

## MEETING REPORT

### 9th Annual Symposium on Catalysts in Petroleum Refining and Petrochemicals

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More than 150 engineers, catalysis researchers, and scientists from Saudi Arabia, Gulf Countries, Japan, Europe, USA, and China participated in the two-day symposium on catalysts in petroleum refining and petrochemicals held on November 29–30, 1999. The symposium was jointly organized by the Center for Refining and Petrochemicals, Dhahran, and the Japan Petroleum Institute, Tokyo. The emphasis of this annual event was on the latest developments and advances in refining and petrochemical catalysts and processes such as FCC, hydroprocessing, paraffins and olefins utilization for petrochemicals, and CO hydrogenation. Twenty-five technical papers from international catalyst suppliers, process licensors, and research centers were presented at the symposium.

#### Catalytic Cracking

Warren Letzsch of Stone & Webster Engineering, USA, discussed short contact time pilot plant testing for FCC. The author reviewed pilot plant testing for the fluid catalytic cracking process and how it has developed over the years. Some of the new pilot plant facilities were described along with data from short contact time systems. A series of variables were covered including feedstock variations, reactor temperature, catalyst-to-oil ratio and contact time.

The modeling and simulation of a downer-type FCC unit was presented by Abdallah Shaikh of KFUPM (Chemical Engineering Department). Mathematical models were developed for a downer-type FCC unit, in which conservation equations for non-isothermal downer and regenerator reactors were linked with applicable hydrodynamic findings, 4-lump cracking kinetics in the downer, and complete combustion kinetics in the regenerator. Furthermore, the mathematical models have been validated against experimental data collected in a pilot plant in which the downer and regenerator are 1m and 3.6m in length, respectively; and operating temperatures of around 875K can be achieved.

Hajime Okazaki of Nippon Mitsubishi, Japan, discussed the design of the downer reactor and regenerator section of a high-severity HS-FCC using a cold flow model. HS-FCC process, which has been developed in the joint project between Japan and Saudi Arabia, produces more light olefins, under short contact time and high catalyst/oil ratio. Back-mixing in a riser reactor becomes greater with increase of catalyst flow ratio, and makes the distribution of contact time broader. A large scale cold flow model, which has the same size as a 30 b/d demonstration plant, was constructed and used for study of pressure balance and structures of devices in the catalyst circulation system. The results confirmed that the cold flow model could control large catalyst circulation ratio with minimum utility consumption.

Ting Chan of ABB Lummus Global, USA, discussed FCC developments to meet increasing propylene demand. As the worldwide growth in propylene demand continues to outpace growth in demand for ethylene, there is increasing interest to produce more propylene from refinery FCC units. Currently, about 70% of the worldwide propylene demand is produced by steam cracking with the remaining 30% of the propylene demand from refinery FCC units. By the year 2015, the propylene production from refinery FCC units is estimated to increase to 38%. While propylene is a natural product of the FCC process, the traditional FCC operation did not maximize propylene. Refiners are now increasing FCC propylene production to improve their profit margins. New developments in FCC process, along with catalyst advancement, make it possible to triple or quadruple the traditional propylene yield.

Sergio Sobrinos of Grace GmbH, Germany, discussed a new FCC catalyst technology for gasoline sulfur reduction. Today's refiners are faced with a number of challenges, the most notable of which is the need to improve the quality of transportation fuels to meet more demanding specifications. Gasoline sulfur reduction is one of the key issues in

this respect. Grace Davison has recently developed FCC catalyst technology that has the potential to reduce gasoline sulfur by as much as 40%. This novel catalyst technology, called GFS-2000, is in the commercialization phase.

*Andrew Chambers* of Intercat, USA, discussed recent technology developments on FCC catalyst additives for enhanced LPG and octane production. A number of advances have been made in ZSM-5 technology over the years; however, with FCC units being pushed to new processing constraints all the time, the ability to adjust the selectivity of these types of catalyst additives would greatly assist the refinery in maximizing profitability. The major advances in ZSM-5 technology include higher Si/Al ratio zeolites, greater additive efficiency through improved binder technology, and higher concentration additives for improved activity per particle. The ZMX additive technology gives a significant benefit to those refiners using ZSM-5, where gasoline has a higher value than distillate.

