REFERENCES

- Alemany, L.J., Lietti, L., Ferlazzo, N., Forzatti, P., Busca,G., Giamella, E., and Breganis, F.(1995). Reactivity and physicochemical characteristic of V2O5-WO3/TiO2 De-NOx catalysts. Journal of catalysis, 155,117-130.
- Amiridis, M.D., Zhang, T., and Farrauto, R.J. (1996). Selective catalytic reduction of nitric oxide by hydrocarbons. <u>Applied Catalysis B: Environmental</u>, 10, 203-227.
- Botsford, C.W. (2001). The Two Faces of NOx Control. <u>Chemical Engineering</u>, pp.66-71.
- Cavani, F., Trifiro, F., and Vaccari, A.(1991). Hydrotalcite-Type Anionic Clays: Preparation, Properties and Applications. <u>Catalysis Today</u>, pp. 173-301.
- Cheng, L.S., Yang, R.T., and Chen, N. (1996). Iron oxide and chromia supported on titania-pillared clay for selective catalytic reduction of nitric oxide with ammonia. Journal of Catalysis, 164, 70-81.
- Cotton, F.A., Wilkinso, G., and Gaus, P.L. (1995) <u>Basic Inorganic Chemistry</u>. 3rd ed. John Wiley & Sons, Inc. pp.154-158.
- Drezdzon, M.A. (1988). Synthesis of isopolymetalate-pillared hydrotalcite via organic-anion-pillared precursor. <u>Inorganic Chemistry</u>, 27, 4628-4632.
- Eatl, G., Knozinger, H., and Wettkamp, J. (Eds.).(1998). <u>Handbook of</u> <u>Heterogeneous Catalysis.</u> A Wiley company.,4, 1633-1665.
- Fornasari, G., Vaccari, A., Prinetto, A., Ghiotti, G., and Centi, G.(2002). Novel low temperature NO storage-reduction catalysts for diesel light-duty engine emissions based on hydrotalcite compounds. <u>Catalysis Today</u>, 75, 421-429.
- Fritz, A., Pitchon, V. (1997). The current state of research on automotive lean NO_x catalysis. <u>Applied Catalysis B: Environmental</u>, 13, 1-25.
- Li, W., Sirilumpen, M., and Yang, R.T. (1997). Selective catalytic reduction of nitric oxide by ethylene in the presence of oxygen over Cu²⁺ ion-exchanged pillared clays. <u>Applied Catalysis B: Environmental</u>, 11, 347-363.
- Lietti, L., Forzatti, P., and Berti, F. (1996). Role of the redox properties in the SCR of NO by ammonia over V₂O₅-WO₃/TiO₂ catalysts. <u>Catalysis Letters</u>, 41(1-2), 35-39.

- Long, R.Q., and Yang, R.T. (1999). Selective catalytic reduction of nitrogen oxides by ammonia over Fe³⁺-exchanged TiO₂-pillared clay catalysts. <u>Journal of</u> <u>Catalysis</u>, 186(2), 254-268.
- Long, R.Q., and Yang, R.T. (2000a). Selective catalytic reduction of NO with ammonia over V₂O₅ doped TiO₂ pillared clay catalysts. <u>Applied Catalysis</u> <u>B: Environmental</u>, 24, 13-21.
- Long, R.Q., and Yang, R.T. (2000b). The promoting role of rare earth oxides on Feexchanged TiO2-pillared clay for selective catalytic reduction of nitric oxide with ammonia. <u>Applied Catalysis B: Environmental</u>, 27, 87-95.
- Long, R.Q., and Yang, R.T. (2000c). Catalytic performance and characterization of VO²⁺-exchanged titania-pillared clays for selective catalytic reduction of nitric oxide with ammonia. Journal of Catalysis, 196, 73-85.
- Marshneva, V.,I., Slavinskaya, E.,M., Kalinkina, O.,V., Odegova, G.,V., Moroz, E.M., Lavrova, G.V. and Salanov, A.,N.(1995). The influence of support on the activity of monolayer vanadia-titania catakysts for selective catalytic reduction of NO with ammonia. Journal of Catalysis, 151, 171-183.
- Kwon, T., Tsigdinos, G.A., and Pinnavaia, T. J.(1988). Structuring of layered double hydroxides (LDH's) by polyoxometalate anoins. <u>Journal of American</u> <u>Chemical Society</u>, 110, 3653-3654.
- Rahkamaa-Tolonen, K., Salmi, T., Murzin, D.Y., Billon, L.B., Lassi, U., and Keiski,
 R.(2002). Investigate of NO reduction by H₂ on Pd monolith with transient and isotopoic exchange techniques:II H₂/D₂ exchange in the reduction of NO. Journal of Catalysis, 210, 30-38.
- Payen, E., Grimblot, J., and Kasztelan, S. (1987). Study of oxidic and reduced alumina-supported molybdate and heptamolybdate species by in Situ Laser Raman spectroscopy. Journal of Physical Chemistry, 91, 6642-6648.
- Radojevic, M. (1998). Reduction of nitrogen oxides in flue gases. <u>Environmental</u> <u>Pollution</u>, 102, 685-689.
- Twu, J., and Dutta, P.K. (1989). Structure and reactivity of oxovanadate anions in layered lithium aluminate materials. <u>Journal of Physical Chemistry</u>, 93, 7863-7868.

