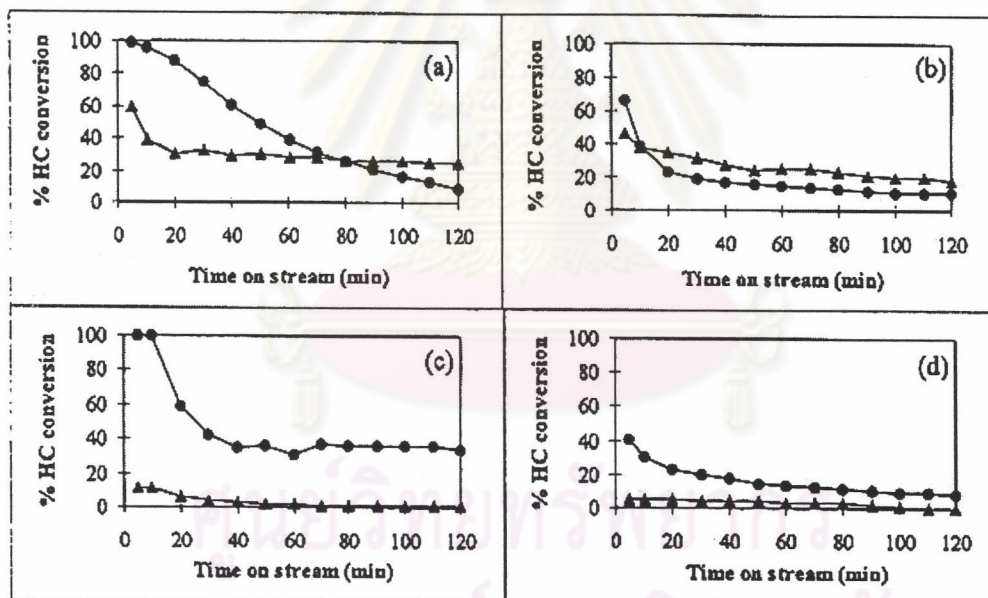


Figure 1. Relationship between % HC conversion versus time on stream. (a) Feed: 3000 ppm HC + He balance, Temperature = 350°C. (b) Feed: 3000 ppm HC + 1000 ppm NO + He balance, Temperature = 350°C. (c) Feed: 3000 ppm HC + 2.5 vol.% O₂ + He balance, Temperature = 170°C. (d) Feed: 3000 ppm HC + 1000 ppm NO + 2.5 vol.% O₂ + He balance, Temperature = 170°C.: (◆) Propane, (●) Propene.

had a larger amount of coke than the reactions with propane as a reactant. However, in the dehydrogenation reaction and NO_x reduction under the absence of oxygen condition, the propene conversion dropped more rapidly than the propane

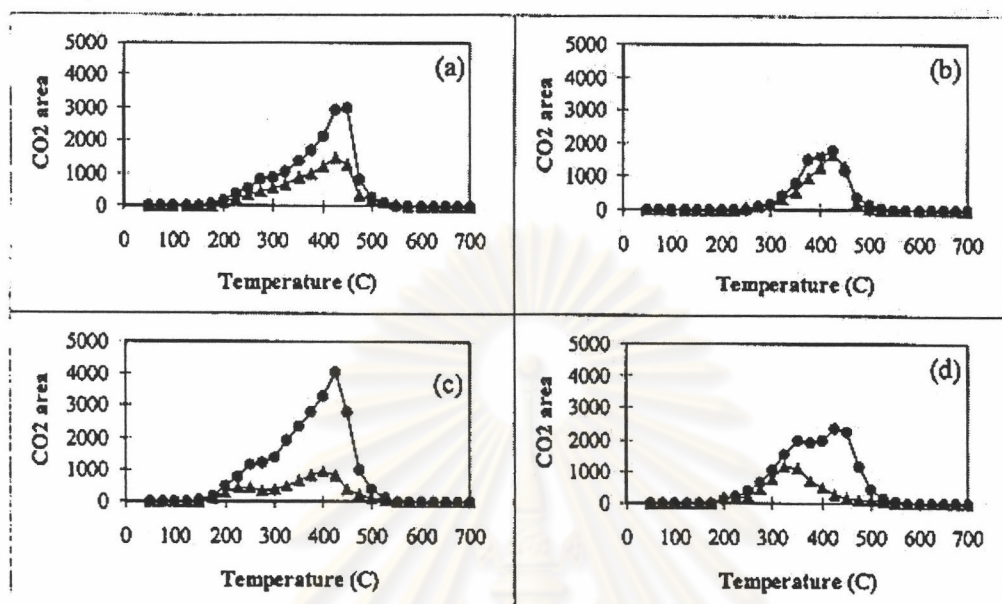


Figure 2. TPO profiles of 0.3 g coked catalyst from reaction. (a) Dhydrogenation, Temperature = 350°C. (b) Reduction of NO_x under absence of oxygen condition, Temperature = 350°C. (c) Combustion, Temperature = 170°C. (d) Reduction of NO_x under absence of oxygen condition, Temperature = 170°C.: (\blacklozenge) Propane, (\bullet) Propene.

conversion. Finally the reaction of propene gave a lower percent of hydrocarbon conversion than the reaction of propane. It meant that propene is more active than propane [6]. Since propene reacted more, there was more opportunity to convert to coke precursor. Additionally, it was clarified that the product of propene from the reaction with the absence of oxygen, propadiene which is converted irreversibly to ethylidyne leading to coke deposition [7,8], was more reactive than propene [6]. Thus the catalysts in the reaction using propene as a reactant were rapidly covered by carbonaceous deposits. The TPO profiles of 0.3% $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts are indicated in Figure 2. Each sample showed a TPO peak around 425°C except the TPO profiles of spent catalyst from reduction of NO_x in the presence of oxygen condition. This TPO profiles showed a TPO peak at a temperature of around 325°C for the reaction with propane as a reactant and two peaks at the temperature around 325°C and 425°C for that with propene as a reactant. Barbier *et al.* [3] suggested that the first peak is the coke on metal and the second peak is the coke on the support. In this paper, we define the selectivity of coke formation as the ratio of carbon atom in coke to carbon atom of feed hydrocarbon converted. It was found that propene had a higher percent of selectivity of coke formation for the reaction with the absence of oxygen, but propane had a higher percent of selectivity of coke

formation for the reaction with the presence of oxygen. Under the presence of oxygen, it suggested that coke is formed in parallel with carbon dioxide formation. Propene or coke precursor is more effectively reacted with oxygen to carbon dioxide [9]. Additionally, for the reaction with the presence of oxygen using propane as a reactant, it was observed that the reaction with the absence of NO gave a higher percent of selectivity of coke formation than the reaction with the presence of NO. On the other hand, in the case of propene, the reactant with the presence of NO gave higher percent selectivity of coke formation. It suggests that propane or propene is first reacted with adsorbed oxygen to be converted to intermediates [10,11]. In the case of propane [10,11], these intermediates are preferably reacted with NO which result in, when NO was added in feed, propane producing less selectively of coke formation. However, in the case of propene [12], NO hardly reacted with the intermediates but it preferred to dissociate into dinitrogen. Thus, since the dissociation of NO hinders the reaction of carbon dioxide formation, the intermediates prefer produce coke rather than carbon dioxide for the case of the presence of NO reaction.

