3. FY2006 Results

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

3.1 Kuwait Institute for Scientific Research (KISR) (Part 1)

3.1.1 Researcher:

Dr. Dawoud Sh. M. Bahzad

Associate Research Scientist at KISR (Petroleum Refining Department)

3.1.2 Organization providing training

Graduate School of Engineering, Kyoto University

(Professor Koichi Eguchi, Department of Energy and Hydrocarbon Chemistry)

3.1.3 Schedule: June 12 - July 7, 2006

3.1.4 Research topic

Catalyst Preparation and Development for Fuel Cell Hydrogen Formation

3.1.5 Training overview

The hydrocarbon steam reforming reaction and partial oxidation reaction are known as hydrogen production processes for fuel cells. The steam reforming reaction is more common as a hydrogen production process, and has been widely adopted for use in hydrogen production plants, but there are problems in startup and stopping because it is an endothermic reaction. On the other hand, the partial oxidation reaction presents no problem with startup because it is an exothermic reaction, but the energy efficiency is low. In applications of fuel cells of recent particular interest, as startup and stopping are expected to occur frequently, we examined both. Kyoto University has examined hexaaluminate-type oxides as heat-resistant reforming catalysts, but we introduced a $BaAl_{12}O_{19-}$. host lattice with Ni and Ru as active species and used a methane partial oxidation reaction and reforming reaction.

Catalysts were prepared using the alkoxide method. This starts from a Ba metal and Al isopropoxide alcohol solution and nitrate of Ni or Ru. For the reaction we used a flow-type reactor.

In terms of the methane partial oxidation reactions, $BaNiAl_{11}O_{19-}$. showed more activity than $BaRuAl_{11}O_{19-}$.. This is thought to be because Ni enters a solid solution state in the hexaaluminate lattice in an oxidized state more easily than does Ru, and therefore a highly dispersed state of Ni was achieved. The reaction proceeds in a reduction status, and therefore it is thought that Ni and Ru particles partially separate from the hexaaluminate phase, but the initial uniformity in the oxidized state is believed to have an impact on the degree of dispersion in the reduction state. Ni exhibits higher catalytic activity than Ru, and there is no problem with activity during temperature drops; during temperature gains, however, Ni oxidation occurs earlier in a partial oxidation reaction and there is marked inactivity. This is because Ru, a precious metal in which a decline in activity has rarely been observed in a Ru catalyst as a result of catalyst oxidation, is easily reduced and goes into a metallic state that is active in reactions. As for the Ni catalyst, if a rising and falling temperature cycle is performed repeatedly during a partial oxidation reaction, a phenomenon is seen wherein activity gradually declines as a result of oxidation in the low-temperature range.

Even in the methane reforming reaction, $BaNiAl_{11}O_{19-}$. exhibited higher activity than $BaRuAl_{11}O_{19-}$.. This is thought to be related to metal dispersion characteristics similar to those that occur during a partial oxidation reaction. In this case, the difference in activity as a result of rising temperature scanning is observed with Ni, but the decline in activity when raising temperature was smaller than in the case of partial oxidation. In the case of Ru, no discrepancy was seen in activity as a result of raising temperature as before.

Through the above research, we have considered and exchanged information on methods of preparing partial oxidation and reforming catalysts for hydrogen production, characteristics of those reactions, catalyst design indicators, catalytic processes in the vicinity of fuel cells, catalyst development, and so on.

3.2 Kuwait Institute for Scientific Research (KISR) (Part 2)

3.2.1 Researcher:

Ms. Khalidah M. S.M. Al-Dalama

Associate Research Scientist at KISR oil refining department

3.2.2 Organization providing training

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University (Professor Yasuaki Okamoto)

3.2.3 Schedule

Schedule: June 12 - July 7, 2006

3.2.4 Research topic

A Fundamental Study on Characterization of HDS Catalysts by CVD Techniques Using $Co(CO)_3NO$

