

REFERENCES

- Bernard, J. R. and Rees, L.V.D. (Eds.). (1980) Proc. 5th Internat. Zeolite Confer. Heyden, London, 686.
- Fung, S. C. and Querini, C. A. (1992) A Highly Sensitive Detection Method for Temperature Programmed Oxidation of Coke Deposits: Methanation of CO₂ in the Presence of O₂. J. Catal., 138, 240.
- http://www.iza-structure.org/databases/, <u>The database of the Structure Commission</u> of the International Zeolite Association, 20 June 2002.
- Ko, Y. S. and Ahn, W. S. (1999) Synthesis and Characterization of Zeolite L. <u>Bull.</u> <u>Korean Chem. Soc.</u>, 20, 1.
- Lobo, R. F., Tsapatsis, M., Freyhardt, C. C., Khodabandeh, S., Wagner, P., Chen, C-Y, Balkus Jr., K. J., Zones, S. I., and Davis, M. E. (1997) Characterization of the Extra-Large-Pore Zeolite UTD-1. J. Am. Chem. Soc., 119, 8474.
- Rase, H. F. (2000) Handbook of Commercial Catalysts.CRC Press LLC.
- Sinfelt, J. H. (1964) Bifunctional Catalysis. Adv. Chem. Eng., 5, 37.
- Wittcoff, H. A. and Reuben, B. G. (1996) <u>Industrial Organic Chemicals</u>. John Wiley: New York.

APPENDICES

Appendix A Structure of Zeolites (http://www.izastructure.org/databases/)

1. LTL Zeolite

Linde Type L: $K_6Na_3[Al_9Si_{27}O_{72}]$. 21 H_2O

Channels: [001] 12 7.1*

Materials with the same topology:

Gallosilicate L(2,3)

(K,Ba)-G,L(4)

LZ-212(5)

Perlialite(6,7)



Fig. 1. Structure of LTL zeolite. (viewed normal to [001])



Fig. 2. Referable XRD pattern for LTL zeolite, x-axis is 20, y-axis is intensity.

2. BEA Zeolite

Beta $[Al_nSi_{64}-n O_{128}]$ with n=7 Channels: [001] 12 5.5 x 5.5* <--> [100] 12 7.6 x 6.4** Materials with the same topology: Borosilicate *BEA(3,4) Gallosilicate *BEA(4) Tschernichite (5)



Fig. 3. Structure of BEA zeolite. (viewed along [100])



Fig. 4. Referable XRD pattern for BEA zeolite, x-axis is 20, y-axis is intensity.

Mazzite (Na2,K2,Ca,Mg)5 [Al10Si26O72] . 28 H2O

Channels:[001] **12** 7.4* | 8 [001] 3.4 x 5.6*

Materials with the same topology:

Gallosilicate MAZ(2)

LZ-202(3)

Omega(1)

ZSM-4(4)



Fig. 5. Structure of MAZ zeolite. (viewed along [001])



Fig. 6. Referable XRD pattern for MAZ zeolite, x-axis is 20, y-axis is intensity.

4. FAU Zeolite

Faujasite (Na2,Ca,Mg)29 [Al58Si134O384] . 240 H2O

Channels: [111] 12 7.4***

Materials with the same topology:

Alumino- and gallo-germanate FAU⁽³⁾

Beryllophosphate X⁽⁴⁾

CSZ-1 (EMT-FAU structural intermediate)⁽⁵⁾

ECR-30 (EMT-FAU structural intermediate)⁽⁶⁾

Linde X^(7,8)

Linde Y ^(9,10)

LZ-210⁽¹¹⁾

SAPO-37⁽¹²⁾

Zincophosphate X⁽⁴⁾

ZSM-20 (EMT-FAU structural intermediate) (13)

ZSM-3 (EMT-FAU structural intermediate) (14)

CAP-FAU, Cobalt-Aluminum-Phosphat⁽¹⁵⁾

and numerous other compositional variants



Fig. 7. Structure of FAU zeolite. (viewed along [111])



Fig. 8. Referable XRD pattern for FAU zeolite, x-axis is 20, y-axis is intensity.