For the Case of Cu/Na-ZSM-5

The experimental results were summarized in Figure 3. It was found that the propene conversion was higher than that of propane. This is particularly obvious for the reaction with the presence of oxygen and absence of NO_x as shown in Figure 3(b). Propane conversion was only 10 %, whereas propene conversion is about 100 %. Figure 3(c),(d) (reduction of NO_x with and without O_2) exhibited the effect of NO_x on the reaction. It was found that the % of propene conversion decreased when NO_x was added, however the % of propene conversion was still higher than that of propane. It means that propene is more active than propane [6]. The temperature program oxidation (TPO) results were shown in Figure 4. It was found that the amount of coke from the four reactions of propene was greater than propane over Cu/Na-ZSM-5 zeolite. The results in Table 2 can suggest that in aromatization, the percentage of propene conversion was greater than that of propane; however, on the other hand, the % coke selectivity of propene was less than that of propane, because propene was converted to product more than to coke while propane formed product less than coke. In the system with absence and presence of oxygen it was found that the addition of oxygen caused a significant change in % of coke selectivity [13-15]. With the presence of NO_x , it was found that the percent conversion of both propane and propene decrease and that the % of coke selectivity of propane decreased whereas that of in propene increased. From this result in the case of propene, we can propose that NO_x was adsorbed on the surface of the catalyst to form an intermediate which is strongly adsorbed and, hence, the desorption rate is slow [16-21]. As a result, the intermediate can not selectively form the product but can be further

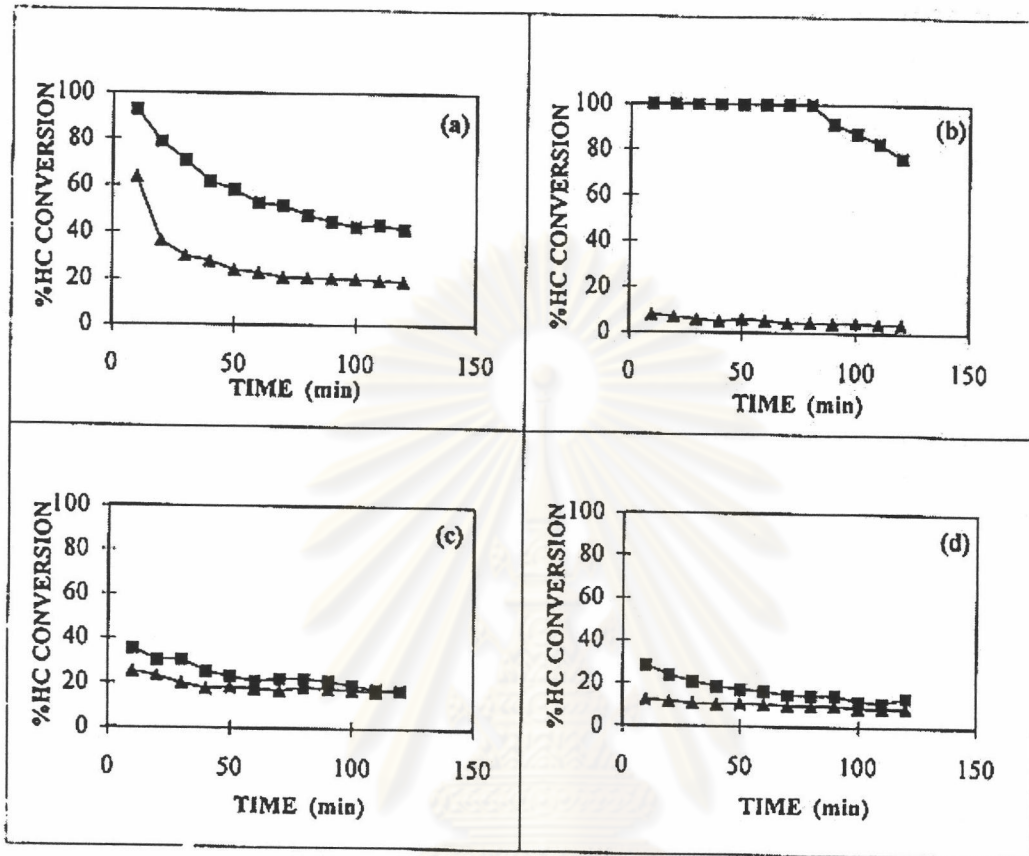


Figure 3. Relationship between % HC conversion versus time over 1.58% Cu/Na-ZSM-5; (a) Feed: 3000 ppm HC + He balance, Temperature = 500°C. (b) Feed: 3000 ppm HC + 2.5 vol.% O₂ + He balance, Temperature = 170°C. (c) Feed: 3000 ppm HC + 1000 ppm NO + He balance, Temperature = 500°C. (d) Feed: 3000 ppm HC + 1000 ppm NO + 2.5 vol.% O₂ + He balance, Temperature = 170°C: (▲) C₃H₈, (■) C₃H₆

converted to coke.

CONCLUSION

Both in the case of Pt/γ Al₂O₃ and in the case of Cu/Na-ZSM-5, propene provided both higher conversion and coke deposition than propane in the presence or the absence of O₂ and/or NO. For Pt/γ Al₂O₃ catalyst, in the case of the absence of oxygen reactions, the propene conversion dropped more rapidly than the propane conversion. Finally, the reaction of propene gave a lower percentage of hydrocarbon conversion than the reaction of propane. Additionally, propene had a higher

