

## REFERENCES

1. Parker, A. *Industrail Air Pollution Handbook*. England : McGraw Hill Book Co., 1978.
2. Kim, E. J. Jpn. Inst. Energy 71 (1992) : 1150.
3. Toyota Human Resource Development Center Project Office (THDC), *Toyota Motor Thailand Co. Ltd. Emission Control for Automobiles*. Bangkok, 1990.
4. Hightower, J.W., and Von Leirsberg, D.A. In R.L. Klimisch and L.G. Larson (eds.), The Catalytic Chemistry of Nitrogen Oxides, 63.
5. Klimisch, R.L., and Komarmy, J.M. In R.L. Klimisch and L.G. Larson (eds.), The Catalytic Chemistry of Nitrogen Oxides, 305.
6. Bosch, H., and Janssen, F. Catal. Today 2 (1988) : 369.
7. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M. Highly selective reduction of nitrogen oxides with hydrocarbons over H-form zeolite catalysts in oxygen-rich atmospheres. Appl. Catal. 64 (1990) : L1-L4.
8. Ukisu, Y., Sato, S., Muramatsu, G., and Yoshida, K. Activity enhancement of copper-containing oxide catalysts by addition of cesium in the reduction of nitric oxide. Catal. Lett. 16 (1992) : 11-16.
9. Iwamoto, M., Mizuno, N., and Yahiro, H. Selective catalytic reduction of NO by hydrocarbon in oxidizing atmosphere. Proc. 10th Int. Cong. Catal., 213-215. Budapest, 1992.

10. 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.
11. 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 cetane. Catal. Lett. 13 (1992) : 87-93.
12. Ishihara, T., Kagawa, M., Mizuhara, Y., and Takita, Y. Selective reduction of nitrogen monoxide with propene over Cu-silicoaluminophosphate (SAPO) under oxidizing atmosphere. Chem. Lett. (1992) : 2119-2122.
13. 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.
14. Bennett, C.J., Bennett, P.S., Golunski, S.E., Hayes, J.W., and Walker, A.P. Selective reduction of nitrogen oxides under oxidizing exhaust-gas conditions. Appl. Catal. 86 (1992) : L1-L6.
15. Petunchi, J.O., and Hall, W.K. Effects of selective reduction of nitric oxide on zeolite structure. Appl. Catal. B 3 (1994) : 239-257.
16. Teraoka, Y., Pgawa, H., Furukawa, H., and Kagawa, S. Influence of cocations on catalytic activity of copper ion-exchanged ZSM-5 zeolite for reduction of nitric oxide with ethene in the presence of oxygen. Catal. Lett. 12 (1992) : 361-388.

17. 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.
18. Lee, C.Y., Choi, K.Y., and Ha, B.H. Catalytic decomposition of nitric oxide on copper/zeolites. Appl. Catal. B 5 (1994) : 7-21.
19. Held, W., Konig, A., Richter, T., and Puppe, L. Catalytic NO<sub>x</sub> reduction in net oxidizing exhaust gas. SAE Paper 900496 (1990).
20. Iwamoto, M. Catalytic decomposition of nitrogen monoxide. Stud. Surf. Sci. Catal. 54 (1990) : 121.
21. Hamada, H., Kindaichi, Y., Sasaki, M., and Ito, T. Chem. Lett. (1990) : 1069.
22. Iwamoto, M., Yahiro, H., and Tanda, K. Catalytic decomposition of nitrogen monoxide over copper ion-exchanged zeolites: influence of zeolite structure and aluminum content on the catalytic activity. In T. Inui (ed.), Successful Design of Catalysis, 219-226. Amsterdam : Elsevier Science Publishers B.V., 1988.
23. Iwamoto, M., Sato, S., Yu-u, Y., Yahiro, H., and Mizuno, N. Cu-ZSM-5 zeolite as highly active catalyst for removal of nitrogen monoxide from emission of diesel engines. Appl. Catal. 70 (1991) : L1-L5.
24. 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.
25. Ault, J.W., and Ayen, R.J. Catalytic reduction of nitric oxide with various hydrocarbons. AIChE J. 17 (1971) : 265-271.