5. VFI Zeolite

VPI-5 [Al₁₈P₁₈O₇₂] . 42 H₂O Channels: [001] 18 12.1* Materials with the same topology: AlPO₄-54(2) H1(4) MCM-9(5)



Fig. 9. Structure of VFI zeolite. (viewed along [001])



Fig. 10. Referable XRD pattern for VFI zeolite, x-axis is 20, y-axis is intensity.

6. AET Zeolite AlPO₄-8 [Al₃₆P₃₆O₁₄₄] Channels: [001] 14 7.9 x 8.7* Materials with the same topology: MCM-37(3)



Fig. 11. Structure of AET zeolite. (viewed along [001])



Fig. 12. Referable XRD pattern for AET zeolite, x-axis is 20, y-axis is intensity.



Appendix B Dual-Function Mechanism for Catalytic Reforming (Sinfelt, 1964)

Acidic Centers

Fig. 1. Dual-function mechanism for catalytic reforming.

Appendix C Experimental Data

1. Atomic Absorption Spectroscopy (AAS)

TABLE 1

AAS data of Pt containing in different catalysts

| Catalyst | % Pt obtained from AAS |
|-----------------------------|------------------------|
| 1%Pt/KL (IWI)-batch 4 | 0.95 |
| 1%Pt/KL (VPI)-batch 11 | 0.88 |
| 1%Pt/Ce-KL (VPI)-batch 9 | 0.82 |
| 1%Pt/Ce-KL (IWI)-batch 15 | 0.85 |
| 1%Pt/Er-KL (VPI)-batch 19 | 0.90 |
| 1%Pt/SiO ₂ (IWI) | 0.94 |

TABLE 2

AAS data of Si/Al, K/Al, and Na of K-exchanged zeolites

| Sample | Si/Al | Si/Al (theory) | K/Al (wt) | K/Al | Na |
|--------|-------|-------------------|--------------|------|-----|
| K-LTL | 2.79 | 3.00 | 1.252 | 0.86 | nil |
| K-BEA | 8.31 | 8.14 | 1.828 | 1.26 | nil |
| K-MAZ | 2.36 | 2.60 | 0.897 | 0.62 | nil |
| K-FAU | 2.12 | 2.31 | 1.410 | 0.97 | nil |

2. Scanning Electron Microscope (SEM)



Fig. 1. SEM images of Catapale B, Al_2O_3 source of VPI-5 synthesis.



Fig. 2. SEM images of Pt/VPI-5 catalyst.



Fig. 3. SEM images of Pt/KL catalyst.

3. X-ray Diffractometer (XRD)



Fig. 4. XRD pattern of K-LTL.



Fig. 5. XRD patterns of MAZ zeolite, before and after exchanged to K-MAZ and after calcination at 400°C for 5 h.



Fig. 6. XRD patterns of FAU zeolite, before and after exchanged to K-FAU and after calcination at 400°C for 5 h.



Fig. 7. XRD patterns of BEA zeolite, before and after exchanged to K-BEA and after calcination at 400°C for 5 h.



Fig. 8. XRD patterns of VPI-5 zeolite; fresh, after BET measurement (heated at 300° C for 5 h, under vacuum), and after TGA-DSC measurement (heated to 1,000°C in the presence of air).

4. DRIFTS of Adsorbed CO



Fig. 9. DRIFTS of CO molecules and CO adsorbed over Pt/KL and Pt/KY (FAU) catalysts reduced in-situ at 500°C. The catalysts were exposed to 3%CO/He for 30 min at room temperature and purging by He for 30 min. The spectra were collected before and after purging by He.

Note; The peak appeared at 2250- 2150 cm⁻¹ represents CO molecules in gas phase while the band at 1900-2150 cm⁻¹ represents CO adsorbed on Pt clusters. After purging by He, the absorbed CO is present for Pt/KL. In contrast, there is no CO absorbed on Pt/KY (FAU) after purging by He.

5. TGA-DSC of Synthesized VPI-5



Fig. 10. TGA and DSC curves of synthesized VPI-5. The zeolite was heated to 1,000°C (10°C/min) in the presence of air.

Note; This experiment was conducted by a NETZSCH STA-409EP simultaneous thermal analyzer.