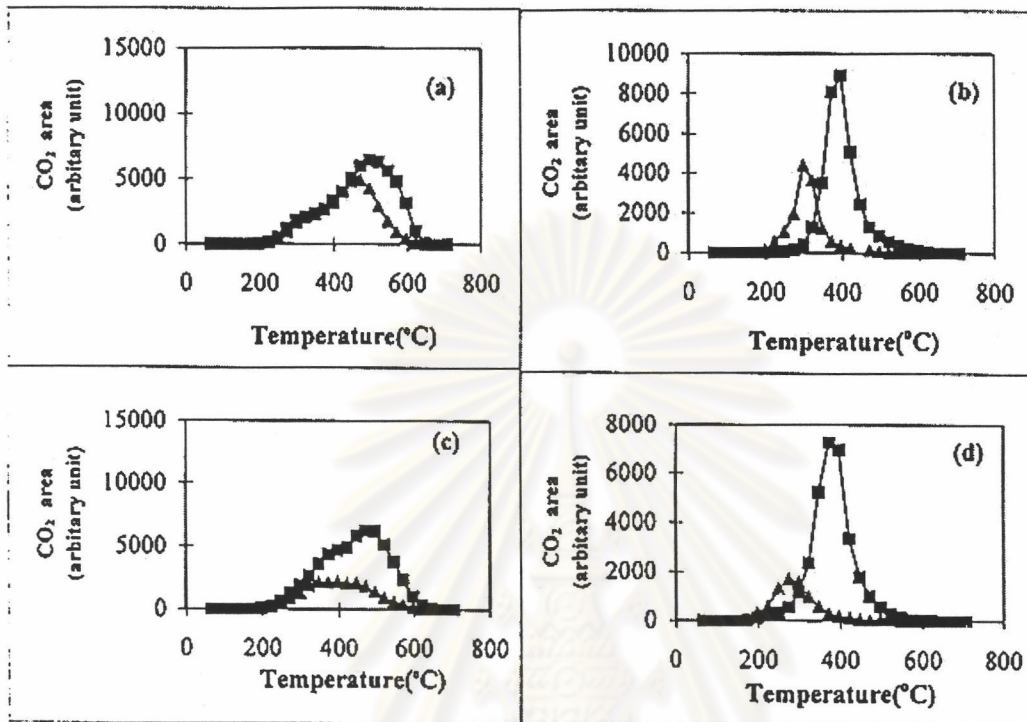


Figure 4. TPO curve of 1.58% Cu/Na-ZSM-5 after the reaction; (a) HC at 500 °C, (b) HC+O₂ at 170 °C, (c) HC+NO at 500 °C, (d) HC+NO+O₂ at 170 °C; (▲) C₃H₈, (■) C₃H₆; In the case of propene (b,d), amount of coked catalyst for TPO is five times than that of propane.

Table 2

Percentage HC conversion and selectivity of coke over 1.58%Cu/Na-ZSM-5

Reaction	Reactant	Temperature (°C)	% HC conversion (at 5 min.)	% Carbon in coke	% Selectivity of coke formation
HC	propane	500	75	0.45	0.74
	propene	500	98	0.68	0.51
HC+O ₂	propane	170	9	0.17	1.43
	propene	170	100	2.03	0.86
HC+NO _x	propane	500	26	0.25	0.45
	propene	500	38	0.67	1.51
HC+NO _x +O ₂	propane	170	15	0.10	0.39
	propene	170	38	1.82	2.80

percentage of selectivity of coke formation for the reaction with the absence of oxygen but propane had higher percent selectivity of coke formation for the reaction with the presence of oxygen. For Cu/Na-ZSM-5, in the system with absence and presence of oxygen, the addition of oxygen caused a significant change in the % of coke selectivity. With the presence of NO_x , the percent conversion of both propane and propene decreased and that of the % coke selectivity of propane decreased, whereas that in propene increased.

REFERENCES

1. W.G. Appleby, J.W. Gibson, and G.M. Good, *I & EC Process Design and Development* 1, 102 (1962).
2. J.N. Beltramini, E.E. Martinelli, E.J. Churin, N.S. Figoli, and J.M. Parera, *Applied Catalysis* 7, 43 (1983).
3. J. Barbies, *Catalyst Deactivation I* (1987).
4. J. Biswas, P.G. Gray, and D.D. Do, *Applied Catalysis* 32, 249 (1987).
5. Mikael Larsson, Magnus Hulten, Edd A Blekkan, and Bengt Andersson, *Journal of Catalysis* 164, 44 (1996).
6. Morrison and Boyd, *Organic Chemistry (sixth edition)*: 122, 287, 410.
7. Gabor A. Somorjai, *Introduction to Surface Chemistry and Catalysis*: 420.
8. B.J. McIntyre, M. Salmeron, and G.A. Somorjai, *Journal of Catalysis* 164, 184 (1996).
9. R. Burch and T.C. Watling, *Catalysis Letters* 43, 19 (1997).
10. Motoi Sasaki, Hideaki Hamada, Yoshiaki Kintaichi, and Takehiko Ito, *Catalysis Letters* 15, 297 (1992).
11. Megumu Inaba, Yoshiaki Kintaichi, and Hideaki Hamada, *Catalysis Letters* 36, 223 (1996).
12. R. Burch, P.J. Millington, and A.P. Walker, *Applied Catalysis B4*, 65 (1994).
13. J.L. d' Itri and W.M.H. Sachtler, *Catal. Lett.*, 15, 289 (1992).
14. H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, and M. Tabata, *Appl. Catal.* 64, L1 (1990).
15. A. Yu Stakheev, C.W. Lee, S.P. Park, and P.J.Chong, *Progress in Zeolite and Microporous Materials.*, Vol 105 , 1579 (1997).
16. H. Hamada, Y. Kintaichi, M. Sasaki, M. Tabata, and T. Ito, *Appl. Catal.*, 70, L15 (1991).
17. C.J. Bennett, P.S. Bennett, S.E. Golunski, J.W. Hayes, and A.P. Wallker, *Appl. Catal. A*, 86 L1 (1992).
18. R.Burch and P.J. Millington , *Appl. Catal B:Env*, 2, 101 (1993).
19. M. Iwamoto, H. Yahiro, H. Khin, M.Watanabe, J Guc, M. Konno, T. Chikabisa and T. Murayama, *Appl. Catal B5.*, L1 (1994).
20. Chikafumi Yokotama and Makoto Misono, *Journal of Catalysis*. 160, 95 (1996).
21. Janos Szanyi and Mark T. Paffett, *Journal of Catalysis*. 164 232 (1996).

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ROLE OF NO ON PROPENE AND NO CONVERSION OVER Pt/Al₂O₃ CATALYST UNDER LEAN-BURN CONDITION AT LOW TEMPERATURE

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Summary: The catalytic activity and the amount of coke on the spent Pt/Al₂O₃ catalysts were investigated for the C₃H₆/O₂ reaction with and without the presence of NO at 150 °C. The addition NO with the concentrations of 212 ppm or 520 ppm decrease percent propene conversion and the amount of coke, but the selectivity of coke formation becomes higher.

Introduction

From the recent literature [1-2], there are still arguments on the reaction mechanisms of NO reduction by hydrocarbon under excess oxygen condition over Pt catalyst. Since coke deposition can also take place on catalyst surface in oxidizing atmosphere, the investigation of coke formation for NO reduction by hydrocarbon may illustrate some aspects that may be useful for the prediction of reaction mechanism.

