3. FY2005 Results

The following exchange programs were held to promote exchanges with researchers in oil-producing nations.

3.1 King Fahd University of Petroleum and Minerals (KFUPM) (1)

3.1.1 Researcher:

Dr. Nadhir A. H. Al-Baghli
Assistant Professor of Chemical Engineering, KFUPM

3.1.2 Organization providing training

Graduate School of Engineering, Hokkaido University
(Professor Takao Masuda)

3.1.3 Schedule: June 18 - July 21, 2005

3.1.4 Research topic

Experimental Investigation of the Diffusion of Benzene, p-Xylene, and m-Xylene in Silicalite-1 and ZSM-5 Zeolites

3.1.5 Overview of training

Zeolite containing various cations was used in a catalytic reaction process. The apparent catalytic activity of zeolite is closely related to its diffusivity coefficient, and information about the diffusivity coefficient provides direction for catalyst design. The host lab is knowledgeable in the vapor phase diffusivity coefficient of monocyclic aromatics in H-type MFI-type zeolite. However, the diffusivity coefficient of zeolite containing metal cations such as Na^+ has not been sufficiently studied. This training measured the diffusivity coefficient of MFI-type zeolite containing Na^+ as a representative cation.

Silicalite-1 containing Na+ (Na-SL) and ZSM-5 containing Na+ (Na-ZSM-5) were prepared as MFI-type zeolite. Using 5.38 g of sodium silicate as the silica source, 1.18 g of tetra-n-butyl ammonium bromide as the template, and 0.60 g (at time of ZSM-5 synthesis) of aluminum sulfate as the alumina source, hydrothermal synthesis was performed at 200°C for 48 h (ZSM-5 SiO_2/Al_2O_3=50). The result was subsequently cleaned with distilled water, fired in the open air at 530°C for 2 h, and used in experiments. Measurement was conducted using a volumetric method at 300-450°C and 2-10 mmHg of pressure. Diffusion substances used were benzene (B), p-xylene (p-X) and m-xylene (m-X). These values were compared with the existing results for H^+ type.

With silicalite, which does not have ion exchange sites, in H-SL, B and p-X have 8-10 times the diffusion speed (intracrystalline diffusivity coefficient) as compared to m-X. Compared to H-SL, the diffusivity coefficient of Na-SL is 1/80 with B and p-X and 1/10 with m-X. Na^+ was positioned at the terminal silanol group of crystal defects, which interfered with adsorption and caused the diffusivity coefficient to decline. This effect was remarkable at the pore mouth (near the zeolite crystal outer surface) and the decline in diffusivity coefficient was great for B and p-X, which easily penetrate pores. The results make it clear that with Na-SL, B and p-X have about the same diffusion speed as m-X. This conclusion is further supported by the fact that Na-SL has 1/10 - 1/50 the adsorption of H-SL. Furthermore, the effective diffusivity coefficient (found by multiplying adsorptive capacity by intracrystalline diffusivity coefficient) was 1/100 - 1/300 for Na-SL as compared to H-SL. This indicates that there is very little diffusion of monocyclic aromatics in Na-type zeolite.

On the other hand, with Na-ZSM-5, p-X was 1/10 of H-ZSM-5. During the period of this training, however, sufficient results were not acquired for m-X and B, so the effect observed with silicalite could not be confirmed. However, Na-ZSM-5's decline in adsorption was 1/50 that of H-ZSM-5, and it is predicted that the above inference will also apply to ZSM-5.

3.2 Kuwait Institute for Scientific Research

3.2.1 Researcher

(1) Mr. Naser Al-Enzi

Research Associate at KISR (Petroleum Production Dept.)

(2) Mr. Jamal N. Al-Fadhli

Research Associate at KISR (Petroleum Production Dept.)

3.2.2 Organization providing training

Central Research Laboratories, Idemitsu Kosan Co., Ltd.

3.2.3 Schedule

June 19 - July 16, 2005

3.2.4 Research topic

Pilot Plant Organization and Management, Pilot Plant Operation and Data Analysis

3.2.5 Training overview

The Kuwait Institute for Scientific Research (KISR), Kuwait's national research institute, is promoting the "Direct Upgrading Process Study for Kuwait Crude Oils (Phase II): Scale up Assessment," a study project led by the Japan Cooperation Center, Petroleum (JCCP). In this project, KISR and the Japan side are sharing the tasks of evaluating process performance with pilot plants; offering qualitative and quantitative analysis of crude oil, raw materials, products, etc.; comparing large-scale and small-scale pilot performance; and analyzing the scale-up benefit.