26. Inui, T., Kojo, S., Shibata, M., Yoshida, T., and Iwamoto, S. NO decomposition on Cu-incorporated A-zeolites under the reaction condition of excess oxygen with a small amount of hydrocarbons. In P.A. Jacobs et al. (eds.) Zeolite Chemistry and Catalysis, 355-364. Amsterdam : Elsevier Science Publishers B.V., 1991.
27. Petunchi, J.O., Sill, G., and Hall, W.K. Studies of the selective reduction of nitric oxide by hydrocarbons. Appl. Catal. B 2 (1993) : 303-321.
28. Cho, B.K. Nitric oxide reduction by hydrocarbons over Cu-ZSM-5 monolith catalyst under lean conditions: steady-state kinetics. J. Catal. 142 (1993) : 418-429.
29. Iwamoto, M., Konno, M., Chikahisa, T., and Murayama, T. Catalytic reduction of NO<sub>x</sub> in actual diesel engine exhaust. SAE Paper 920091 (1992) : 1-8.
30. d'Itri, J.L., and Sachtler, W.M.H. Selective reduction of nitric oxide over Cu/ZSM-5 : the role of oxygen in suppressing catalyst deactivation by carbonaceous deposits. Appl. Catal. B 2 (1993) : L7-L15.
31. Burch, R., and Scire, S. Selective catalytic reduction of nitric oxide with ethane and methane on some metal exchanged ZSM-5 zeolites. Appl. Catal. B 3 (1994) : 295-318.
32. Iwamoto, M., Mizuno, N., and Yahiro, H. Removal of nitrogen monoxide over copper ion-exchanged zeolite catalysts. Sekiyu Gakkaishi 34 (1991) : 375-390.
33. d'Itri, J.L., and Sachtler, W.M.H. Reduction of NO over impregnated Cu/ZSM-5 in the presence of O<sub>2</sub>. Catal. Lett. 15 (1992) : 289-295.

34. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M. 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.
35. Li, Y., and Armor, J. Selective catalytic reduction of NO<sub>x</sub> with methane over metal exchanged zeolites. Appl. Catal. B 2 (1993) : 239-256.
36. Iwamoto, M., and Mizuno, N. NO<sub>x</sub> emission control in oxygen-rich exhaust through selective catalytic reduction by hydrocarbon. Proc. Instn. Mech. Engrs. 207 (1993) : 23-33.
37. Flanigen, E.M. Zeolites and molecular sieves : an historical perspective. In H.V. Bekkum (ed.), Stud. Sur. Sci. Catal., 58 : Introduction to Zeolite Science and Practice, 13-34. Netherlands : Elsevier Science Publishing, 1991.
38. Breck, D.W. Zeolite Molecular Sieves. New York : Robert E. Krieger Publishing Co., 1984.
39. Szostak, R. Molecular Sieves : Principles of Synthesis and Identification. New York : Van Nostrand Reinhold, 1989.
40. Gates, B.C. Catalytic Chemistry. Singapore : John Wiley & Sons, 1992.
41. Satterfield, C.N. Heterogeneous Catalysis in Practice. New York : McGraw-Hill Book Co., 1980.
42. Tanabe, K., Misono, M., Ona, Y., and Hattori, H. Acid and base centers : structure and acid-base property. In B. Delman and J.T. Yates (eds.), Stud. Sur. Sci. Catal., 51 : New Solid Acids and Bases, 142-161. Tokyo : Elsevier, 1989.
43. Khouw, C.B., and Davis, M.E. Shape-Selective catalysis with zeolites and molecular sieves. J. Am. Chem. Soc. 115 (1993) : 207-221.