3.2.5 Training overview

This research examined the benefits of adding citric acid, a chelating agent, on the hydrodesulfurization (HDS) activity of $Al_2O_3$and B_2O_3-Al_2O_3 supported Co-Mo and Ni-Mo catalysts. We prepared a series of catalysts in which citric acid (CA) had been added to Al_2O_3 and B_2O_3-Al_2O_3 (1.2wt% B) that had been prepared by impregnation. The number of prepared catalysts was 33, including those used for reference purposes. CA/Co (Ni) mole ratios were 0.4, 0.7, 1.0, 1.5, 2.0, 3.0 and 4.0. The thiophene HDS activity of these catalysts was evaluated using a closed-circuit reactor. The reaction temperature was 350°C. Analysis of reaction gas was by gas chromatography. Catalysts were sulfurated preliminarily at 400°C for 1.5 hours, and were not exposed to air during the reaction. It was found that adding citric acid caused the activity of the Co-Mo/B_2O_3-Al_2O_3 and Ni-Mo/B_2O_3-Al_2O_3 to rise. An increase in activity as a result of adding citric acid was observed. Results showed that the Co-Mo catalyst series underwent a larger effect from the adding of citric acid as compared to using the same carrier. Both the Co-Mo and Ni-Mo catalyst series showed an increase in activity as a result of adding boron. In order to understand the reason for the increase in activity, we evaluated the catalyst surface structure by CVD using $Co(CO)_3NO$. When Co was added by CVD to the catalysts that had undergone preliminary sulfuration and these were then sulfurated again, an increase in HDS activity was observed with the catalysts to which citric acid had not been added, and it was understood that the Co coverage ratio of the MoS_2 particle edge was not 100%. However, no increase in activity was seen in catalysts to which citric acid had been added, so it was understood that the MoS_2 edges were completely covered by Co. It is conjectured that citric acid forms complexes with Co. To confirm this, we used FTIR to perform a characterization of catalysts with citric acid added. The results indicate that with catalysts with a small amount of citric acid, the peak, which suggests the formation of citric acid and Co complexes, was seen at 1600 cm^{-1}, but with catalysts with a large amount of citric acid, free citric acid was also seen. This suggests that the fact that Co (Ni)-citric acid complex formation causes Co coverage of MoS_2 edges to increase is connected to increased activity.

3.3 King Fahd University of Petroleum and Minerals (Part 1)

3.3.1 Researcher:

Dr. Abdulaziz Abdullah Al-Shuaibi

Associate Professor of Mathematics Department at KFUPM

3.3.2 Organization providing training

Faculty of Engineering, Gunma University

(Professor Saburo Saito)

3.3.3 Schedule: June 19 - August 18, 2006

3.3.4 Research topic

Numerical Real Inversion Formulas of the Laplace Transform by the Sinc Method

3.3.5 Training overview

Professor Peter Valkó of Texas A & M University's Harold Vance Department of Petroleum Engineering (one of the most renowned petroleum engineering centers in the world) is a specialist in Laplace transform and has focused his research on petroleum engineering and this transform. For his research he works closely with the Wolram Information Center. One can see his direct influence in a recent PhD dissertation at Iwate University Faculty of Engineering.

The Laplace transform method is essentially used to solve integral equations such as appear in petroleum engineering; however, particularly when inverse-transforming the Laplace transform, the information is real information, so it is necessary to find inversions using real numbers. This is a famously difficult question in which many people have an interest.

Dr. Alshuaibi's research specifically seeks a real inversion with the Laplace transform. For about one week after arriving in Japan, he performed numerical value experiments using Mr. V. K. Tuan's formula, but these were difficult and unsuccessful. We undertook to use our own method combining Tikhonov regularization with the theory of reproducing kernels. Because we were able to successfully use computers to solve the similarly famous problem of heat conduction inversion, we felt confident that we would also be successful with a real inversion Laplace transform.

Dr. Alshuaibi suggested the so-called sinc method, and we found a concrete formula and repeated the numerical value experiment by computer. Since we achieved a certain degree of success, we performed a follow-up experiment on a larger computer. Based on the results, we understood that there is a type of coincidence at work, and decided that there are still problems. While we were able to put together a thesis, we have determined to continue further numerical value experiments with great caution.