*Iacovos Vasalos* of the University of Thessaloniki, Greece, discussed the effect of catalyst feedstock interactions on laboratory evaluation procedures of FCC catalysts. Catalyst selection remains one of the most important ways of shifting the product selectivity in an integrated refinery. Procedures have been established involving the design and operation of several experimental units leading to state of the art technology for catalyst selection. These include: modified ASTM D3907 microactivity test for obtaining a full range of products as a function of conversion; catalyst aging procedure for deactivating a fresh catalyst with or without metals; pilot plant evaluation in a circulating fluid bed with the capability of using a variety of reactors matching the residence time of traditional or short contact time units.

*Takahisa Horie* of Catalysts & Chemicals Industries, Japan, presented a new technology of resid FCC catalyst. RFCC technology is attracting attention for the upgrading process of residual oil. The feed oil in RFCC usually contains large amounts of contaminant metals and Conradson carbon residue. The production of high quality gasoline and LCO fraction requires a high performance FCC. The requirements in RFCC catalyst are: treatment for heavy and low quality oil; effective cracking for feed oil; stable and flexible operation (at the oil factory). In order to fill these requirements, the following concepts are needed in developing RFCC catalyst: design of porosity; design of acidity; and high metal tolerance.

*Huiping Tian* of RIPP-Sinopec, China, discussed breakthroughs in RFCC catalysts development. RFCC technology has been evolving at a great pace since mid 1980's. The most concerned subject of RFCC in commercial practice is the percentage of resid fraction that can be charged into the FCCU to obtain the highest yield of value added products, *i.e.* LPG, gasoline, LCO. This implies that the catalyst should be good in bottoms cracking, metals tolerance, and coke and dry gas selectivity. Recent practice at RIPP has further advanced the art to a higher level; a novel catalyst for cracking 100% vacuum residue of Daqing crude oil has been developed. It has a unique pore architecture and acidity, and shows excellent hydrothermal stability and cracking activity.

*Yasukazu Ohkatsu* of Kogakuin University, Japan, discussed the development of new phenolic antioxidants for the stabilization of cracked oil. A new effect of *ortho*-substituents of a phenolic antioxidant has been found and reported; the substituent having alpha-hydrogen exhibits the ability of regeneration of a phenolic hydroxyl group. New high-performance phenolic antioxidants are designed and developed on the basis of the concept of the above-mentioned finding. The designed phenols are *ortho*-benzyl- and 3-(*o*-hydroxyphenyl)allyl-substituted phenols which have an activated methylene group (labile hydrogens) on an *ortho* substituent. Both groups of phenols exhibited very high antioxidative activities, and especially the latter were found to have a new function of trapping carbon-centered radicals in addition to oxygen-centered radicals.

## Hydroprocessing

*Narinobu Kagami* of Idemitsu Kosan, Japan, presented R&D results on active catalysts for resid upgrading process. Highly active catalysts have been developed for integrated resid upgrading HDS and FCC process. Resid HDS catalyst was developed through studying new impregnation method using water soluble organic compound and phosphorus addition. With the further optimization of pore diameter of resid HDS catalyst, both HDS activity and HDM activity were improved. RFCC catalyst was also developed to increase the yield of gasoline and middle distillates, by the addition of meso pore in matrix pore distribution. These catalysts were tested in a commercial plant, and have been showing good performance, as estimated.

*Toru Saitoh* of Japan Energy Corporation discussed new resid hydroprocessing catalysts with high HDM activity and large metal uptake capacity. The solution to a decrease in resid hydrotreating cost lies in increasing catalyst life.

Since the life of a resid HDS catalyst is dominated by metal fouling, a HDM catalyst should be placed prior to the desulfurization catalyst. However, to extend catalyst life, the limited volume of a reactor obviously requires increasing both demetallation activity and metal uptake capacity of the demetallation catalyst. The authors succeeded in developing such a demetallation catalyst by optimizing pore structure, hydrogenation activity, and distribution of active components. Combining this demetallation catalyst with the existing desulfurization catalyst will increase the run length of a resid HDS unit by 25%.

*Kaoru Fujimoto* of the University of Tokyo discussed the selective production of middle distillates from VGO by hydro-thermal cracking. Liquid-phase cracking of VGO was performed over NiMo supported nonacidic catalysts in a batch reactor. Compared to VGO thermal cracking under the same reaction conditions, the new process showed suppressed naphtha yield and VGO conversion and increased the middle distillate yield. At the same conversion level, the yield ratio of middle distillates to naphtha for this new process was two times higher than that for VGO hydrocracking. The reaction mechanism for this new process was assumed to consist of thermal cracking of hydrocarbon molecules *via* the free radical chain mechanism and the catalytic hydroquenching of free radicals.

