

Session 1

Abstract (#19432)

Title: Advances in Crude to Chemicals

Authors: Keith Couch, Joao Alves

Honeywell UOP

With softening demand for transportation fuels, petrochemicals production provides an alternative path to profitability for refiners and creates the maximum value uplift from crude. In this presentation, we will

- Review current global and Middle East refining and petrochemical trends, highlighting crude to chemicals strategies that would enhance diversification towards petrochemical production
- Explore recent advances in crude to chemicals technology, including Bottom of the Barrel processing and Refining and Petrochemical Integration
- Present project case studies that highlight the importance of intimate domain knowledge when determining the highest value integration strategy and show how we identified solutions that delivered increased value.

Abstract (#19703)

Title: Crude to Chemicals – The Way Forward.

Authors: Musaed Al-Thubaiti, Asma Tahlawi, Fahad Al-Mansour

Saudi Aramco

Petroleum refining and the petrochemical industry account for a major share in the energy and industrial markets globally. Refinery-petrochemical integration is characterized by a number of drivers, including availability and price volatility of feedstock, heavier feedstock qualities, high capital, energy and operating costs, environmental regulations, operational efficiency and flexibility. Additionally, the high production of fuels, which are currently declining in demand world-wide, present another disadvantage in the current market. There are many challenges facing conventional refining-petrochemical integration including the selection of technologies and proper configurations to achieve business targets and capex. Emerging “Direct Crude Oil to Chemicals” technologies provide solutions to such challenges. With competitive and sustainable lower capex and opex, they have the potential to significantly increase the efficiency and yields of chemicals produced from a barrel of crude oil, converting more than 60% of a barrel into

chemicals. Moreover, the direct Crude Oil to Chemicals technologies offers a competitive advantage in the market and create new opportunities of diversification and expansion into higher growth markets.

This paper will provide an overview of conventional refining and petrochemical integration as well as alternative approaches of converting crude oil directly to chemicals. Additionally, it will discuss the challenges in the selection of the proper process configuration during early stage of facility design. The importance and criticality of reliability, availability and maintainability (RAM) modelling will be discussed in detail. This paper will show the value added by RAM modeling to (i) predict the overall site performance when process units, storage, utilities and manufacturing rules are fully operational, (ii) perform sensitivity analysis and comparison scenarios, (ii) quantify design/technical modifications contribution toward improving site performance during design phase.

Abstract (#19433)

Title: Paving The Way to More Efficient Crude to Chemical Complex via Innovative Materials.

Authors: Fabrice Bertoncini

IFPEN

The lecture will briefly comment the changing market dynamics for fuels & chemicals leading to higher interest to crude to chemical routes.

Based on new approaches from heavy fractions to chemicals, this lecture will emphasize relevant R&D challenges in term of innovation for materials for achieving more efficient solutions for crude's conversion to chemical. R&D options to tackle these challenges will be discussed. Illustrations from recent R&D works will be discussed to demonstrate how innovations on materials, mainly metal based nanostructured catalyst's active phases, mesostructured materials or oxidic divided carriers, could provide significant improvements in both bottom of barrel conversion yields and chemical production in a zero-fuel perspective.

Abstract (#19401)

Title: Pressurized, Long-term Steam Reforming of Heavy Naphtha – Challenges and Solutions

Authors: Joongmyeon Bae, Jae Young Yoo, Jaemyung Lee, Aadesh Harale, and Sai Katikaneni

KAIST

Hydrogen has recently gained wide attention as an important energy carrier for developing a low-carbon society in the future. Due to its high energy storage capacity, it can efficiently store a substantial amount of energy. Even with many advantages, hydrogen economy needs to reduce its production cost to be