Results and Discussion

For the reaction without NO (with a feed containing 3000 ppm C₃H₆, 2.5%O₂ and He balance at a GHSV of 4000 for 2 hrs at 150°C), 100% and 37.5% of propene were converted to CO at 5 mins and 2 hrs, respectively. When 212 ppm or 520 ppm NO was added, percent propene conversion decreased. In the case of NO at 212 ppm, 17.6% and 2.4% of propene were converted to CO₂ at 5 mins and 2 hrs, respectively. In case of 520 ppm, a percent of propene conversion was 24.2% and 1% at 5 mins and 2 hrs, respectively. Additionally, 10% and 21.5% of NO were approximately converted to N₂ in case of 212 ppm and 520 ppm NO, respectively. After the reaction, the coked catalyst was analyzed by temperature programmed oxidation technique (TPO) performed by burning it in 1 vol.% O₂ in He. It was found that the amount of carbon in coked catalysts were as follows: 0.48% (no NO), 0.27% (212 ppm NO) and 0.34% (520 ppm NO). The TPO profile of the spent catalyst from the reaction without NO showed two TPO peaks at the temperature around 225°C and 425°C. Similarly, the TPO

Role of NO on Propene and NO Conversion Over Pt/Al₂O₃ Catalyst Under
Lean-Burn Condition at Low Temperature

profiles of the coked catalyst from the reaction with NO (both 212 ppm NO and 500 ppm NO) demonstrated two peaks, but the first peak was shifted to a higher temperature (325 °C). Barbier et al [3] suggested that the first peak is the coke on metal and the second peak is the coke on the support. Additionally, it was found that propene conversion decreased with the increase of the amount of coke but NO conversion to N₂ was nearly constant. It was possible that propene reacts with O₂ on the sites on which coke was formed. In this paper, we define the selectivity of coke formation as the ratio of carbon atoms in coke to carbon atoms of feed hydrocarbon converted. It was found that the reaction with NO had higher percent selectivity of coke formation than the reaction without NO (0.86% for 212 ppm NO, 1.70% for 520 ppm NO and 0.26% for no NO). From the results, it suggested that NO would compete with C₃H₆ and O₂ to adsorb on metal active sites [1,2] leading to the decrease of percent propene conversion and the amount of coke and to react with adsorbed O₂ to NO₂ [2] leading to the decrease of propene combustion or the increase of percent selectivity of coke formation. Since the adsorbed O₂ which prevents the deposition of carbonaceous deposits [4] decrease, the peak of the coke on metal shifted to a higher temperature. It does not believe that an active carbonaceous material, which is formed from the propene, was responsible for the formation of N₂ [5] because the percent propene conversion decreased whereas the percent NO conversion to N₂ were almost constant as time on stream increased.

Conclusions

It was concluded that the reaction between propene and oxygen carried out on the sites rely on coke formation and that the reaction between propene and NO₂ proceed on the sites do not relate to coke formation.

References

1. Megumu Inaba, Yoshiaki Kintaichi and Hideaki Hamada, Catal. Lett. 36 (1996), 223-227.
2. R. Burch and T.C. Watling, J. Catal., 169 (1997), 45-54.
3. Barbies J., Catalyst Deactivation (1987) 1-18.
4. J.O Petunchi and W.K. Hall, Appl. Catal. B 3 (1993), 239-257.
5. C.J Bennett, P.S. Bennett, S.E. Golunski, J.W. Hayes and A.P. walker, Appl. Catal. A 86 (1992) L1-L6.

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THE EFFECT OF NO ON COKE FORMATION OVER Pt CATALYST IN NO REDUCTION BY PROPENE UNDER LEAN-BURN CONDITION.

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ABSTRACT

The catalytic activity and the amount of coke on the spent Pt/Al₂O₃ catalysts were investigated for the C₃H₆/O₂ reaction with and without the presence of NO at 170 °C. The addition of NO with the concentration of 1000 ppm decreased percent propene conversion and the amount of coke, but the selectivity of coke formation became higher. Additionally, the peak of the coke on metal and support shifted to a higher temperature in even of the presence of NO. It was also found that organic NO₂ groups was the main species detected after the reaction with NO thus it was suggested to be the intermediates.

INTRODUCTION

The emission of NO_x from stationary and automotive sources has serious environmental implications and therefore, various catalysts have been developed for NO_x control. Ammonia has used as a reducing agent to remove NO_x under net-oxidizing conditions but this technology can only be conveniently used on stationary sources. The three-way automotive catalyst has been highly successful in controlling exhaust emissions from conventional petrol engines which operate close to stoichiometric conditions. However, this catalyst is no longer effective for NO_x control in oxygen-rich exhaust gases such as the exhaust from diesel and lean-burn gasoline engines. To reduce NO_x under these conditions alternative catalytic systems must be developed. Various zeolites [1,2], metal oxide [3], and noble metals [4] have been reported to have catalytic activity for the selective reduction of nitrogen monoxide with hydrocarbon in the presence of excess oxygen. The platinum group metals supported on metal oxide are among the most important catalysts. Although the supported platinum catalyst does not have as high activity as Cu-ZSM-5 catalyst at high temperature, Cu-ZSM-5 catalyst has poorer thermal and hydrothermal stability. It has been emphasized that the activities of the Pt catalysts were little diminished by the introduction of SO₂ [5,6] or water [6]. From the recent literature [7-12], there are still arguments on the reaction mechanisms of NO reduction by hydrocarbon under excess oxygen condition over Pt/Al₂O₃ catalyst. In general, many mechanisms have been proposed for NO reduction in the presence of oxygen, for example:

1. The hydrocarbon may remove the surface oxygen poisoning the active site, while nitrogen is formed through NO decomposition [7].
2. The hydrocarbon may react with oxygen to partially oxidized hydrocarbon which then reacts with NO (or NO₂) to form nitrogen [8].
3. The hydrocarbon may react with NO₂ [4] formed by NO oxidation to intermediates such as isocyanate [9] and organic nitro compound [10] leading to the formation of nitrogen.

4. The hydrocarbon may be converted to an active carbonaceous material [11] and then it is rely on the formation of nitrogen, while oxygen may prevent the deposition of carbonaceous deposits which would cover the active sites [12].

In general, most researches have emphasized only on coke formation in reducing atmosphere e.g. dehydrogenation [13], cracking [14], reforming [15] etc. Nevertheless under these net-oxidizing condition it appears that coke deposition can take place on catalyst surface. The investigation of coke formation for NO reduction by hydrocarbons may illustrate some aspects that may be useful for the prediction of reaction of reaction mechanism. Therefore, in the present work, coke formation on Pt/Al₂O₃ catalyst for propene combustion (without NO) and NO reduction by propene under lean-burn condition (with NO) were studied.

