3. FY2004 results

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

3.1 Kuwait Institute for Scientific Research

3.1.1 Researcher

(1) Dr. Mahmoud Al-Shamali

Associate Research Scientist, KISR (Petroleum Production Dept.)

(2) Mr. Ayyad Toman Al-Dhafeeri

Technician ,KISR (Petroleum Production Dept.)

3.1.2 Organization providing training

Petroleum Refining Research and Technology Center, Japan Energy Corporation

Japan Energy Analytical Research Center Co., Ltd.

3.1.3 Schedule

June 28 - July 5, 2004 (Petroleum Refining Research and Technology Center)

July 6 - 8, 2004 (Analytical Research Center)

July 9 - 16, 2004 (Petroleum Refining Research and Technology Center)

3.1.4 Research topic

Petroleum Evaluation Training Program

3.1.5 Training overview

KISR researchers perform qualitative and quantitative analysis of crude oil, raw materials, products and oil.

The two members from KISR were a researcher who evaluates analysis results and another researcher engaged in actual analysis. Japan Energy's Toda laboratory contains the Petroleum Refining Research and Technology Center, under the jurisdiction of the same company, and the affiliated company Japan Energy Analytical Research Center. The researchers received instruction from both companies as they learned analysis and management techniques.

The training included an explanation of the analytical objectives and functions of the 23 types of advanced analysis equipment owned by the two companies, as well as actual performance of analysis and instruction in operations methods. This training did not consist merely of performing analysis and obtaining the results; we also learned management techniques to enable us to manage the results. The Japan Energy Analytical Research Center has developed an analysis management system named "Lab-Aid." This software manages the entire series of tasks from taking customer requests for analysis to receiving samples, processing the samples in the laboratory for analysis, compiling the results derived from the various analysis equipment, confirming the reliability of data and sending the results to the customer. This training was very fruitful in terms of analysis data management, which was the major theme of the training.

3.2 United Arab Emirates University (UAEU)

3.2.1 Researcher

Dr. Ali H. M. Hassan Al-Marzouqi

Assistant Professor of Chemical and Petroleum Engineering Department ,United Arab Emirates University

3.2.2 Organization providing training

Research Center of Supercritical Fluid Technology, Graduate School of Engineering, Tohoku University

(Professor Hiroshi Inomata)

3.2.3 Schedule: July 5 - August 13, 2004

3.2.4 Research topic

Characterization of C_7^+ Fraction of Crude Oil

3.2.5 Training overview

With the objective of applying EOR (Enhanced Oil Recovery) using supercritical CO_2 secondarily or tertiarily for crude oil remaining in UAE oil wells, our goal was to establish a characterization method for crude oil in order to allow establishment and simulations of operating conditions.

Because crude oil can generally be separated into various compounds from C_1 - C_6, substances are classified as either those ingredients or as ingredients with higher boiling points. The properties of these high-boiling-point ingredients (C_7^+) depend upon the oil well, volume of crude oil residue, etc., so they vary widely with the crude oil concerned. Therefore, we examined a methodology for estimating properties (supercritical temperature, supercritical pressure and eccentricity coefficient) for enabling a simulation that includes these C_7^+ ingredients based on the minimal amount of property data for these ingredients.

The characteristics of crude oil that are easiest to measure are molecular weight (Mw) and specific gravity (SG). We also decided which of the methods capable of estimating hopeful properties as reported in the literature offered the highest application precision, in the order

“Molecular weight”/“specific gravity” ———→ “boiling point” —→ “supercritical constant”/“eccentricity factor”

as one property that is relatively dependent on the C7+ composition is boiling point (Tb). We also wrote software capable of evaluating these properties using actual crude oil data, establishing an estimation method, making simple estimates on a spreadsheet and graphing the results.

We focused on Twu et al.’s method and Riazi’s method as specific techniques, evaluated them using data for n-paraffin (~C7), for which sufficient data has been derived for these properties, then confirmed the precision of application to data limited to crude oil’s C7+ ingredients as reported in the literature.