attractive. One possible approach is to reduce the equipment complexity of the current hydrogen generation process. A simplified process, which has a pre-reformer (PR) and a membrane reformer (MR), performs reforming, separation, and purification in two processes. The PR produces a methane-rich reformat gas from liquid hydrocarbons. The product gas is then fed to the MR to crack the remaining methane and permeate high-purity hydrogen. The PR must operate at high pressure since the MR must be pressurized to permeate hydrogen. The high-pressure operation causes several engineering issues, especially in lab-scale equipment. These issues may prohibit long-term, stable operation of the PR-MR system. In order to find solutions for the engineering issues, two separate long-term experiments were conducted. Their pressure, temperature, steam-to-carbon ratio, and GHSV were 25 bar(g), 565°C, 3.5, and 3,000/h, respectively. The lab-scale pre-reformer used a Ni-Ru/CGO catalyst. The first experiment experienced failure due to carbon coking in the fuel supply line even though the fuel inlet was in contact with steam. The second experiment lowered the temperature of the fuel supply line and decreased the fuel supply rate while keeping the GHSV constant. These improvements resulted in more stability.

Session 2

Abstract (#19316)

Title: Catalytic Dealkylation of Alkyl Polycyclic Hydrocarbons Towards Innovation of Petroleum Refinery.

Authors: Naonobu Katada

Totori University

Separation of aromatic and aliphatic hydrocarbons on the initial stage of petroleum refinery, followed by the conversion of naphthalene, phenanthrene and anthracene into tetralin derivatives and the distillation of aliphatic parts into fractions, will provide the following advantages; maximizing the yield of benzene derivatives, minimizing the hydrogen consumption, minimizing the yield of LPG and lighter compounds; separation of sulfur-containing aromatics which are difficult to desulfurization from fuel fractions; maximizing the gasoline and diesel yields in the alkane parts; maximizing the yield of alkanes possible to convert into benzene derivatives. The key for this process is development of active and selective solid acid catalyst for the dealkylation of alkyl polycyclic hydrocarbons. A silica monolayer catalyst was found to be active for this reaction without undesired cracking of alkyl parts. The stability in the reaction of practical vacuum gas oil was also observed.

Abstract (#801)

Title: Single Step Catalytic Cracking of Crude to Chemicals in a Packed Bed Reactor

Authors: Ahmet R. Özdural* (1) & Halil Kalkan (2)

Hacettepe University

This innovative technology, from here on shall be called “Packed Bed Catalytic Cracking - PBCC”, is built over a proprietary catalysts mixture that contains, amongst others, metal oxides and enriched zeolites. The system operates under mild vacuum. The most striking feature of PBCC is its catalysts structure which is immune to poisoning. PBCC technology doesn't require hydrogen or water-vapor supply. All the experiments are carried out in a bench scale specially designed reactor. Feed flow rate is changed between 1 to 1.5 L/hr, where catalyst bed temperature on the cracking effect is investigated between 210 to 390 C. The catalyst system maintains its initial activity for over two years and realizes a highly

efficient one step crude oil catalytic cracking to chemicals. Almost 95 per cent of the crude feed is converted to valuable goods as gas and liquid products. Analysis of PBCC cracked liquid points out that it is particularly rich in higher-octane hydrocarbon stocks such as aromatics, olefins, branched chain paraffin and cycloalkanes.

Abstract (#19470)

Title: Optimization of Gasoline Yield Produced from Plastic Mixture Waste by Catalytic Cracking.

Authors : Muhammad Faisal Irfan, S. A. Habib, Y. Ali, S. M. Z. Hossain, S. Haji

University of Bahrain

The production and consumption of plastics is increasing due to the increase in the population and the variety amount of applications. Plastic is non-biodegradable material and that makes its life cycle ends in waste landfills. The increase in the demand of oil on the other hand for industrial and domestic applications is rising the need for an alternative source of energy. Pyrolysis is one of the processes that could be used to solve the environmental problems of plastics and turn it into effective source of energy. In this study, catalytic pyrolysis of plastic mixture waste is studied to produce liquid oil with the optimum yield percentage in the gasoline range hydrocarbons. The plastic mixture used is 19.5% LLDPE, 19.5% LDPE, 24% HDPE, 28% PP and 8.5% PS. Different catalysts were prepared and screened for the catalytic reaction of plastics. The pyrolysis reaction is performed by using a designed system of stainless steel reactor with a collector immersed in ice-bath. The parameters studied are temperature, plastic to catalyst ratio and the hydrogen flow rate. The catalyst is chosen based on the percentage of gasoline yield from Gas-Chromatography-Mass-Spectrometer (GC-MS) analysis. The chosen catalyst is used for the design of experiments (DOE) analysis with Central-Composite design model to find the optimum parameters. A kinetic study is also performed using Thermogravimetric Analyzer (TGA) data for finding the kinetic parameters for the plastic waste mixture along with the best catalyst by using different models. The catalyst with the best gasoline yield is Co-Ni- HZSM-5. The best gasoline yield achieved experimentally is 91.8% with a liquid yield of 79%. The optimum parameters using the model of the Design of Experiment are 3:1 plastic to catalyst ratio, 426 °C and 0.128 mL/min hydrogen flow in which the gasoline yield is equal to 92.3%. Friedman model is the best fitting model with value of activation energy and pre-exponential factor values of 193 kJ/mol and $1.645 \times 10^{13} \text{ s}^{-1}$, respectively.