At the international conference at Hokkaido University, we were able to meet many people concerned and exchange research, and by meeting with Professor Sugihara of the University of Tokyo we were able to exchange detailed research into numerical value analysis.

3.4 United Arab Emirates University (UAEU)

3.4.1 Researcher:

Dr. Mohamed Humaid Mohamed Hassan Al-Marzouqi

UAEU

3.4.2 Organization providing training

Department of Applied Science, Faculty of Engineering, Kobe University

(Professor Hideto Matsuyama)

3.4.3 Schedule: July 12 - August 22, 2006

3.4.4 Research topic

Membrane Preparation, and Establishment of Simulation Program for CO_2 Removal from Contaminated Gas Stream by Gas-Liquid Membrane Contactors

3.4.5 Training overview

We produced porous membranes for a gas-liquid membrane contactor. We studied production of polyether sulfone (PES) and polyvinylidene fluoride (PVDF) membranes using two methods, nonsolvent induced phase separation (NIPS) and thermally induced phase separation (TIPS). In the NIPS process, we pressed out a polymer solution from the clasp of a double tube and induced phase separation by immersion in a water bath to form a porous hollow fiber membrane. We made a detailed examination of the membrane production conditions (polymer concentration, polymer pressing speed, hollow membrane take-up speed, etc.) that have an effect on membrane structure and performance (permeability, obstruction rate, strength, etc.). In addition, using TIPS, we produced mainly PVDF hollow fiber membranes under various conditions. TIPS is a technique for preparing uniform polymer solutions at high temperatures and subsequently cooling them to induce phase separation and form pores.

This was the first time for the trainee, Dr. Al-Marzouqi, to make this kind of porous membrane, and he took much interest in producing the various membranes, in part because he felt this knowledge would be very useful for his future research.

In addition to making such hollow fiber membranes, we performed simulations of membrane reactor performance using membrane modules with the hollow fiber membranes. The solution is an amine solution, which is an absorbent, and the gas is a mixture of CO_2/CH_4. Because only the CO_2 can react with amine, the CO_2 is selectively absorbed. In actual operation, the amine solution would flow in the opposite direction from the gas, so we simulated this situation. At first we struggled to set the necessary boundary conditions for the simulation, but we were able to complete a stable program thanks to advice from Masaaki Teramoto, an academic researcher from the laboratory. Simulation results clarified the effect of amine and gas flow volumes on CO_2 absorption volume and CO_2/CH_4 selectivity. They also demonstrated the membrane surface area (that is, the number of hollow fiber membranes) needed to obtain the target absorption volume. These simulation results make it possible to actually design membrane contactors without changing operating conditions on a trial-and-error basis. Dr. Al-Marzouqi plans to continue studying this type of simulation after returning home.

3.5 King Fahd University of Petroleum and Minerals (KFUPM) (Part2)

3.5.1 Researcher:

Dr. Hasan Ali Al-Muallem

Assistant of Chemistry Department at KFUPM

3.5.2 Organization providing training

School of Engineering, The University of Tokyo Graduate School

(Professor Takuzo Aida, Department of Chemistry and Biotechnology)

3.5.3 Schedule: July 30 - August 31, 2006

3.5.4 Research topic

Dendritic Polymers

3.5.5 Training overview

Shortly after arriving in Japan, we took part in ZMPC2006 (in Yonago), an international conference concerned with zeolite, where we received information on recent developments in solid catalysts and related mesoporous inorganic substances.