EXPERIMENT

The 0.3 % Pt/Al₂O₃ catalyst used in this study was prepared by dry impregnation method using hexchloroplatinic acid as the salt precursor. The sample was calcined at 500 °C for 3 hr. in air. Catalytic testing was carried out using a quartz tubular downflow microreactor (i.d. 6 mm). The sample (0.5g) was held between plugs of quartz wool. Prior to the reactor, the catalyst was reduced with a flow of H₂ at 500 °C for 1 hr. Then it was cooled down from 500°C to reaction temperature, 170 °C. Both reactions, propene combustion and NO reduction by propene under lean-burn condition, were performed at the pressure close to the atmospheric pressure. A feed gas mixture was fed at the volumetric flow rate of 60 cm³/min or with gas hourly space velocity (GHSV) of 4000 hr⁻¹. The feed gas consists of propene (3000 ppm) and oxygen (2.5 %vol) with He balance for propene combustion. NO (1000 ppm) was added in feed stream for selective catalytic reduction of NO with propene in the presence of excess oxygen. The time on stream of both reactions was varied at 1, 2, and 4 hr. The products were analyzed using a SHIMADZU GC-8ATP gas chromatograph equipped with molecular sieve 5A for the separation of O₂, N₂ and CO and a SHIMADZU GC-8AIT gas chromatograph equipped with Porapak QS for the separation of CO₂, N₂O and C₃H₆.

The coke catalysts from both reactions were characterized by temperature programmed oxidation technique (TPO) performed by burning it in 1 vol% oxygen in helium. Before starting the TPO, 0.3 g of spent catalyst was pretreated at 120°C for 3 hr under helium atmosphere. During testing the TPO, the temperature was raised from 50 °C to 700 °C and the effluent stream was sampled by an on-line gas sampling valve every 5 minutes. Carbon dioxide produced was measured by a thermal conductivity detector (TCD) gas chromatography (GC 8AIT, SHIMADZU) with Porapak QS column. The percentage of carbon in coke can be calculated from TPO curves. CO₂ area is divided by a internal time in which CO₂ formation is, hence, obtained. The area under the curve of CO₂ formation rate versus time gives the value of total CO₂ formation. Finally, this value is converted to milligram carbon or percentage of carbon by using a calibration curve.

Infrared spectra of the adsorbed species on the spent catalysts from both reactions were recorded on an FT-IR spectrometer (The Micolet model Impact 400) equipped with a deuterated triglycine sulfate (DTGS) detector. About 50 mg of the spent catalyst was set in the IR cell. The resolution of 4 cm⁻¹ with 500 scans was employed for every experiment.

RESULTS AND DISCUSSIONS

The effect of time on stream on the $C_3H_6 + O_2$ and $C_3H_6 + O_2 + NO$ reactions over 0.3 %Pt/Al₂O₃ at 170 °C is shown in Figure 1. It was observed that the reaction without NO gave significantly higher percent hydrocarbon conversion than the reaction with NO.

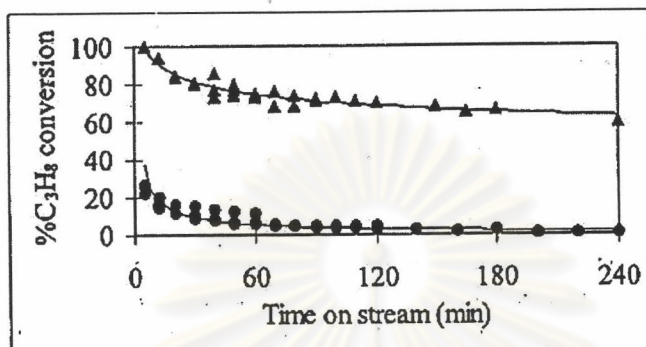


FIGURE 1 Relationship between %C₃H₆ conversion and time on stream on Pt/Al₂O₃.

Given: (▲) The reaction without NO (C₃H₆+O₂),

(●) The reaction with NO (C₃H₆+O₂+NO)

After the reaction, the spent catalysts were characterized by temperature-programmed oxidation technique (TPO) and then percentage of carbon in catalyst was calculated as shown in Table 1. It was noticed that the $C_3H_6 + O_2$ reaction provided higher amount of coke than the $C_3H_6 + O_2 + NO$ reaction (at the same time on stream). Additionally, the amount of coke increase with time on stream in both reactions. In this paper, we define the selectivity of coke formation as the ratio of carbon atom in coke to carbon atom of hydrocarbon feed converted. From Table 1, it was found that the reaction with NO had higher percent selectivity of coke formation than the reaction without NO. For the $C_3H_6 + O_2$ reaction, the percent selectivity of coke formation decreased with time on stream. When NO was added, it appeared that the percent selectivity of coke formation was not related simply to time on stream.

TABLE I

Hydrocarbon conversion, amount of coke and selectivity of coke formation of Pt/Al₂O₃.

Reaction	Time on stream (hr)	% C ₃ H ₆ conversion	% Coke	% Selectivity of coke formation
C ₃ H ₆ +O ₂	1	74.08	0.45	0.31
	2	70.34	0.67	0.23
	4	59.76	0.98	0.19
C ₃ H ₆ +O ₂ +NO	1	10.97	0.28	0.80
	2	3.18	0.41	1.27
	4	0.51	0.47	1.08

The TPO profiles of 0.3 %Pt/Al₂O₃ catalysts are indicated in Figure 2. The spent catalyst from the reaction without NO showed a shoulder at 250 °C and a TPO peak around 425 °C, while the TPO profiles of spent catalysts from the reaction with NO demonstrated two TPO peaks at the temperature around 325 °C and 450 °C. Barbier et al. [16] suggested that the first peak is the coke on metal and the second peak is the coke on the support. It was noticed that the reaction without NO provided higher amount of coke on support than the reaction with NO but coke on support for C₃H₆ + O₂ reaction was burnt harder than coke on support for C₃H₆ + O₂ + NO reaction. It was also found that the peak of the coke on metal shifted to a higher temperature in even of the presence of NO; besides, for C₃H₆ + O₂ + NO reaction the amount of coke on metal is higher than the amount of coke on support.

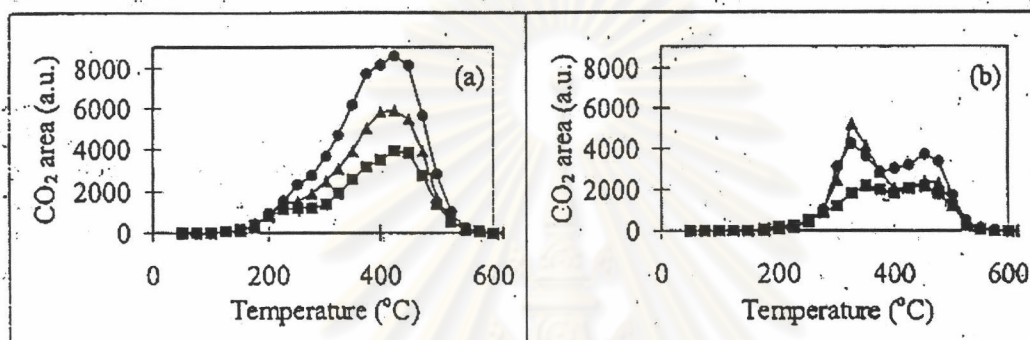


FIGURE 2 (a) TPO profiles of coked catalyst from the reaction without NO (C₃H₆+O₂).
 (b) TPO profiles of coked catalyst from the reaction with NO (C₃H₆+O₂+NO).
 Given : (■) Time on stream = 1 hr., (▲) Time on stream = 2 hr.,
 (●) Time on stream = 4 hr.