We were unable to establish a final estimation method by the time the training was finished, but the direction to proceed had become clear. The Riazi distribution shown below gave the best results as a formula expressing C7+ residue composition distribution, and we based our estimation method accordingly.

$$P^* = \left[\frac{A}{B} \ln\left(\frac{1}{1-x} \right) \right]^{1/B} \qquad \begin{aligned} B(SG) &= 3.0 \\ B(Tb) &= 1.5 \\ B(Mw) &= 1.0 \end{aligned}$$

P: various properties

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

3.3.1 Researcher

Mr. Musaed Salem M. Al-Ghamdi

Chemical engineer Center for Refining and Petrochemicals, Research Institute, KFUPM

3.3.2 Organization providing training

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University

(Professor Yasuaki Okamoto)

3.3.3 Schedule: July 20 - August 20, 2004

3.3.4 Research topic

The Effect of Boron Addition and Preparation Method on the Hydrodesulfurization Activity of MoS_2/Al_2O_3 and $CoMoS_2/Al_2O_3$ Catalysts

3.3.5 Training overview

Mo/Al_2O_3 and $CoMo/Al_2O_3$ catalysts (3%CoO, 13%MoO_3) were prepared using a pore volume impregnation method and an ordinary simultaneous impregnation method. Catalysts were also prepared containing boron 0.6wt%. A hydrodesulfurization (HDS) of thiophene reaction was instigated at 350°C. Catalyst characterization was performed by NO adsorption; we evaluated CoMoS coverage ratio at MoS_2 particle edges and the degree of blocking caused by Co sulfide clusters at active sites, based on changes in activity due to a CVD method using $Co(CO)_3NO$. No change in the order of boron HDS activity was found in either catalyst's preparation. However, regardless of the presence of boron, the catalyst prepared by pore volume impregnation showed higher activity. It is conjectured that this is because Mo was concentrated near the mouth of pores. The $CoMo/Al_2O_3$ and $CoMo/B/Al_2O_3$ that were prepared by simultaneous impregnation showed 42% and 53% increases in respective activity as a result of adding Co by CVD, while in both catalysts the CoMoS coverage ratio on the MoS_2 particle edge was limited, and declined specifically as a result of adding boron. On the other hand, a 13% increase in activity was observed with the pore volume impregnation method. This fact indicates that with pore volume impregnation, the CoMoS coverage ratio is higher than in the case of catalysts prepared by the ordinary simultaneous impregnation method. Based on comparison of HDS activity with CVD-Co/Mo/Al_2O_3 or CVD-Co/Mo/B/Al_2O_3 catalysts, we estimated the percentage decline in activity that would occur as a result of blocking caused by Co sulfide clusters at active sites. In all cases it was 22-26%, and it was shown that neither catalyst preparation method nor the addition of boron had significant impact. We further evaluated activity (TOF) at active sites as related to NO adsorption and HDS activity. The results indicated that TOF declined in the following order: pore volume impregnation (boron added) > pore volume impregnation (no boron) > simultaneous impregnation. However, even the TOF of pore volume impregnation with boron added was only 1.2-1.3 times more than that of simultaneous impregnation, suggesting that in catalysts prepared by pore volume impregnation, especially those with boron added, CoMoS Type I has been converted to some of the CoMoS Type II. This agrees with the finding of Usman, et al., that adding boron changes CoMoS Type I into CoMoS Type II. Furthermore, the fact that TOF is so high with the pore volume impregnation method agrees with the inference that Mo becomes concentrated near the mouth of pores and makes it easy for CoMoS Type II to form.

We conducted training in the development of catalysts that shift the carbon monoxide formed in the synthesized gas production process to carbon dioxide. Three types of catalysts were prepared during the training, and the activity of these was compared with that of commercially available catalysts. As a result, we learned that catalysts can have greater activity than commercially available catalysts, depending on operating conditions.

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

3.4.1 Researcher:

Dr. Sulaiman S. Al-Khataff
Assistant Professor at KFUPM

3.4.2 Organization providing training

Department of Materials—Process Engineering & Applied Chemistry for Environments, Faculty of Engineering and Resource Science, Akita University
(Professor Shinichi Nakata)

3.4.3 Schedule: July 26 - August 16, 2004

3.4.4 Research topic

Study on the Perovskite-type Catalyst for Propylene Oxidation

3.4.5 Training overview

We prepared a Perovskite-type catalyst generally represented by the chemical formula ABO_3, performed a model reaction test by oxidizing propylene CO/CO_2 with the idea of using this as an environmental catalyst, and evaluated the catalyst. The catalyst was prepared by solid-state reaction. Metal oxides and palladium nitrate were mixed by ball mixer with water as solvent and calcined at 1100°C for 12h in air. Using powder X-ray diffraction (XRD), we confirmed that the crystal phase we were targeting had formed, and then subjected the material to a reaction experiment. The reaction experiment was carried out in a fixed-bed flow reactor system, using a quartz tube of 10mm in diameter. Particle size of the catalyst was 0.36-0.6mm, and 0.05-0.2g was used (GSHV = 2.6×10^5 - 1.3×10^6 h-^{1}). Treatment of the catalyst before reaction was performed by heating at 580°C with 1.5% O_2 / He gas for 10 minutes, and the reaction experiment was then performed with a feed gas stream consisting of 1000 vol-ppm C_3H_6 / 4500 vol-ppm O_2 with total gas flow rate of 200 cm^3 min-^{1}. The composition of the reaction product was analyzed by a gas chromatograph (GC) with methanizer and a flame ionization detector (FID). The results showed that the propylene conversion rate increased as the temperature increased and GSHV declined, and in particular, when the reaction temperature reached 275°C, the conversion rate rapidly increased from 13% to 70% when GSHV 3.24×10^5 h-^{1}. At 350°C, the conversion rate reached almost 100% at GSHV 3.24×10^5 - 6.48×10^5 h-^{1}. Additionally, our investigation of the CO_2/CO rate showed that under conditions GSHV 3.24×10^5 h-^{1} and 350°C, when the conversion rate was 13.4%, 70% and 100%, the CO_2/CO rate was 17.3, 63 and 200, respectively. Thus, we were able to evaluate the performance of Perovskite-type oxides through a propylene CO/CO_2 oxidization reaction and obtain basic data.