Afterwards, we witnessed a series of experiments on the synthesis of dendrimers in Professor Aida's lab at the University of Tokyo, and learned basic technology concerning reaction, isolation, refining and analysis. We concluded that the measurement of molecular weight of dendrimers by weight analysis was particularly significant. In addition to these experiments, during our stay we attended and joined the discussion in a meeting for presenting research papers at Prof. Aida's laboratory, a midterm conference for presenting Master's theses at the same department, and a meeting for presenting research papers at the ERATO Aida Nanospace project in the National Museum of Emerging Science and Innovation. Through these experiences, we were exposed to the latest information on dendrimer research and other organic nanomaterial science. To further deepen our studies, Mr. Al-Muallem visited Prof. Yamamoto's lab at Keio University and Prof. Aoi's lab at Nagoya University, both known as leading laboratories in dendrimer research, and also took part in discussions through their graduate students' research reports concerning azomethine dendrimers and sugar dendrimers (sugar bowls). We also received comprehensive explanations of both professors' research projects. Additionally, we visited the ERATO project headed by Prof. Eiji Yashima of Nagoya University, where advanced research is taking place on helical molecules. Although our stay was very short, the exposure to dendrimer synthesis, the in-person reports from many researchers and students, as well as the lively discussions, were very meaningful experiences for Mr. Al-Muallem. We additionally visited two different ERATO projects promoted by the Japan Science and Technology Agency, and these were useful for understanding the state of Japan's science and technology policies. And of course the chance to stay in Japan, with its different culture, language and lifestyle customs, was very meaningful. We had various opportunities to discuss many scientific and cultural matters, and overall, these events were undertaken enthusiastically and helped to build good relationships.

3.6 King Abdulaziz University (KAAU)

3.6.1 Researcher:

Dr. Mohammed Ismail Abdulsalam

Director in Academic Assessment Unit at KAAU (Saudi Arabia)

3.6.2 Organization providing training

Faculty of Engineering, Yokohama National University

(Emeritus Professor Shukuji Asakura)

3.6.3 Schedule: August 3 - September 12, 2006

3.6.4 Research topic

The Method of Corrosion Education of the Technical Directors in Petroleum Industries

3.6.5 Training overview

The objective of this training was to teach a methodology for educating oil industry managers about corrosion and its prevention. Corrosion and prevention education covers many fields, but this training focused on the following two points, which are particularly important to the oil industry.

The first point was to learn the state and methods of corrosion prevention training as it is presently practiced in Japan. This refers specifically to training given by concerned groups, including universities, private enterprises and local governments.

First, we visited the Yokohama City Environmental Observation Center, the Sludge Treatment and Recycling Center in Yokohama, Kanazawa Sewage Treatment Plant in Yokohama, Kanazawa Incinerator Plant in Yokohama and the Tokyo Metropolitan Research Institute for Environmental Protection. We studied the current state of these facilities and learned about the problems they face. These facilities all suffer from a number of corrosion problems, and they indicated how difficult it is to train non-specialist employees in preventing corrosion. The Yokohama City Environmental Observation Center in particular works with enterprises to monitor atmospheric pollution, and as part of that provides a great deal of information on atmospheric corrosion near oil refining facilities, where there are high levels of sulfur oxides. This facility made us aware of the importance of corrosion prevention training as it relates to the use of that data. We realized that the corrosion prevention education given by these facilities was similar to that practiced by the oil industry on many points, and that this would be informative for us.

Next, we visited New Cosmos Electric and Horiba, Ltd. to learn about techniques for measuring atmospheric and water corrosion, and we received training in equipment-based corrosion evaluation methods and operator education methods. We also visited the Tokyo Electric Hitachinaka Thermal Power Station, built with the most advanced technology, and the relatively older Kashima Power Station, and received training in the corrosion prevention education that is given to their operators. Here, we learned that if equipment and systems are adequately managed, the corrosion problem can be kept to extremely insignificant levels. To achieve that, we learned how important it is to provide detailed instructions on corrosion prevention in manuals and to provide sufficient training on equipment and system usage.

We also attended corrosion prevention education given by visiting university teachers and related parties at a private enterprise (Maezawa Industries); our training included the reaction of the trainees to the methods and know-how provided. We also attended a corrosion prevention training that included lab learning in an open course where engineers who are members of society meet at the Yokohama National University Graduate School of Engineering, and we learned know-how there as well.

Second, we learned methods for educating people about the mechanism of corrosion in stainless steel, which is used in oil extraction and refining equipment and systems that are exposed to severely corrosive environments, and how to help people understand the related evaluation methods. On this occasion, the topic was the mechanism and evaluation methods of crevice corrosion of stainless steel, which has become a particular problem recently.