- Yang, R.T.and Li, W. (1995). Ion-exchange pillared clays: A new class of catalysts for selective catalytic reduction of NO by hydrocarbons and by ammonia. <u>Journal of Catalysis</u>, 155, 414-417.
- Yang, R.T., Tharappiwattananon, N., and Long, R.Q. (1998). Ion-exchanged pillared clays for selective catalytic reduction of NO by ethylene in the presence of oxygen. <u>Journal of Catalysis</u>, 19, 289-304.
- Van den Brink, R.W., Booneveld, S., Verhaak, M.J.F.M., and DeBruijn, F.A.(2002). Selective catalytic reduction of N₂O and NOx in a single reactor in the nitric acid industry. <u>Catalvsis Todav</u>, 75, 227-232.

APPENDIX A

Calculation of NO conversion and N₂ selectivity



1. NO Conversion

NO Conversion =
$$\frac{y_{NO}^{o}F_{t}^{o} - y_{NO}^{'}F_{t}^{'}}{y_{NO}^{o}F_{t}^{o}}$$

2. N2 Selectivity and N2O selectivity

water amount produced per run = A g (from experiment) volume of water produced = A g*0.0821 Latm/molK*623K

18 g/mol*1atm

= **B** Litre

volume of water produced per min =
$$\mathbf{B} g^{*1000} cm^{3}$$

time run (min)
= $\mathbf{C} cm^{3} / min$
nce In reactor = Out reactor

O₂ balance

actor = Out reactor $2y_{O_2}^{o}F_t^{o} = 2y_{O_2}^{i}F_t^{'} + y_{NO}^{i}F_t^{'} + y_{N_2O}^{i}F_t^{'} + y_{H_2O}^{i}F_t^{'}$

$$y_{N_{2}O} = 2y_{O_{2}}^{o} \frac{F_{i}^{o}}{F_{i}} - 2y_{O_{2}}^{i} - y_{N_{0}}^{i} - y_{H_{2}O}^{i}$$

 N_2 selectivity = mole N_2 produced mole NO converted

N₂ selectivity
$$= \frac{y'_{N_2}}{y'_{NO}} \frac{F'_t}{F'_t} - y'_{NO}$$
H₂O selectivity
$$= \frac{y'_{H_2O}}{y'_{NO}} \frac{F'_t}{F'_t} - y'_{NO}$$
N₂O selectivity
$$= \frac{y'_{N_2O}}{y'_{NO}} \frac{F'_t}{F'_t} - y'_{NO}$$