Abstract (#19707)**Title:** Catalyst for Dealkylation–transalkylation of Heavy Alkyl-aromatics**Authors:** Veera Venkata Ramakrishna Tammana, Mohammed Thamer, Zhonglin Zhang, Ali Abdali, Ahmad Jazzar, Ahmad Al Mahdi, Abdul Aziz Alaqeel, Raed AbuDawoud and Sohel Shaikh**Saudi Aramco**

The production of xylenes via the disproportionation of toluene or the transalkylation of heavy aromatics (with or without toluene or benzene) offers refiners an excellent opportunity to add value to their product streams. Other advantages include compliance with the more stringent gasoline specifications (less heavy aromatics) and the expected decline in gasoline demand.

The main applications of xylenes are in the production of synthetic fibers, plasticizers, solvents and gasoline blending. Currently, p-xylene accounts for ca. 83% of the global demand for xylenes, which exceeds 42 million tons per year.

Transalkylation is a prominent process for the inter-conversion of aromatics by alkyl group transferring reactions, especially for the production of dialkylbenzenes directly invoking the conversion of heavy aromatics (particularly C9 alkylbenzenes) to xylenes.

This study displays the zeolite based bi-functional novel catalyst development using High Throughput Technologies and compares its performance to that of catalysts known in the literature for the conversion of heavy reformat containing mainly of C9+ alkylbenzenes in to xylene rich product.

Session 3

Refining & Chemicals:

Abstract (#19300)

Title: Effects of Titania Coatings on Hydrodesulfurization Catalysts, Insights from First-principles

Authors: Hiroki Iriguchi

JXTG Nippon Oil & Energy Corp.

To establish guidelines for the development of high activity hydrodesulfurization catalysts, first-principles calculations were carried out with Al₂O₃ as the catalyst support and MoS₂ as the supported metal species, focussing on the TiO₂ coating and support-metal interaction.

Abstract (#19313)

Title: Meeting IMO 2020 Imposed Challenges by Employing Oxidative Desulfurization of Heavy Oils

Authors: Saumitra Saxena, Claudia Hernandez, Paolo Guida, Abdul Gani Abdul Jameel, Long Jiang, Saumitra Saxena, Pedro Castano, William Roberts

King Abdullah Uni of Sci & Tec

International Maritime Organization (IMO), the United Nations (UN) established regulatory body for maritime shipping, has mandated the use of low sulfur fuels (0.5 wt % sulfur) throughout the world starting 1st January 2020 to reduce health and environmental costs engendered by sulfur oxides (SO_x) emissions. In certain emission controlled areas (ECA), 0.1 wt % sulfur regulation is already effective. Heavy fuel oil (HFO), a residual product generated from the crude refining which contains up to 4.5 wt% sulfur, has been used as a marine fuel for nearly five decades due to its high availability and low price. The emerging concerns related to its use are pushing refineries to re-assess their refining strategies to produce low sulfur fuels or to risk losing a significant market. Desulfurization of high sulfur-fuel oil, if technologically feasible at lower costs, can enable its continued economic utilization for both shipping and power generation industries. The presence of refractory organo-sulfurous compounds like polyaromatic sulfur heterocycle (PASH) species, render conventional desulfurization strategies like hydrodesulfurization (HDS) ineffective on HFO. Consequently, in recent years, one of the most promising technologies, namely Oxidative Desulfurization (ODS), has been widely studied for deep or ultra-deep desulfurization of transportation fuels. Compared to HDS, ODS offers several advantages: It has shown to be effective in the removal of sulfides/disulfides, thiols, thiophenes and their derivatives present in HFO