6. TPD of Adsorbed Ammonia

Fig. 11. TPD profiles of adsorbed ammonia on NaH-BEA, K-exchanged BEA, and H-exchanged BEA. The samples were exposed to 10%NH₃/He for 30 min and purged by He for 30 min.



Fig. 12. TPD profiles of adsorbed ammonia on K-LTL and Pt/K-LTL. The samples were exposed to 10%NH₃/He for 30 min and purged by He for 30 min.



Fig. 13. TPD profiles of adsorbed ammonia on K-BEA and Pt/K-BEA. The samples were exposed to 10%NH₃/He for 30 min and purged by He for 30 min.



Fig. 14. TPD profiles of adsorbed ammonia on K-MAZ and Pt/K-MAZ. The samples were exposed to 10%NH₃/He for 30 min and purged by He for 30 min.



Fig. 15. TPD profiles of adsorbed ammonia on K-FAU and Pt/K-FAU. The samples were exposed to 10%NH₃/He for 30 min and purged by He for 30 min.



Fig. 16. TPD profiles of adsorbed ammonia on SiO_2 and Pt/SiO_2 . The samples were exposed to $10\%NH_3$ /He for 30 min and purged by He for 30 min.

Appendix D Equipment

1. Reaction Testing System



Fig. 1. Schematic diagram of overall reaction testing system.



Fig. 2. Schematic diagram of auto-sampling system.





Fig. 3. Electronic connection designed for auto-sampling-controlled system.

Note; This system was invented to control solenoid valve for driving sampling valve automatically. It was first applied for Shimadzu GC-17A. Since it works efficiently and the cost (approximately 3,000 baht) is much cheaper than commercial system (approximately 30,000 baht). The system was then duplicated for the other two gas chromatographs (HP 5890 series II) in room 606.

2. Hydrogen Chemisorption System



Fig. 4. Schematic diagram of hydrogen chemisorption system.

Note; The experiments were conducted in Catalysis laboratory at the University of Oklahoma.



3. Temperature Programmed Oxidation (TPO) System (Fung, et al., 1992)

Fig. 5. Schematic diagram of temperature programmed oxidation (TPO) system.

4. DRIFTS Cell



Fig. 6. Image of DRIFTS cell (Spectra-Tech 0030-103; high temperature/ vacuum chamber).

Note; The cell is fit in reflection collector consisting of reflection mirrors in FT-IR spectroscopy. With this cell, samples can be pretreated in-situ at maximum temperature of 900°C and vacuum to 10^{-5} torr.

5. EXAFS Cell



Fig. 7. Image of EXAFS cell.

Note; The experiments were conducted at the national synchrotron light source (NSLS), Brookhaven national laboratory, Upton, New York. The EXAFS cell consists of sample holder, gas inlet/outlet, heater, and cables for temperature controller. The samples can be pretreated in-situ at a certain temperature and gas flow. The data were obtained at liquid nitrogen temperature. Therefore there is a liquid nitrogen tank on the top of the cell for circulation liquid nitrogen to the sample.

6. Microwave Oven and Teflon Vessel Set



Fig. 8. Images of equipment and tools for VPI-5 synthesis. (a) Microwave oven, (b) Assemblies of Teflon vessel set, (c) Teflon vessel set, and (d) Cross-section of Teflon vessel set.

CURRICULUM VITAE

| Ms. Siriporn Jongpatiwut | | | | |
|---|--|--|--|--|
| April 4, 1975 | | | | |
| Thai | | | | |
| University Education: | | | | |
| B.Sc. in Chemical Engineering, Faculty of Science, | | | | |
| Chulalongkorn University, Bangkok, Thailand | | | | |
| M.Sc. in Petrochemical Technology, The Petroleum and | | | | |
| Petrochemical College, Chulalongkorn University, Bangkok, | | | | |
| Thailand | | | | |
| | | | | |

Working Experience:

| 1998-1999 | Position: Program Officer |
|-----------|---|
| | The Thailand Research Fund (TRF), Bangkok, Thailand |

Publications:

- Jongpatiwut, S., Sackamduang, P., Rirksomboon, T., Osuwan, S., and Resasco,
 D. E. "Aromatization of n-Octane Over Pt/KL Prepared by Vapor-phase Impregnation Method", Submitted to *Journal of Catalysis*, April 2002.
- Jongpatiwut, S., Sackamduang, P., Rirksomboon, T., Osuwan, S., Alvarez, W. E., and Resasco, D. E. "Sulfur- and Water-Tolerance of Pt/KL Aromatization Catalysts Promoted with Ce and Yb", *Applied Catalysis A General*, 2002, 230 (1-2), pp.177-193.