*Syed A. Ali* of KFUPM-Research Institute discussed the acquisition of improved batch reactor data for hydrocracking catalyst development. The paper described various improvements made in the reactor configuration and procedures in order to minimize the thermal cracking reactions as well as to enhance the macroscopic mixing and microscopic diffusion. These include installation of a stainless steel mesh along the length of the impeller, premixing of feedstock and catalyst particles, and reduction of reaction time. The improvements have resulted in suppression of thermal cracking and secondary reactions resulting in a reliable technique for rational screening and ranking of semi-developed catalysts. The batch reactor data thus obtained was used for hydrocracking catalyst development.

*George J. Antos* of Universal Oil Products (UOP), USA, presented tools and methodologies for successful commercial hydrocracking catalysts. Theories have been proposed which discuss ideal hydrocracking behavior and the necessity of balancing the two functions in a hydrocracking catalyst. The paper explored some of the methodology employed in starting with new ideas for catalysts with unknown potential, and determining which, if any, have commercial possibilities. Methods involving

reaction studies as well as the more routine characterization tools were discussed. Some examples of the information obtained and how the information is used were presented.

*Takashi Fujikawa* of Cosmo Research Institute, Japan, discussed aromatic hydrogenation of diesel fuel over noble metal catalysts. In order to develop a new sulfur-tolerant noble-metal catalyst with significantly increased catalytic activity for the hydrogenation of aromatics in diesel fuel, screening tests of various non-zeolitic noble-metal catalysts were carried out. The feed was hydrotreated light cycle oil (LCO)/straight-run light gas oil (SRLGO) containing 30–34 vol% aromatics and 100–474 ppm sulfur at a temperature of 573 K, hydrogen pressure of 4.9 MPa, and LHSV of 1.5/h. The Pt–Pd/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> was the most highly active catalyst for aromatic hydrogenation under the conditions applied. Long-term stability tests demonstrated the excellent stability of this catalyst.

*Saad Akashah* of Kuwait Catalyst Company presented an overview on technologies used in hydroprocessing. Hydroconversion processes have been seen as the most attractive tools to meet these concerns since they offer the best carbon yield to product upgraded while minimizing unconverted residual fuel. Although they are characterized by their high investment and operating costs, hydroconversion processes yield significant conversion into distillates. Several types of hydroconversion processes have been commercially proven, but the fixed bed process is still the most widely employed. In hydrotreating different feeds, it is necessary to have the catalyst designed to minimize fixed bed reactor pressure drop and maximize HDS activity, HDM activity, metal retention capacity, cycle length, and conversion level, as well as product stability.

*Shinichi Inoue* of Chiyoda, Japan, discussed a new reaction model and its simulation results for ultra-deep desulfurization employing the *n*th order. When the optimum design of the ultra-deep HDS is made, the conventional reaction model is no longer suitable. A further reinforcement of reaction simulator for reactor design was attempted. The developed model is the Distribution Function Model. In the model the distribution of rate constants is expressed with a distribution function. It is observed that the predictions agreed well with the observed data down to the ultra-deep desulfurization range. Reactor size was estimated using both the distribution function model and the *n*th order reaction model in order to obtain diesel oil of the sulfur level required by European Auto-Oil II Program. The results indicate that reactor sizes calculated by the Distribution Function Reaction Model are smaller than those estimated by the conventional 1.7th order.

David Mc Namara of Criterion Catalyst, UK, discussed fitting the technology to the chemistry of future fuels. A prerequisite of any hydrogen-in refining process is a thorough understanding of the chemistry involved, the presentation provided an overview of the chemistry required to meet the proposed specifications. Innovative solutions are required to overcome the demonstrated chemical incompatibility of some of the 2005 diesel specifications. This means that ensuring maximum utilization of high performing catalyst is the most important reactor internal. The SynSat and SynShift diesel upgrading technologies offered through the Syn Alliance involving Criterion/ABB Lummus/Shell Global Solutions with Exxon as a special licensee, are based on making the necessary chemistry in the existing unit in the most cost effective and creative 'customized solutions' approach.

### Paraffins and Olefins Utilization

A. Matsuoka of Showa Shell, Japan, discussed the transalkylation of benzene with C9 aromatics over zeolite catalysts. Various types of zeolites (MOR-type, BEA-type, and MFI-type) have been used as catalyst for the transalkylation of benzene with C9 aromatics. MOR-type and BEA-type zeolites showed high initial activity, but the activity was decreased with an increase of time on stream. On the other hand, the MFI-type zeolite showed stable activity. The influence of the space velocity, reaction pressure, reaction temperature, and molar ratio of reactants are discussed.