under mild reaction conditions (25-90 °C and ambient pressure) without hydrogen consumption, thus, reducing capital costs. In this work, we report a preliminary study of ODS of heavy fuel oil (HFO) using H₂O₂ as an oxidant in the presence of acetic acid as a catalyst. A polar solvent, Acetonitrile, was utilized as an extractant to remove the oxidized sulfur compounds from the fuel. The desulfurized HFO was analyzed using advanced analytical platforms like Fourier transform-Ion cyclotron resonance (FT-ICR) mass spectrometry, ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy and inductively coupled plasma - optical emission (ICP-OES) spectrometry, to study the molecular and functional group distribution of the fuel to determine ODS efficiency and fuel properties. The results show a promising outcome of reduced sulfur content in the ODS treated HFO and forms the basis for further evaluation and optimization of the ODS technology. Clean Combustion Research Center (CCRC) and KAUST Catalysis Center (KCC) at KAUST have formed a consortium of several international universities and industrial partners, and presently, working on a demonstration of 1 kg/min ODS of HFO utilizing ultrasonic cavitation technology. The consortium's goal is to optimize this pilot unit and enable the foundation of a scientific approach for further strides in ODS technology and its commercialization.

Abstract (#19515)

Title: Trace Helium Recovery from Natural Gas Using Membranes

Authors: Jason Ploeger, Jin Cao, Don Henry, Erin Sorensen

Air Products and Chemicals

Using membranes to extract helium from natural gas is appealing since the bulk of the natural gas suffers only a minimal pressure drop. We have developed several process cycles utilizing an initial membrane stage to concentrate the helium in a permeate stream that can then be purified at lower cost via distillation or adsorption. Cycle selection for a given project may be influenced by any number of parameters including feed flow rate, pressure, contaminant concentration, and desired products. In almost all cases the initial membrane stage is capital intensive due to the large size, so any reduction in that cost is vital for optimizing process economics. In an effort to reduce these costs, we have built a new experimental apparatus that will test membrane performance in a range of simulated feeds to aid in our design.

Abstract (#19417)

Title: Development of Thermo-neutral Reforming Catalyst for Hydrogen Production: Low Pressure Structured ca

Authors: Shakeel Ahmed, Sai P. Katikaneni, and Aadesh Harale

KFUPM

Hydrogen production is gaining increased importance from the viewpoints of ultimate clean and high caloric energy sources, and especially for the use in fuel cells. Hydrogen demand in the refining sector is also expected to continue its growth driven mainly by stricter fuel specifications. In addition, hydrogen-based fuel cells for automotive and stationary applications are gaining popularity for various reasons including their higher efficiencies and lower emissions. Use of liquid hydrocarbon fuels to generate hydrogen is being considered as an immediate solution for large scale hydrogen production. The main objective of this study is to develop a reforming catalyst for on-board generation of hydrogen for transportation applications. In this study, we have investigated the preparation of new reforming catalysts using a monolith support. Compared to any other catalyst structures such as pellets or extrudates, a significantly lower pressure drop is observed when monolithic catalysts are used. The use of liquid hydrocarbons as fuel in conventional processes such as steam reforming requires heavy and large equipment. This makes them unsuitable for transportation vehicles and remote portable power applications. A highly active catalyst is required for the purpose of making a compact on-board reformer. For this purpose, a multi-components thermo-neutral reforming (TNR) catalyst in various sizes and shapes was used to convert liquid hydrocarbons into hydrogen rich syngas for fuel cell based power applications. Monolith and microlith (brand name form PCI, USA) coated TNR catalysts were prepared, characterized and evaluated for syngas production. Monolith or microlith based structured catalysts are expected to withstand the rugged environment in which these fuel processors on-board vehicles are subjected for applications. The following figures show the results of monolith coated TNR catalyst for low sulfur heavy naphtha conversion to hydrogen rich syngas

Session 4

Refining & Chemicals:

Abstract (#19704)

Title: Novel Cobalt Catalyst to Produce Cyclohexane by the Hydrogenation of Benzene.