Using laboratory measurement equipment, we practiced assessing crevice corrosiveness of SUS304, a form of stainless steel used up to now, and of NSSC312L, a stainless steel that is highly resistant to crevice corrosion. This gave us many ideas on how to teach executive-level engineers after returning home. It also became clear to us that JIS standards were better than several US standards for crevice corrosion assessment methods. We hope that JIS standards will be adopted in Saudi Arabia in the future. We have also been asked to give an introduction to materials from the training that has been given for so many years at the Yokohama National University Graduate School of Engineering for engineers who are members of society, and to implement these at Mr. Mohammed Ismail Abdulsalam’s university.

3.7 King Abdulaziz City for Science and Technology

3.7.1 Researcher:

Mr. Ahamad Abdullah Al-Omar

Researcher in oil refining research department at KACST

3.7.2 Organization providing training

Department of Chemical and Environmental Engineering, University of Kitakyushu

(Professor Sachio Asaoka)

3.7.3 Schedule: August 7 - September 11, 2006; August 3 - September 12, 2006

3.7.4 Research topic

Catalytic Hydrodesulfurization of Diesel Oil

3.7.5 Training overview

We received training in the basic technology for investigating and optimizing light oil desulfurization catalyst exploration and usage conditions. The focus of the research was on a series of techniques from catalyst preparation to evaluation based on usage conditions. We also performed dynamics research on the desulfurization reaction process for basic knowledge.

We prepared a catalyst that used beta zeolite as a zeolite component, which we chose from among the "three elemental compounding nano-uniform porous test-produced catalysts" being studied for the deep desulfurization of light oil at Prof. Asaoka's research lab. Catalysts used were preliminarily sulfurated. 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. We learned about experimental methods for preparing catalysts for the deep desulfurization of light oil, starting with the assumption that such catalysts would be produced industrially.

2. We determined that the LHSV effect of the desulfurization reaction with new catalysts could be adjusted by a primary reaction formula, and that the new catalysts had about three times the activity of our predecessors' catalysts.

3. Based on the activation energy value calculated, it was found that the reaction temperature, as a factor that impacts desulfurization rate, has little impact on the new catalyst because of diffusion.

4. It was shown that although hydrogen partial pressure has little impact on the speed constant in the new catalyst, it does have a linear relationship to it.

5. It was found that the new catalyst shows marked deterioration in the early stages, but that activity quickly stabilizes.

6. In our research on catalysts for the deep desulfurization of light oil, we understood what study items have to be pinned down and learned procedures for addressing them.

By using the results of our predecessors during the training period, we were able to learn data about the latest improved catalysts. We finished the training with a promise to continue a cooperative relationship in the future.

4. Attachment (training report)

4.1 Kuwait Institute for Scientific Research (KISR) (Part 1)

Reporter: Dr. Dawoud Sh. M. Bahzad

Reported theme: Catalyst Preparation and Development for Fuel Cell Hydrogen Formation

4.2 Kuwait Institute for Scientific Research (KISR) (Part 2)

Reporter: Ms. Khalidah M. S.M. Al-Dalama

Reported theme: A Fundamental Study on Characterization of HDS Catalysts by CVD Techniques using $Co(CO)_3NO$

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

Reporter: Dr. Abdulaziz Abdullah Al-Shuaibi

Reported theme: Numerical Real Inversion Formulas of the Laplace Transformation by the Sinc Method

4.4 United Arab Emirates University

Reporter: Dr. Mohamed Humaid Mohamed Hassan Al-Marzouqi

Reported theme: Membrane Preparation, and Establishment of Simulation Program for CO_2 Removal from Contaminated Gas Stream by Gas-Liquid Membrane Contactors

4.5 King Fahd University of Petroleum and Minerals (Part 2)

Reporter: Dr. Hasan Ali Al-Muallem

Reported theme: Dendritic Polymers

4.6 King Abdulaziz University (KAAU)

Reporter: Dr. Mohammed Ismail Abdulsalam

Reported theme: The Method of Corrosion Education of the Technical Directors in Petroleum Industries

4.7 King Abdulaziz City for Science and Technology

Reporter: Mr. Ahamad Abdullah Al-Omar

Reported theme: Catalytic Hydrodesulfurization of Diesel Oil