APPENDIX B

Raw data

Table B.1 The d-spacing of all catalysts

Types of pillared clay	2 $\Theta(^{\circ})$	d-spacind (Å)
1. TA clay		
- fresh	6.16	14.33
- dried	6.16 / 6.32*	14.33 / 13.97*
- calcined 350 °C 6hr	6.16 / 6.2*	14.33 / 14.24*
2. Fe TA clay		
2.1 Fe TA clay Imp1		
- calcined 350 °C 6hr	6.16 / 9.36*	14.33 / 9.44*
2.2 Fe TA clay Imp 2		
- calcined 350 °C 6hr	6.16 / 34.34*	14.33/2.61*
3. V clay		
- fresh	7.56	11.68
- dried	7.56 / 8.68*	11.68 / 10.18*
- calcined 350 °C 6hr	7.56 / 18.76*	11.68 / 4.73*
4. Fe V clay		
4.1 Fe V clay Ion		
- calcined 350 °C 6hr	7.56 / 34.78*	11.68 / 2.57*
4.2 Fe V clay Imp1		
- calcined 350 °C 6hr	7.56 / 34.6*	11.68 / 2.59*
4.3 Fe V clay Imp 2		
- calcined 350 °C 6hr	7.56 / 34.98*	11.68 / 2.56*
5. Mo clay		
- fresh	7.08	12.47
- dried	7.08 / 9.6*	12.47 / 9.21*
- calcined 350 °C 6hr	7.08 / 9.48*	12.47 / 9.32*

Table B.1 continued

Types of pillared clay	2 $\Theta(^{o})$	d-spacing (Å)
6. Fe Mo clay		
6.1 Fe Mo clay Ion		
- calcined 350 °C 6hr	7.08 / 61.2*	12.47 / 1.51*
6.2 Fe Mo clay Imp1		
- calcined 350 °C 6hr	7.08 / 8.58*	12.47 / 10.29*
6.3 Fe Mo clay Imp 2		
- calcined 350 °C 6hr	7.08 / 14.38*	12.47 / 6.15*
7. Mo V clay		
- fresh	9.08	9.73
- dried	9.08 / 9.56*	9.73 / 9.24*
- calcined 350 °C 6hr	9.08 / 14.92*	9.73 / 5.93*
8. Fe Mo V clay		
8.1 Fe Mo V clay Ion		
- calcined 350 °C 6hr	9.08 / -*	9.73 / -*
8.2 Fe Mo V clay Imp1	7	
- calcined 350 °C 6hr	9.08 / 9.36*	9.73 / 9.44*
8.3 Fe Mo V clay Imp 2		
- calcined 350 °C 6hr	9.08 / 9.48*	9.73 / 9.32*

NOTE : * means first peak observed

- : All catalysts show d-spacing at $6.16^{\circ} = 14.33$ Å
- : Mo V clay also show the same value of d-spacing of V clay and Mo clay at 7.56° and 7.08°

Catalysts	Surface area ^a	Pore volume ^b	Avrage Pore
	(m^2/g)	(cc/g)	diameter (Å)
TA-clay	68.51	0.12370	72.25
Fe-TA-clay Imp1	84.90	0.11530	54.33
Fe-TA-clay Imp2	102.3	0.12740	49.81
V-clay	49.50	0.07248	63.09
Fe-V-clay Ion	83.53	0.13180	63.13
Fe-V-clay Imp1	116.10	0.13420	46.25
Fe-V-clay Imp2	99.97	0.12830	51.32
Mo-clay	39.45	0.04229	42.88
Fe-Mo-clay Ion	110.6	0.1862	67.34
Fe-Mo-clay Imp1	59.27	0.06172	41.65
Fe-Mo-clay Imp2	48.00	0.06916	57.03
Mo-V-clay	48.23	0.04932	40.90
Fe-Mo-V-clay Ion	73.73	0.12960	70.30
Fe-Mo-V-clay Imp1	75.03	0.05821	41.72
Fe-Mo-V-clay Imp2	73.25	0.10100	55.15

Table B.2 BET characterization

a : from 5 pionts BET

b : Total pore volume for pores with diameter less than 388.8 Å at $\ensuremath{P/P^o}=0.948$



Figure B.1 Amount of iron on clay by atomic adsorption spectroscopy.