Figure 3 shows IR spectra of the surface species after C₃H₆ + O₂ and C₃H₆ + O₂ + NO reactions at 170 °C. It was observed that three main peaks appeared at 1460, 1570 and 1630 cm⁻¹ for both reactions. Besides, it was noticed that two broad peaks also appeared approximately at 1350 and 1410 cm⁻¹ for the presence of NO.

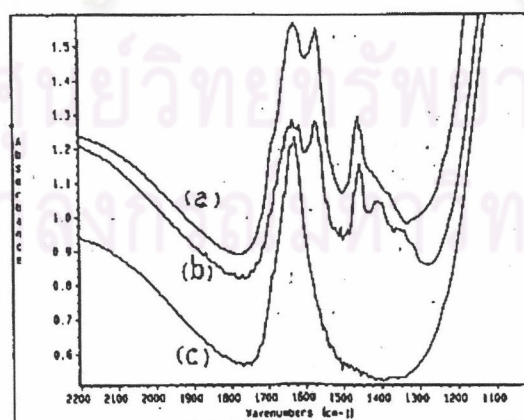


FIGURE 3 IR spectra of the surface species, (a) Spent catalyst C₃H₆+O₂ reaction,
 (b) Spent catalyst C₃H₆+O₂+ NO reaction, (c) Fresh catalyst.

For all the catalyst, both fresh and spent catalysts, the band at 1630 cm^{-1} disappeared after pretreatment under vacuum at $150\text{ }^{\circ}\text{C}$. It is believed that this band can be assigned to OH deformation (adsorbed water on catalyst surface) [17]. Two bands at 1460 and 1570 cm^{-1} can be assigned to carbonaceous deposits because these bands appeared on spent catalyst from the reactions with the presence of NO and the absence of NO. Normally, the band in the region of $1500\text{-}1600\text{ cm}^{-1}$ are very specific to stretching mode of aromatic systems [18]. The in-phase blending vibration of the carbon-hydrogen bands of methyl or methylene groups occur in the regions of $1340\text{-}1470\text{ cm}^{-1}$ [18]. Thus, two bands at 1460 and 1570 cm^{-1} can be assigned to methyl or methylene groups and aromatic ring, respectively. As reported previously, it was speculated that two bands at 1350 and 1410 cm^{-1} can be assigned to organic NO_2 groups (stretching mode) [10].

From literature, on account of the fact that Al_2O_3 is not active to hydrocarbon combustion at this temperature [19], propene should react with oxygen on the metal sites. Furthermore, NO oxidation also takes place on the metal sites [20]. Therefore, it is possible that both NO and propene may compete to adsorb and react with oxygen on metal active sites. R. Burch et al. [20] found that NO conversion to NO_2 was independent of contact time for NO oxidation over Pt/ Al_2O_3 catalyst. They believed that conversion of NO to NO_2 was faster than the other reactions, e.g. hydrocarbon combustion, NO conversion to N_2 etc., occurring on the Pt/ Al_2O_3 catalyst. From the results above, it was suggested that oxygen would preferably react with NO leading to the decrease of percent propene conversion. Since propene from $\text{C}_3\text{H}_6 + \text{O}_2$ reaction was more reacted than that from $\text{C}_3\text{H}_6 + \text{O}_2 + \text{NO}$ reaction, there are more opportunities to be converted to coke precursor. Because the catalysts in the $\text{C}_3\text{H}_6 + \text{O}_2$ reaction were rapidly covered by carbonaceous deposits, they gave higher amount of coke than the catalysts in the $\text{C}_3\text{H}_6 + \text{O}_2 + \text{NO}$ reaction. From the previous [21] work, it was concluded that the higher production rate of coke precursor appeared in the gas product, the lower coke deposited on the catalyst surfaces is. On the other hand, if the deactivation is found significantly, product of coke precursor would be found in amount of trace. This is consistent with the results above which it was found that the $\text{C}_3\text{H}_6 + \text{O}_2 + \text{NO}$ reaction had higher percent selectivity of coke formation than that of $\text{C}_3\text{H}_6 + \text{O}_2$ reaction. From TPO results of both reactions, it is speculated that shifting and decreasing of coke on support after the addition NO may have three reasons as follows:

1. NO_2 spill over [20] will suppress the drain off effect.
2. The coke on support will be burnt by oxygen [12].
3. The active carbonaceous material on support will react with the other species

[11].

It is expected that the first reason are more possible than the other reasons. Because the coke on the support is a complex structure coke, there are opportunities to be burnt or reacted hardly. On the other hand, the peak of the coke on metal shifted to a higher temperature since the adsorbed O_2 which prevents the deposition of carbonaceous deposits decrease. Finally, it is suggested that adsorbed NO on metal active sites reacted with oxygen to NO_2 and then it may be transferred from metal active sites to support. Indeed, it hindered the drain off effect and related to the formation of intermediates to nitrogen production which it will correspond to the formation of organic nitro species.

CONCLUSION

It was concluded that the addition NO affect to coke formation as follow;

1. NO would complete with C_3H_6 to adsorb and react rapidly with O_2 on metal active sites leading to the decrease of present propene conversion and the amount of coke.
2. NO would suppress C_3H_6 combustion leading to the increase of present selectivity of coke formation.
3. NO would difficultly lead to burn coke on metal and support.
4. NO would correspond to the formation of organic nitro species.

ACKNOWLEDGEMENTS

This research was supported in financial by The Thailand Research Fund and National Science and Technology Development Agency (NSTDA).