The two trainees from KISR are researchers involved in pilot plant operation and management and evaluation of operation/analysis results; the Central Research Laboratories of Idemitsu Kosan provided guidance to help them learn management and data analysis techniques for said pilot evaluation.

Training in pilot plant equipment included (1) an explanation of functions for automating and improving the precision of Idemitsu's pilot equipment, followed by instruction in operation methods. Results of this training will be reflected in the design of pilot plants to be implemented this fiscal year at KISR.

(2) Training in pilot plant evaluation management helped the trainees to learn a wide range of management techniques, from requesting a series of pilot evaluations to experiment plan establishment, operation management, sample recovery, analysis requests and filing of operations results. Similar training was given in 2002, but it was clear that KISR's management techniques had advanced remarkably since that time, and that the previous training had been put to good use.

(3) The trainees additionally performed comparative analysis of results from an actual large-scale pilot plant with Idemitsu's small-scale pilot plant and practiced compiling reports. Through this training, the trainees were able to acquire practical analysis technology. The training also helped to advance KISR's analysis technology by explaining examples of construction of life-span simulators using analysis technology and pilot evaluation results from an agitating-type reactor, such as has been practiced at Idemitsu. This training was very successful because it included pilot plant equipment training, pilot plant management technology training, and, in addition, practical training using real pilot plant data.

3.3 United Arab Emirates University (UAEU)

3.3.1 Researcher:

Dr. Samir I. Abu-Eishah
Associate Professor of Chemical and Petroleum Engineering Department , UAEU

3.3.2 Organization providing training

Graduate School of Science and Engineering, Tokyo Institute of Technology
(Associate Professor Hitoshi Kosuge, Department of Chemical Engineering)

3.3.3 Schedule: June 22 - July 22, 2005

3.3.4 Research topic

Azeotropic VLE Data Measurement and Simulation

3.3.5 Training overview

The participant wrote a program for estimating two-ingredient and three-ingredient vapor/liquid equilibrium and liquid/liquid equilibrium, and checked the validity of the program using water/1-butanol system and 2-butanol-water system data. To do this, he used a program conforming to the two-constant mixing rule in the revised Pen-Robinson-Stryjek-Vera equation of state (PRSV-2 equation of state). The results showed that calculated values were a good fit with measured values for both vapor/liquid equilibrium and liquid/liquid equilibrium. When, for comparison purposes, Aspen Plus (a typical commercial simulator) was used to estimate vapor/liquid equilibrium and liquid/liquid equilibrium, it was able to estimate vapor/liquid equilibrium with no problem, but unable to estimate liquid/liquid equilibrium correctly, indicating that the liquid/liquid equilibrium estimation program created in this research is superior. When the program developed for this research was applied to cyclohexane-aromatics-sulfolane, benzene-toluene-ethylbenzene and benzene-toluene-cumene, the calculated values were a good fit with measured values. In addition, a program was created to decide parameters for an activity coefficient model for two-ingredient and three-ingredient series. When the parameters found by this program were used to calculate vapor/liquid equilibrium and liquid/liquid equilibrium, the calculated values were a good fit with measured values.

We prepared measurements of vapor/liquid/liquid equilibrium of a carbonic acid dimethyl-water heterogenous azeotropic mixture, changed the composition, and measured. The two-liquid phase field and vapor/liquid equilibrium largely fit past data (regarding which there is one report). However, this system is notoriously difficult to measure, and a certain amount of skill is required to measure vapor/liquid/liquid equilibrium, so we were not able to obtain very precise data.