3.5 King Abdulaziz University (KAAU)

3.5.1 Researcher:

Dr. Mohammed Ismail Abdulsalam

Currently: Director of Academic Assessment Unit – Executive Administration, KAAU

3.5.2 Organization providing training

Department of Marine Electronics and Mechanical Engineering, Faculty of Marine Technology, Tokyo University of Marine Science and Technology

(Associate Professor Shin'ichi Motoda)

3.5.3 Schedule: August 11 - September 8, 2004

3.5.4 Research topic

Corrosivity of Zinc-Coated Steel and Aluminum Alloy in Marine Atmosphere

3.5 5 Training overview

With the objective of evaluating corrosion of metal materials used in oil refining plant buildings and storage tanks situated in coastal areas of the Persian Gulf, we examined the use in desert regions of an ACM (Atmospheric Corrosion Monitor) corrosion sensor developed in Japan.

The ACM corrosion sensor was developed at the University of Tokyo in 1993 as an environmental corrosion monitor for marine atmospheric environments. It works as an environmental monitoring sensor, measuring hours of condensation, dryness and precipitation on metal surfaces as a result of climatic changes. It is also capable of real-time monitoring of the amount of sea salt particles on the sensor surface. It is also known that in indoor environments such as residences, besides these environmental corrosion monitors, the corrosion speed of substrate metal carbon steel and plating zinc can be measured using the correspondence relation with sensor output. This means that it is possible to build a monitoring system with such sensors in place of exposure testing using flat panel specimens such as have been used in various atmospheric environments, but in a regional environment with as little rainfall as the Middle East, it is possible to use such a system outdoors.
The ACM corrosion sensor consists of an Fe-Ag couple, combining carbon steel (the sensor substrate anode) with silver (the cathode), but there is concern that in the desert, sensor life will be shortened due to the harsh climatic conditions severely corroding the substrate metal. For that reason, we considered switching the sensor substrate metal from carbon steel to zinc or aluminum, and examined how to establish methods of producing these and their relative humidity characteristics in relation to sensor output.
For this study, we used a screen printer to test-produce sensors at Tokyo University of Marine Science and Technology and evaluated their characteristics in the laboratory. We also took the finished sensors to the university's Shimizu Station—Marine Experimental Center in Shizuoka City to examine their characteristics and measurement techniques in a real-life marine environment.
By the time the training was over, we had not yet established mass production technology for zinc substrate sensors, but it was clear that screen-printing technology could similarly be applied to metal substrates with different levels of surface activity. In addition, based on measurement results from the laboratory and real-life environments, we foresee the possibility of using this sensor to monitor environmental corrosion even in the Middle East's desert, with its dramatic fluctuations in temperature and humidity and local condensation due to radiation cooling.

4 Attachment (training report)

4.1 Kuwait Institute for Scientific Research (KISR)
Petroleum Evaluation Training Program
Dr. Mahmoud Al-Shamali
Mr. Ayyad Toman Al- Dhafeeri

4.2 United Arab Emirates University (UAEU)
Characterization of C_7^+ Fraction of Crude Oil
Dr. Ali H. M. Hassan Al-Marzouqi

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

The Effect of Boron Addition and Preparation Method on the Hydrodesulfurization Activity of MoS_2/Al_2O_3 and $CoMoS_2/Al_2O_3$ Catalysts
Mr. Musaed Salem M. Al-Ghamdi

4.4 King Fahd University of Petroleum and Minerals (KFUPM) (Part 2)
Study on the Perovskite-type Catalyst for Propylene Oxidation
Dr. Sulaiman S. Al-khataff

4.5 King Abdulaziz University, KAAU)
Corrosivity of Zinc-Coated Steel and Aluminum Alloy in Marine Atmosphere
Dr. Mohammed Ismail Abdulsalam