% NO Conversion	0	% Selectivity	
	N ₂	N ₂ O	NO ₂
0	0	0	0
64.9	41.7	58.3	0
64.3	40.5	59.5	0
64.5	40.5	59.5	0
64.3	45.0	55.0	0
64.3	49.6	50.4	0
64.2	47.9	52.1	0
64.3	53.8	46.2	0
	% NO Conversion 0 64.9 64.3 64.3 64.3 64.3 64.3 64.3 64.3 64.3	% NO ConversionN200 64.9 41.7 64.3 40.5 64.3 40.5 64.3 45.0 64.3 49.6 64.2 47.9 64.3 53.8	% NO Conversion% Selectivity0 N_2 N_2O 00064.941.758.364.340.559.564.540.559.564.345.055.064.349.650.464.247.952.164.353.846.2

Table B.3 Activity Test of TA-clay calcined 350 °C 12 hr

Table B.4 Activity Test of V-clay calcined 350 °C 12 hr

Time-on-stream (min)	% NO Conversion _	0	% Selectivity	
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	59.3	62.0	38.0	0
30	65.2	62.4	37.6	0
45	64.5	62.8	37.2	0
60	64.5	63.1	36.9	0
75	64.5	61.9	38.1	0
105	64.5	61.1	38.9	0
135	64.5	57.6	42.4	0

Time-on-stream (min)	% NO Conversion	0	% Selectivity	
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	61.3	13.7	86.3	0
30	62.6	29.2	70.8	0
45	63.3	26.5	73.5	0
60	62.2	28.6	71.4	0
75	63.0	33.4	66.6	0
105	62.6	25.6	74.4	0
135	63.0	23.9	76.1	0

Table B.5 Activity Test of Mo-clay calcined 350 $^{\rm o}{\rm C}$ 12 hr

Table B.6 Activity Test of Mo-V-clay calcined 350 °C 12 hr

Time-on-stream	% NO Conversion	O	% Selectivity	,
(min)		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	75.9	36.1	73.9	0
30	75.2	32.0	68.0	0
45	75.8	36.7	63.3	0
60	75.8	25.8	74.2	0
75	75.8	27.2	72.8	0
105	75.7	22.2	77.8	0
135	75.6	26.1	73.9	0

Time-on-stream (min)	% NO Conversion		% Selectivity	7
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	27.1	100	0	0
30	29.2	100	0	0
45	26.8	100	0	0
60	28.1	100	0	0
75	29.3	100	0	0
105	30.5	100	0	0
135	30.5	100	0	0

Table B.7 Activity Test of Fe-V-clay Ion calcined 350 °C 6 hr

Table B.8 Activity Test of Fe-Mo-clay Ion calcined 350 °C 6 hr

Time-on-stream	% NO Conversion	0	% Selectivity	,
(min)		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	12.3	100	0	0
30	13.4	100	0	0
45	13.8	100	0	0
60	13.8	100	0	0
75	13.7	100	0	0
105	13.4	100	0	0
135	13.7	100	0	0

Time-on-stream (min)	% NO Conversion	0/	6 Selectivity	,
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	11.9	100	0	0
30	11.5	100	0	0
45	11.5	100	0	0
60	11.9	100	0	0
75	11.9	100	0	0
105	11.5	100	0	0
135	11.9	100	0	0

Table B.9 Activity Test of Fe-Mo-V-clay Ion calcined 350 °C 6 hr

Table B.10 Activity Test of Fe-TA-clay Imp 1 calcined 350 °C 6 hr

Time-on-stream	% NO Conversion	0	% Selectivity	
(min)		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	12.1	100	0	0
30	15.4	100	0	0
45	7.6	100	0	0
60	7.6	100	0	0
75	7.8	100	0	0
105	8.7	100	0	0
135	8.7	100	0	0

Time-on-stream (min)	% NO Conversion	0	% Selectivity	7
		N_2	N ₂ O	NO ₂
0	0	0	0	0
15	3.6	100	0	0
30	5.3	100	0	0
45	5.6	100	0	0
60	8.2	100	0	0
75	7.4	100	0	0
105	7.4	100	0	0
135	7.4	100	0	0