REFERENCES

1. Hideaki Hamada, Yoshiki Kintaichi, Motoi Sasaki and Takehiko Ito; Appl. Catal.A; 64; L1; 1990.
2. Shinya Sato, Yoshihiro Yu-u, Hidenori Yahiro, Noritaka Mizuno and Masakazu Iwamoto; Appl. Catal.A; 70; L1; 1991.
3. Yoshiaki Kintaichi, Hideaki Hamada, Mitsunori Tabata, Motoi Sasaki and Takehiko Ito; Catal. Lett; 6; 239; 1990.
4. Shuichi Naito and Mitsutishi Tanimoto; Chem. Lett.; 1935; 1993
5. Geng Zhang, Toshio Yamagushi, Hiroshi Kawakami and Takao Suzuki; Appl. Catal.B; 1; L15; 1992.
6. Akira Okushi, Akihiko Ohi, Masato Nakamura, Atsushi Ogata, Koichi Mizuno and Hideo Okuchi; Appl. Catal. B; 2; 71; 1993.
7. R-Burch, P.J. Millington, A.P. Walker; Appl. Catal. B; 4; 65; 1994.
8. Motoi Sasaki, Hideaki Hamada, Yoshiaki Kintaichi and Takehiko Ito; Catal. Lett; 15; 297; 1992.
9. Gratian R. Bamwenda, Akira Obuchi, Atsushi Ogata and Koichi Mizuno; Chem. Lett.; 2109; 1994.
10. T. Okukara, Y. Hasada and M. Misono; Catal. Today; 35; 83; 1997.
11. C. J. Bennett, P. S. Walker; Appl. Catal.A; 86; L1; 1992.
12. Juan O. Petunchi and W. Keith Hall; Appl. Catal. B; 3; 239; 1994.
13. Mikael Larsson, Magnus Hulten, Edd A Blekkan and Bengt Andersson; J. Catal.; 164; 44; 1996.
14. W. G. Appleby, J. W. Gibson and G. M. Good, I & EC Process Design and Development; 1; 102; 1962.
15. J.N. Beltramini, E.E. martinelli, E.J. Churin, N.S. Figoli and J.M. Parera; Appl. Catal.; 7; 43; 1983.
16. Barbies J.; Catalyst Deactivation ; 1; 1987
17. Neil W. Hayes, Richard W. Joyner, Efim S. Shpiro; Appl. Catal. B; 8; 343; 1996.
18. Douglas A. Skoog and James J. Leary; Principles of instrumental analysis (4 th ed.) ; Harcourt Brace College Pabbishers; Philaadelphia; 1992.
19. Megummu Inaba, Yoshiaaki kintaichi and Hideaki Hamada; Catal. Lett.; 36; 223, 1996.
R. Burch and T. C. Watling; J. Catal.; 169; 45; 1997.
21. Wilaiwan Yuangsawatdikul; Effect on reactants on coke formation in dehydrogenation reaction; M. Eng. Thesis; Chulalongkorn University; 1997.

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

**Quebec, May 17-20, 1998
Québec, 17-20 mai, 1998**

COMPARATIVE STUDY OF COKE DEPOSITION ON Pt CATALYSTS IN REACTIONS WITH AND WITHOUT OXYGEN.

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ABSTRACT

Coke deposition is an important deactivation mode in hydrocarbon conversion process. In general, most researchers (1-5) have emphasized only on coke formation in reducing atmosphere e.g. dehydrogenation, cracking, reforming etc. Nevertheless, in oxidizing atmosphere, coke deposition can also take place on catalyst surface. Therefore, in the present work, it is set up to compare the amount of coke formed on Pt/Al₂O₃ catalysts for reactions with the absence and presence of oxygen. The catalytic activity and the amount of coke on the spent Pt/Al₂O₃ catalysts were investigated for reactions with oxygen, i.e. hydrocarbon combustion and reduction of NO_x, and without oxygen, i.e. dehydrogenation and reduction of NO_x. Propane and propene were used as the hydrocarbon sources for all four reactions. Pt/Al₂O₃ (0.3 wt.% Pt) catalyst in this study was prepared by dry impregnation method using H₂PtCl₆ as the salt precursor. The catalytic test is carried out in a 0.6 I.D. quartz microreactor where a 0.5 g of the catalyst was packed. The reactor was heated from room temperature to 500°C at the heating rate of 5 °C/min. Then, the catalyst was reduced at 500°C for 1 hr using hydrogen as the reductant gas. The reactor was cooled down from 500°C to reaction temperature as 350°C and 170°C for the case of the presence and absence of oxygen reaction, respectively. All four reactions were performed at the pressure close to the atmospheric pressure. A feed gas mixture was fed at the volumetric flow rate of 50 cm³/min or with gas hourly space velocity (GHSV) of 4000 hr⁻¹. Its hydrocarbon (propane or propene) composition was fixed at 3000 ppm. The time on stream was fixed at 2 hr. The coked catalyst from each reaction was analyzed by temperature program oxidation technique (TPO) performed by burning it in 1 vol.% oxygen in helium. The temperature was raised to 700°C at the heating rate of 5°C/min. When temperature was 50°C, the effluent stream was sampled every 5 minutes by an on-line gas sampling valve. Carbon dioxide produced was measured by a thermal conductivity detector (TCD) gas chromatography (GC 8AIT, Shimadzu) with Parapak-QS column.

The experimental results were shown in Table 1, Figure 1 and Figure 2. In all four reactions, it was observed that the reactions with propene as a reactant gave more percent hydrocarbon conversion in the initial interval of time on stream and also had more amount of coke than the reactions with propane as a reactant. However, in the dehydrogenation reaction and NO_x reduction under the absence of oxygen condition, the propene conversion was dropped more rapidly than the propane conversion. Finally the reaction of propene gave less percent hydrocarbon conversion than the reaction of propane. It meant that propene is more active than propane (6). Since propene was more reacted, there is more opportunity to be converted to coke precursor. Additionally, it was clarified that the product of propene from the reaction with the absence of oxygen, propadiene which is converted irreversibly to ethylidyne leading to coke deposition (7,8), was more reactive than propene (6). Thus the catalysts in the reaction using propene as a reactant were rapidly covered by carbonaceous deposits. The TPO profiles of 0.3% Pt/Al₂O₃ catalysts are indicated in Figure 2. Each sample

showed a TPO peak around 425° C except the TPO profile of spent catalyst from reduction of NO_x in the presence of oxygen condition. This TPO profiles showed a TPO peak at the temperature around 325°C for the reaction with propane as a reactant and two peaks at the temperature around 325 °C and 425 °C for that with propene as a reactant. Barbier et al. (3) suggested that the first peak is the coke on metal and the second peak is the coke on the support. In this paper, we define the selectivity of coke formation as the ratio of carbon atom in coke to carbon atom of feed hydrocarbon converted. It was found that propene had higher percent selectivity of coke formation for the reaction with the absence of oxygen but propane had higher percent selectivity of coke formation for the reaction with the presence of oxygen. Under the presence of oxygen, it suggested that coke is formed in parallel with carbon dioxide formation. Propene or coke precursor is more effectively reacted with oxygen to carbon dioxide (9). Additionally, for the reaction with the presence of oxygen using propane as reactant, it was observed that the reaction with the absence of NO gave higher percent selectivity of coke formation than the reaction with the presence of NO. On the other hand, for the case of propene, the reactant with the presence of NO gave higher percent selectivity of coke formation. It suggested that propane or propene is first reacted with adsorbed oxygen to be converted to intermediates (10,11). For the case of propane (10,11), these intermediates are preferably reacted with NO which result in, when NO was added in feed, propane less selectively produce coke. However, for the case of propene (12), NO is hardly reacted with the intermediates but it prefer dissociate into dinitrogen. Thus, since the dissociation of NO hinders the reaction of carbon dioxide formation, the intermediates prefer produce coke rather than carbon dioxide for the case of the presence of NO reaction.