44. Barthomeuf, D. Acidic catalysis with zeolites. In F.R. Ribeiro et al. (eds.), Zeolites : Science and Technology, 317-346. Netherlands : Martinus Nijhoff Publishers, 1984.
45. Chang C.D. Hydrocarbons from methanol. Catalysis Reviews 25 (1983): 9
46. Kokotailo G.T. Zeolite crystallography. In F.R. Ribeiro et al. (eds.), Zeolites : Science and Technology, 83-108. Netherlands : Martinus Nijhoff Publishers, 1984.
47. Ashton, A.G., Batmanian, S., Dwyer, J. Acidity in zeolites. In B. Imelik et al. (eds.), Catalysis by Acids and Bases, 101-109. Amsterdam : Elsevier, 1985.
48. Sano, T., Fujisawa, K., and Higiwara, H. High steam stability of HZSM-5 type zeolite containing alkaline earth metals. In B. Delmin and G.F. Fromant (eds.), Stud. Sur. Sci. Catal., 34 : Catalyst Deactivation, 613- 624. Amsterdam : Elsevier, 1987.
49. Derouane, E. G. New aspects of molecular shape selectivity. In B. Imelik et al. (eds.), Catalysis by Zeolites, 5-27. Amsterdam : Elsevier, 1980.
50. \_\_\_\_\_. Molecular Shape Selectivity Catalysis by Zeolites. In F.R. Rebeiro et al. (eds.), Zeolites Science and Technology, 347-371. The Hague : Martinus Nijhoff Publishers, 1984.
51. Inui, T., Vamase, O., Fukuda, K., Itoh, A., Tarumoto, J., Morinaga, N., Hagiwara, T., and Takegami, Y., Proc. 8th Int. Cong. Catal., Berlin, 1984, 569. Frankfurt-am-Main, Germany : Decema, 1984.
52. Iwamoto, M., Mizuno, N., Yahiro, H., and Yoshioka, T. Ion exchange properties of copper with sodium on ZSM-5 zeolite and application of resulting Cu-ZSM-5 as NO decomposition catalyst. New Developments in Ion Exchange, 407-412. Kodansha, Tokyo, 1991.

53. Accomazzo, M.A. and Nobe, K. Catalytic combustion of C<sub>1</sub> to C<sub>3</sub> hydrocarbons. I&EC Process Design and Development 4 (1965) : 425-430.
54. W. Pattaraprakorn. Master's Thesis, Chulalongkorn University, to be submitted.
55. W. Engopasanan. Performance of ion-exchanged zeolite and metallosilicate catalysts on nitric oxide decomposition. Master's Thesis, Chulalongkorn University, 1994.
56. Argauer, R.J. and Landolt, G.R. Crystalline zeolite ZSM-5 and method of preparing the same. U.S. Patent 3,702,886, November 14, 1972.
57. Kirszensztein, P., Foltynowicz, Z., and Wachowski, L. Peculiar pore structure of the coke coating formed on Pt-Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Ind. Eng. Chem. Res. 30 (1991) : 2276-2279.

## **APPENDIX**

## APPENDIX A

### SAMPLE OF CALCULATIONS

#### A-1 Calculation of Si/Metal Atomic Ratio for ZSM-5 and Cu-silicate

The calculation is based on weight of Sodium Silicate ( $\text{Na}_2\text{O SiO}_2 \text{H}_2\text{O}$ ) in B1 and B2 solutions.

$$\text{M.W. of Si} = 28.0855$$

$$\text{M.W. of SiO}_2 = 60.0843$$

$$\text{Weight percent of SiO}_2 \text{ in Sodium Silicate} = 28.5$$

$$\text{M.W. of Al} = 26.9815$$

$$\text{M.W. of AlCl}_3 = 133.3405$$

$$\text{Weight percent purity of AlCl}_3 = 97$$

$$\text{M.W. of Cu} = 63.54$$

$$\text{M.W. of Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} = 241.60$$

$$\text{Weight percent purity of Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} = 99.5$$

For example, to prepare ZSM-5 at Si/Al atomic ratio of 50.