Table B.11 Activity Test of Fe-V-clay Imp 1 calcined 350 °C 6 hr

Table B.12 Activity Test of Fe-Mo-clay Imp 1 calcined 350 °C 6 hr

Time-on-stream	9/ NO Conversion	0	% Selectivity	
(min)		N ₂ N ₂ O	NO ₂	
0	0	0	0	0
15	2.7	100	0	0
30	5.8	100	0	0
45	5.5	100	0	0
60	6.1	100	0	0
75	6.1	100	0	0
105	6.1	100	0	0
135	6.1	100	0	0

Time-on-stream (min)	% NO Conversion	0	% Selectivity	
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	1.3	100	0	0
30	3.1	100	0	0
45	2.5	100	0	0
60	4.3	100	0	0
75	2.7	100	0	0
105	4.1	100	0	0
135	3.9	100	0	0

Table B.13 Activity Test of Fe-Mo-V-clay Imp 1 calcined 350 °C 6 hr

Table B.14 Activity Test of Fe-TA-clay Imp 2 calcined 350 °C 6 hr

Time-on-stream (min)	% NO Conversion	% Selectivity		7
		N ₂	N ₂ N ₂ O N	NO ₂
0	0	0	0	0
15	29.1	100	0	0
30	28.3	100	0	0
45	27.9	100	0	0
60	27.7	100	0	0
75	28.0	100	0	0
105	27.2	100	0	0
135	28.3	100	0	0

Time-on-stream (min)	9/ NO Conversion	% Selectivity		,
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	9.4	100	0	0
30	9.4	100	0	0
45	10.1	100	0	0
60	10.6	100	0	0
75	10.4	100	0	0
105	10.6	100	0	0
135	10.1	100	0	0

Table B.15 Activity Test of Fe-V-clay Imp 2 calcined 350 °C 6 hr

Table B.16 Activity Test of Fe-Mo-clay Imp 2 calcined 350 °C 6 hr

Time-on-stream	% NO Conversion	0	% Selectivity	
(min)		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	8.6	100	0	0
30	9.5	100	0	0
45	9.4	100	0	0
60	9.5	100	0	0
75	9.8	100	0	0
105	9.3	100	0	0
135	9.4	100	0	0

Time-on-stream (min)	% NO Conversion	0	% Selectivity	
		N ₂	N ₂ O	NO ₂
0	0	0	0	0
15	9.4	100	0	0
30	6.5	100	0	0
45	7.5	100	0	0
60	7.9	100	0	0
75	7.8	100	0	0
105	7.9	100	0	0
135	7.9	100	0	0

Table B.17 Activity Test of Fe-Mo-V-clay Imp 2 calcined 350 °C 6 hr

Catalysts	NO conversion(%)	N ₂ selectivity (%)	N ₂ yield (%)
1. TA -clay	64.4	49.0	31.6
2. V-clay	64.6	61.6	39.8
3. Mo-clay	62.6	24.9	17.5
4. Mo-V-clay	75.5	25.3	19.1
5. Fe-V-clay Ion	27.4	100	27.4
6. Fe-Mo-clay Ion	13.4	100	13.4
7. Fe-Mo-V-clay Ion	10.1	100	10.1
8. Fe-TA-clay Imp1	9.7	100	9.7
9. Fe-V-clay Imp 1	6.4	100	6.4
10. Fe-Mo-clay Imp1	5.5	100	5.5
11. Fe-Mo-V-clay Imp 1	3.1	100	3.1
12. Fe-TA-clay Imp2	28.1	100	28.1
13. Fe-Vclay Imp 2	10.2	100	10.2
14. Fe-Mo-clay Imp 2	9.4	100	9.4
15. Fe-Mo-V-clay Imp 2	7.8	100	7.8

Table B.18 The SCR activity of unloaded and Fe-loaded pillared catalysts

Note : Imp 1 = Fe impregnation on dried clay

Imp 2 = Fe impregnation on calcined clay

Ion exchange = Fe ion exchange on calcined clay

CURRICULUM VITAE

Name:	Ms. Sasinotai Rochanutama
Date of Birth:	February 3,1979
Nationality:	Thai
University Education	:
1997-2001	Bachelor Degree of Science in Chemical Engineering,
	Faculty of Science, Chulalongkorn University, Bangkok,
	Thailand