3.4 King Fahd University of Petroleum and Minerals (KFUPM) (Part 2)

3.4.1 Researcher:

Mr. Abdul-Rahman F. Al-Betar
Lecturer at KFUPM

3.4.2 Organization providing training

Graduate School of Engineering, Hiroshima University
(Professor Takeshi Shiono, Division of Materials Chemistry and Chemical Engineering)

3.4.3 Schedule: June 28 - July 27, 2005

3.4.4 Research topic

Research topic:
Olefin Polymerization with Single-Site Catalysts

3.4.5 Overview of training

With the purpose of learning polymerization techniques and polymer structure analysis methods for olefin polymerization with transition metal complex catalysts known as single-site catalysts, we used complex catalysts developed by the laboratory to polymerize syndiospecific propylene with a titanium catalyst as an example of an early transitional metal, and to polymerize ethylene with a nickel complex as an example of a late transitional metal. We studied molecular weight/molecular weight distribution, thermal properties and primary structure analysis technology through analysis of living polymers using gel permeation chromatography (GPC), a differential scanning calorimeter and nuclear magnetic resonance (NMR) spectrometer. For propylene polymerization, we confirmed the characteristics of living polymerization through GPC measurement and determined the stereoregularity of polypropylene with 13C NMR spectrometry. For ethylene polymerization, on the other hand, we examined techniques for investigating the effect of polymerization temperature on polymerization activity, molecular weight and primary structure of the living polymer and techniques for using 1H NMR to find the number of branches of polyethylene.

3.5 King Abdulaziz University (KAAU)

3.5.1 Researcher:

Dr. Hisham Saeed Bamufleh
Assistant Professor, Chemical and Materials Engineering, KAAU (Saudi Arabia)

3.5.2 Organization providing training

Department of Chemical and Environmental Engineering, University of Kitakyushu
(Professor Sachio Asaoka)

3.5.3 Schedule: July 4 - 29, 2005

3.5.4 Research topic

Diesel Desulfurization Operating Conditions Research

3.5 5 Training overview

We performed research to study the impact of operating conditions during deep desulfurization of light oil and to gain basic knowledge about the associated optimization technology. The particular focus of the research was on technology to achieve targeted low sulfur content with minimal hydrogen consumption. We also performed dynamics research on the desulfurization reaction process for basic knowledge.
The catalyst selected for this work was a "titania composite uniformly porous alumina-supported test-produced Ni-Mo catalyst" (developed by Prof. Asaoka's research lab for deep desulfurization of light oil), which underwent preliminary sulfuration before use. For the reaction test, we used high-pressure testing equipment with a fixed-bed-delivery downstream trickle. A specified amount of 4,6 dimethyl-dibenzothiophene was dissolved in cetane as testing material.
The following is a summary of results; a large number of results were achieved in a short period of time.
1. Desulfurization reaction is a first-order reaction.
2. Desulfurization was found to be greatly dependent on ppH2, reaction temperature, LHSV and H2/oil ratio.
3. ppH2 directly and proportionally increases oil’s effective residence time. It was also shown to have negligible

effect on the effective residence time base rate constant.
4. The H_2/oil ratio has an inverse proportional effect lowering oil's effective residence time, but nonetheless it has a proportional effect on the rate constant and a secondary effect on the effective residence time base rate constant.
5. If the sulfur compound contained is all the same, sulfur feedstock concentration has a negligible effect on the rate constant.
6. H_2S concentration in H_2 has a positive linear relationship to conversion rate, and it was observed that the desulfurizing catalyst is activated by the H_2S.

Because of time limitations, we were unable to acquire data on the latest improved catalysts, but we agreed to continue our cooperative relationship in the future.

4. Attachment (training report)

4.1 King Fahd University of Petroleum and Minerals (KFUPM) (Part 1)

Reporter: Dr. Nadhir A. H. Al-Baghli

Reported theme:

Experimental Investigation of the Diffusion of Benzene, p-Xylene, and m-Xylene in Silicalite-1 and ZSM-5 Zeolites

4.2 Kuwait Institute for Scientific Research (KISR)

Reporter: Mr. Naser Al-Enzi and Jamal N. Al-Fadhli

Reported theme:

Pilot Plant Organization and Management, Pilot Plant Operation and Data Analysis

4.3 United Arab Emirates University (UAEU)

Reporter: Dr. Samir I. Abu-Eishah

Reported theme:

Azeotropic VLE Data Measurement and Simulation

4.4 King Fahd University of Petroleum and Minerals (KFUPM) (Part 2)

Reporter: Mr. Abdul-Rahman F. Al-Betar

Reported theme:

Olefin Polymerization with Single-Site Catalysts

4.5 King Abdulaziz University (KAAU)

Reporter: Dr. Hisham Saeed Bamufleh

Reported theme:

Diesel Desulfurization Operating Conditions Research