Akio Tada of Kitami Institute of Technology, Japan, presented oligomerization of light olefins over solid acid catalysts under mild reaction conditions. Light olefins can be converted to liquid fuels consisting of nonaromatic high-octane number gasoline fraction by their oligomerization. Light olefin oligomerization is now significant from the standpoint of effective utilization of heavy oil and natural gas as well as of chemical conversion of CO<sub>2</sub>, a greenhouse effect gas. The paper described the performances of various catalysts and then focused on the characteristics of boron phosphate which was found to be a promising catalyst under mild reaction conditions. The oligomerization of olefins was carried out using a closed recirculation reactor at 0–200°C. It was found that BPO<sub>4</sub> was superior in activity to other catalysts.

K. Takehira of Hiroshima University discussed the partial oxidation of CH<sub>4</sub> into synthesis gas on Ni/Perovskite catalysts prepared by the solid phase crystallization (SPC) method. Ni-supported catalysts on perovskite-type oxides have been prepared and tested for partial oxidation of CH<sub>4</sub>

into synthesis gas. The catalyst, Ni<sub>0.2</sub>/CaTiO<sub>3</sub>, Ni<sub>0.2</sub>/SrTiO<sub>3</sub>, and Ni<sub>0.2</sub>/BaTiO<sub>3</sub> were obtained in situ from the precursor prepared by citrate method and the catalytic activities were compared with those prepared by the impregnation method or by changing the calcination temperature. The high and stable activity may be due to highly dispersed and stable Ni metal particles (diameter <1 nm) on the perovskite, where the nickel species thermally evolve from the cations homogeneously distributed in an inert perovskite matrix as the precursors during the reaction.

Kazunari Domen of Tokyo Institute of Technology presented an infrared study on the mechanism of hydrocarbon activation on zeolites. The H/D isotope exchange reaction between *n*-alkanes (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>6</sub>H<sub>14</sub>) and the acidic hydroxy groups on D-form ferrierite (FER) was observed by infrared (IR) spectroscopy, and the apparent activation energies were obtained. The real activation energy for the isotope exchange reaction was estimated by adding the heat of adsorption of each alkane. The values of the activation energy in the rate determining step resulted in almost the same value (130–143 kJ·mol<sup>-1</sup>) for all alkanes. The nature and the structure of the transition state for the isotope exchange reaction were discussed in comparison with theoretical predictions.

### CO Hydrogenation

Takashi Tatsumi of Yokohama National University discussed CO hydrogenation over zeolites loaded with Mo<sub>3</sub>S<sub>4</sub><sup>4+</sup> clusters modified by solid-state reaction between zeolites and KCl. By aqueous ion exchange, the cationic molybdenum sulfide Mo<sub>3</sub>S<sub>4</sub><sup>4+</sup> clusters were successfully introduced into KY and KL without destruction of the zeolite structures as verified by the XRD measurements. During sulfidation of the KCl-added samples, the solid-state reaction occurs to a greater extent without loss of zeolite crystallinity, eliminating nearly all the acidic protons and partly suppressing the production of Lewis acid sites in the zeolites. The KCl-added catalysts produce a significant amount of alcohols in CO hydrogenation, which is considered to reflect the decrease in the acid sites in the zeolites by the solid-state ion exchange.

Y. Sugi of Gifu University, Japan discussed the activity and selectivity of C<sub>2</sub>-oxygenates in CO hydrogenation over rhodium catalysts. Metal dispersion has a striking influence on the activity and the selectivity for high pressure CO hydrogenation over Rh/SiO<sub>2</sub>. Turnover frequency of CO conversion does not change up to 0.5 of dispersion, but increases abruptly at around 0.45. Methanol was predominant product at high dispersion such as 0.8, however the

selectivity for MeOH decreased markedly with decreased dispersion. As the dispersion was decreased below about 0.5, the formation of acetaldehyde increased abruptly at around 0.5. The formation of acetic acid and ethanol has the maximum selectivities at Rh dispersions between

0.4–0.5. Methane (CH<sub>4</sub>) formation increases steadily with decrease of Rh dispersion. The results indicate that the optimal Rh dispersion for the formation of C<sub>2</sub>-oxygenates (C<sub>2</sub>-O) in CO hydrogenation over Rh/SiO<sub>2</sub> catalysts is in the range of 0.3–0.5.