Using Sodium Silicate 69 g with 45 g of water as B1 solution.

$$\text{mole of Si used} = \frac{\text{wt. (\%)} \cdot (\text{M.W. of Si}) \cdot (1 \text{ mole})}{100 \cdot (\text{M.W. of SiO}_2) \cdot (\text{M.W. of Si})} \quad (\text{A-1.1})$$

$$= 69 \cdot (28.5/100) \cdot (1/60.0843)$$

$$= 0.3273$$

Si/Al atomic ratio = 50

$$\text{mole of AlCl}_3 \text{ required} = 0.3273/50 = 6.5458 \cdot 10^{-3} \text{ mole}$$

$$\text{amount of AlCl}_3 = 6.5458 \cdot 10^{-3} \cdot 133.34 (100/97)$$

$$= 0.8998 \text{ g}$$

This is the amount of AlCl<sub>3</sub> used in A1 and A2 solutions

Si/Cu atomic ratio = 50

$$\text{mole of Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O required} = 0.3273/50 = 6.5458 \cdot 10^{-3} \text{ mole}$$

$$\text{amount of Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O} = 6.5458 \cdot 10^{-3} \cdot 241.60 \cdot (100/99.5)$$

$$= 1.5894 \text{ g}$$

This is the amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O used in A1 and A2 solutions.

## A-2 Calculation of Metal ion-exchanged ZSM-5 and Metallosilicate

Cu ion-exchange

Determine the amount of Cu into catalyst = 0.2 wt. %

the catalyst use = x g

So that : from the equation

$$\text{Cu}/(x+\text{Cu}) = 0.2/100$$

$$100 \cdot \text{Cu} = 0.2 \cdot (x+\text{Cu})$$

$$(100-0.2) \cdot Cu = 0.2 \cdot x$$

thus  $Cu = 0.2 \cdot x / (100-0.2)$  g

use  $Cu(NO_3)_2 \cdot 3H_2O$  (M.W. 241.60, 26.30%Cu, purity 99.5%)

$$\text{weight of } Cu(NO_3)_2 \cdot 3H_2O = [0.2 \cdot x / (100-0.2)] \cdot [(100/26.30) \cdot (100/99.5)]$$

### A-3 Calculation of Reaction Flow Rate

The catalyst used = 0.50 g

packed catalyst into quartz reactor (diameter = 0.6 cm)

determine the average high of catalyst bed = x cm

So that, volume of catalyst bed =  $\pi * (0.3)^2 \cdot x$  ml-catalyst

used GHSV (Gas Hourly Space Velocity) =  $4,000 \text{ h}^{-1}$

$$GHSV = \frac{\text{Volumetric flow rate}}{\text{Volume of Catalyst}} = 4,000 \text{ h}^{-1}$$

$$\begin{aligned} \text{Volumetric flow rate} &= 4,000 \cdot \text{Volume of catalyst} \\ &= 4,000 \cdot \pi (0.3)^2 \cdot x \text{ ml/h} \\ &= 4,000 \cdot \pi (0.3)^2 \cdot x / 60 \text{ ml/min} \end{aligned}$$

$$\text{at STP : Volumetric flow rate} = \frac{\text{Volume flow rate} \cdot (273.15+t)}{273.15}$$

where : t = room temperature,  $^{\circ}\text{C}$

#### A-4 Calculation of NO and C<sub>3</sub>H<sub>8</sub> conversion

The effluent gas was analyzed by gas chromatography, the NO reduction activity was evaluated in terms of the conversion of NO into N<sub>2</sub>.

$$\text{NO Conversion (\%)} = (2[N_2]_{\text{out}} / [\text{NO}]_{\text{in}}) \cdot 100$$

The C<sub>3</sub>H<sub>8</sub> oxidation activity was evaluated in terms of the conversion of C<sub>3</sub>H<sub>8</sub> into CO and CO<sub>2</sub>.

$$\text{C}_3\text{H}_8 \text{ Conversion (\%)} = \frac{([C_3\text{H}_8]_{\text{in}} - [C_3\text{H}_8]_{\text{out}}) \cdot 100}{[C_3\text{H}_8]_{\text{in}}}$$

## APPENDIX B

### PHYSICAL PROPERTIES OF NITRIC OXIDE

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Property	Value
mol. wt.	30.1
m.p., °C	-161
b.p., °C	151.18
heat of fusion, kcal/mole	0.550
heat of vaporization, kcal/mole	3.293
heat of formation, kcal/mole	21.50
density [0 °C, 1 atm], g/L	1.2536
sp. gr., gas, [0 °C, 1 atm], (air = 1)	-93
critical temperature, °C	1.018
critical pressure, atm	64
color	colorless gas, blue liquid and solid