Proceedings:

Jongpatiwut, S., Sackamduang, P., Rirksomboon, T., Osuwan, S., Alvarez, W. E., and Resasco, D. E. "Aromatization of n-Hexane and n-Octane over Pt/KL and Pt/SiO₂ Catalysts" *Proceedings of the AIChE Spring Meeting 2002*, New Orleans USA, 10-14 March 2002, pp. 1-8.



- Sackamduang, P., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Resasco, D. E. "A Comparative Study of n-Hexane and n-Octane Aromatization over Pt/KL Catalysts" *Proceedings of the 11th National Chemical Engineering and Applied Chemistry Conference*, Nakhon Ratchasima, Thailand, 9-10 November 2001, CD ROM.
- Lertrojanachoosit, B., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Resasco, D. E. "n-Hexane Aromatization to Benzene on Pt/KL And Pt/Ce-KL Prepared By VPI Method" *Proceedings of the Regional Symposium on Chemical Engineering 2000*, Singapore, 10-12 December 2000, CD ROM.
- Thongsrikate, T., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Resasco, D. E. "n-Hexane Aromatization to Benzene on Pt/KL and PtYb/KL Catalysts Prepared by CVD Method" *Proceedings of the 10th National Chemical Engineering and Applied Chemistry Conference*, Bangkok, Thailand, 26-28 October 2000, pp. 197-206.
- Santipornvit, P., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Lobban L.
 L. "Ozone Degradation of Aqueous Contaminants in Bonded Admicelles" Proceedings of the Regional Symposium on Chemical Engineering 2000, Songkhla, Thailand, 22-24 November 1999, pp. B28-1-6.
- Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Lobban L. L. "Formation and Adsolubilization of Hydrocarbon and Fluorocarbon Aggregates Chemically Bonded on Silica Surface" *Proceedings of the 8th National Chemical Engineering and Applied Chemistry Conference*, Nakhonpatom, Thailand, 17-18 December 1998, pp. 358-373.

Presentations:

 Jongpatiwut, S., Sackamduang, P., Rirksomboon, T., Osuwan, S., Alvarez, W.
 E., and Resasco, D. E. "Promotion of Pt/KL catalysts with rare earth oxides for the aromatization of C6 and C8 feeds" 46th Annual Pentasectional Meeting; Oklahoma Sections of the American Chemical Society, Oklahoma, USA, 3 March 2001.

- Jongpatiwut, S., Sackamduang, P., Rirksomboon, T., Osuwan, S., and Resasco, D. E. "Comparative Study of n-Hexane Aromatization on Pt/KL Catalysts Prepared by Vapor Phase Impregnation and Containing Rare Earth Elements: Clean, Sulfur-Containing, and Water-Containing Feeds", *Bangkok International Conference on Heterogeneous Catalysis*, Bangkok, Thailand, 7-9 January 2001.
- Lertrojanachoosit. B., Thongsrikate, T., Jongpatiwut, S., Rirksomboon, T., Osuwan, S., and Resasco, D. E. "Increased Sulfur Tolerance of Pt/KL Catalysts Containing Rare Earth Promoters for n-Hexane Aromatization", *AIChE Annual Meeting 2000*, Los Angles, USA, 12-17 November 2000.
- Jongpatiwut, S., Lertrojanachoosit, B., Thongsrikate, T., Rirksomboon, T., Osuwan, S., and Resasco, D. E., "Increased Sulfur Tolerance of Pt/KL Catalysts Containing Rare Earth Promoters for n-Hexane Aromatization", *RGJ-Ph.D. Congress I*, Karnjanaburi, Thailand, 2-4 May 2000.