Table 1 : Hydrocarbon conversion, amount of coke and coke selectivity of 0.3% Pt/Al₂O₃

Reaction	Reactant	Temperature (°C)	% HC conversion (at 5 min.)	% Coke	% Selectivity of coke formation
HC	Propane	350	59.36	0.1759	0.223
	Propene	350	98.88	0.3236	0.269
HC+NO	Propane	350	46.17	0.1336	0.192
	Propene	350	66.14	0.1633	0.338
HC+O ₂	Propane	170	11.71	0.1319	1.131
	Propene	170	100.00	0.4795	0.294
HC+NO+O ₂	Propane	170	5.59	0.1213	1.069
	Propene	170	40.12	0.3289	0.542

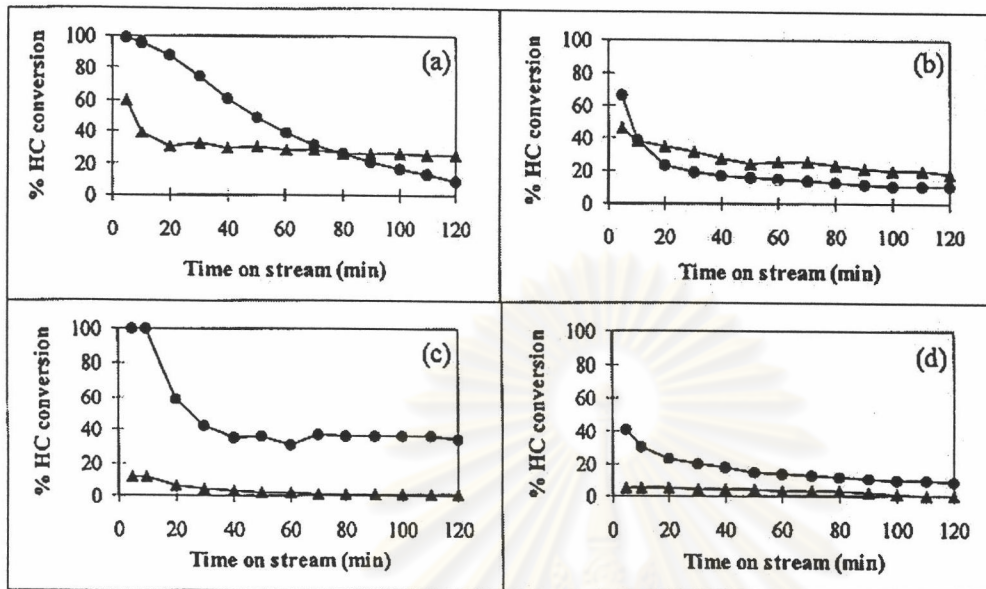


Figure 1 : Relationship between % HC conversion versus time on stream (a) Feed : 3000 ppm HC + He balance, Temperature = 350 °C (b) Feed : 3000 ppm HC + 1000 ppm NO + He balance, Temperature = 350 °C (c) Feed : 3000 ppm HC + 2.5 vol.% O₂ + He balance, Temperature = 170 °C (d) Feed : 3000 ppm HC + 1000 ppm NO + 2.5 vol.% O₂ + He balance, Temperature = 170 °C : (▲) Propane , (●) Propene

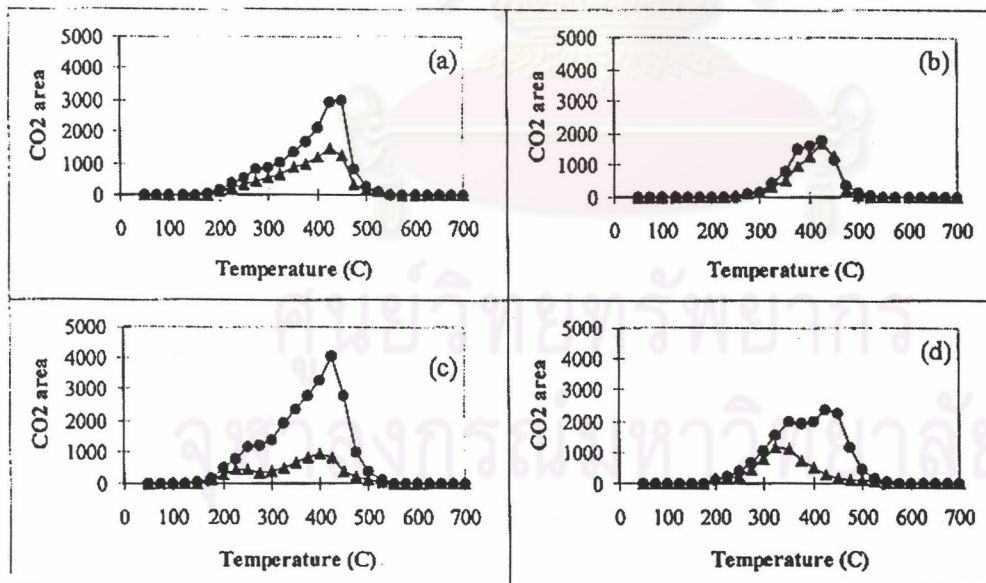


Figure 2 : TPO profiles of coked catalyst from reaction (a) Dehydrogenation, Temperature = 350 °C (b) Reduction of NO_x under absence of oxygen condition, Temperature = 350 °C (c) Combustion, Temperature = 170 °C (d) Reduction of NO_x under absence of oxygen condition, Temperature = 170 °C : (▲) Propane , (●) Propene

REFERENCES

1. W.G. Appleby, J.W. Gibson and G.M. Good, *I & EC Process Design and Development* 1 (1962) : 102-110.
2. J.N. Beltramini, E.E. martinelli, E.J. Churin, N.S. Figoli and J.M. Parera, *Applied Catalysis* 7 (1983) : 43-55.
3. Barbies J., *Catalyst Deactivation* (1987) : 1-18.
4. J. Biswas, P.G. Gray and D.D. Do, *Applied Catalysis* 32 (1987) : 249-274.
5. Mikael Larsson, Magnus Hulten, Edd A Blekkan and Bengt Andersson, *Journal of Catalysis* 164 (1996) : 44-53.
6. Morrison and Boyd, *Organic Chemistry* (sixth edition) : 122, 287, 410.
7. Gabor A. Somorjai, *Introduction to Surface Chemistry and Catalysis* : 420.
8. B.J. McIntyre, M. Salmeron and G.A. Somorjai, *Journal of Catalysis* 164 (1996) : 184-193.
9. R. Burch and T.C. Watling, *Catalysis Letters* 43 (1997) : 19-23.
10. Motoi Sasaki, Hideaki Hamada, Yoshiaki Kintaichi and Takehiko Ito, *Catalysis Letters* 15 (1992) : 297-304.
11. Megumu Inaba, Yoshiaki Kintaichi and Hideaki Hamada, *Catalysis Letters* 36 (1996) : 223-227.
12. R. Burch, P.J. Millington and A.P. Walker, *Applied Catalysis B4* (1994) : 65-94.



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