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## APPENDIX C

### AMBIENT AIR QUALITY STANDARD OF THAILAND (1981)

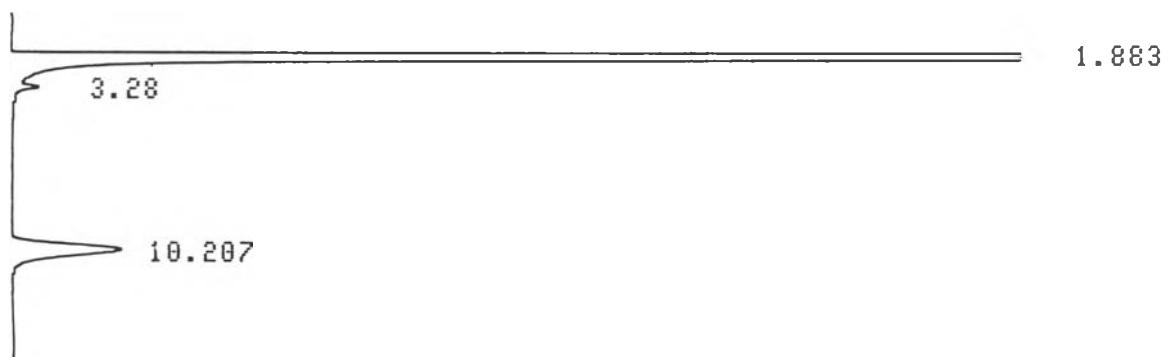
Pollutants	average value (mg/m <sup>3</sup> )				methods of measurement
	1 h	8 h	24 h	1 year	
Carbon Monoxide (CO)	50	20	-	-	Non Dispersive Infrared Detection
Nitrogen Dioxide (NO <sub>2</sub> )	0.32	-	-	-	Gas Phase Chemiluminescence
Sulfur Dioxide (SO <sub>2</sub> )	-	-	0.3	1*	Pararosanniline
Suspended Particulate Matter (SPM)	-	-	0.33	0.1*	Gravimetric
Photochemical Oxidant (O <sub>3</sub> )	0.20	-	-	-	Chemiluminescence
Lead (Pb)	-	-	-	0.01	- Wet Ashing

Note : \* = Geometric mean

## APPENDIX D

### SAMPLE OF CHROMATOGRAMS

10/12/01 01:03:54



COLUMN MS-5A

PKNO	TIME	AREA	CONC	NAME
1	1.883	213659	98.1127	O <sub>2</sub>
2	3.28	348	0.1597	N <sub>2</sub>
3	10.207	3691	1.6948	CO



COLUMN PORAPAK-Q

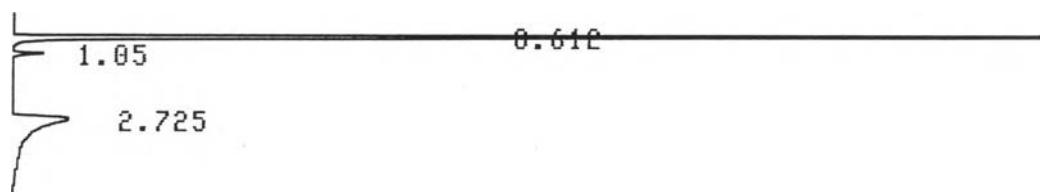
PKNO	TIME	AREA	CONC	NAME
1	0.553	60275	89.9274	AIR
2	1.02	1549	2.3108	CO <sub>2</sub>
3	2.495	2191	3.2683	H <sub>2</sub> O
4	6.188	3012	4.4935	C <sub>3</sub> H <sub>8</sub>

12/11/94 18:41:54



COLUMN VZ-10

PKNO	TIME	AREA	CONC	NAME
1	1.995	57115	100	C <sub>2</sub> H <sub>4</sub>



COLUMN PORAPAK-QS

PKNO	TIME	AREA	CONC	NAME
1	0.612	11850	91.4212	AIR
2	1.05	120	0.925	CO <sub>2</sub>
3	2.725	992	7.6538	H <sub>2</sub> O

## VITA

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