Authors: Ahmad Alshammari, Rashid M. Altamimi, Rajenahally V. Jagadeesh

KACST

Multimillion tones of cyclohexane produced per annum represents highly privileged chemical used for the production of value added products. Cyclohexane is principally produced in industry by the hydrogenation of benzene. In general, precious metal based catalysts are used for the production of cyclohexane from benzene at 220°C and above in presence of 25 to 35 bar hydrogen. The catalyst mainly used is the combination of supported platinum and nickel. Due to higher price and less availability of precious metals, the development catalysts based on more cost-effective and earth abundant metals is highly required for the advanced production of cyclohexane. In addition, conditions used in the commercialized processes are drastic and hence the development of mild reaction conditions is highly important. In this regard, we have developed more earth abundant and cheaper cobalt-based heterogeneous catalyst for the production of cyclohexane and substituted cyclohexane under mild reaction conditions with complete conversion and quantitative yield. Developed catalyst contains cobalt nanoparticles supported on commercial silica. Again, the use of silica is also advantageous regards to its more abundance and cheaper price.

Abstract (#19197)

Title: Core Shell Nanomaterial as Heterogeneous Catalysts for Industrial Application

Authors: Noor Almana

Saudi Aramco

Dry reforming of methane ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$) is one of the most attractive technologies to produce syngas (H_2 and CO) because it consumes greenhouse gases (CH_4 and CO_2), producing a low H_2/CO ratio that can be useful for the following, e.g., methanol synthesis or Fischer-Tropsch synthesis. The main drawback of catalysts for dry reforming is coke formation on the surfaces, which leads to reactor plugging and deactivation of the catalysts. Moreover, dry reforming of methane is endothermic reaction and thus

requires high temperatures ($\approx 900^\circ\text{C}$) to achieve high conversion, lowering the lifetime of the catalysts due to sintering of the metallic particles.

The metal sintering not only causes loss of active sites, but also builds up large particles that favor formation of carbon filament. Thus if small nanoparticles were trapped in a thin porous layer of oxide to form a core-shell structure, extent of sintering at high temperature may be reduced as no contact between nanoparticles would be allowed. Additionally, some oxides such as titania, zirconia, ceria or mixed oxides are known to promote carbon oxidation by activating CO_2 , thus reducing coke formation during DRM reaction. Therefore, trapping metal nanoparticles in this type of oxide shell would be the way to produce catalysts that are tolerant to both sintering and coking.

The core-shell design has attracted a lot of attention due to their distinct structure where the oxide layer encapsulates the metal active site. The protective oxide layer suppresses catalyst deactivation, which is attributable to metal growth (sintering) at elevated temperatures, as it acts as a protective shield to metal migration. Also, the unique design might enhance the activity of the catalysts, as new active sites are created at the interfaces between the metal and oxide, especially oxide with redox properties as TiO_2 and CeO_2 . Controlling the thickness of this oxide shell is crucial for gases and reactant diffusion through it to reach the active metal site.

To achieve the structure with protected metal nanoparticles, reverse micro-emulsion system was chosen to give metal@oxide core-shell materials. This method allows synthesizing fine and monodispersed metal nanoparticles, followed by control coating of metal nanoparticles by oxides matrix. The reverse micro-emulsion method consists of forming nano-sized droplets of water as a nanoreactor in a mixture of organic solvent (cyclohexane) and surfactant (IGEPAL CO-520). To precisely control the size and thickness of the metal@oxide nanoparticles, different parameters play a role in this synthesis, such as the surfactant and organic solvent nature, pH, water/surfactant ratio and reducing agent. Initial attempts involve synthesis of Pt@ SiO_2 core-shell particles, which have been extensively studied, and then the method is extended for developing non-noble metals (Ni, Co) and other oxides (TiO_2 , CeO_2 , ZrO_2). The method successfully produces fine metal particles with well-structured shell using Pt and SiO_2 with controllable thickness (~ 15 nm). The presentation will discuss the challenges of designing metal@oxide core-shell structure with different oxides.

Abstract (#19479)

Title: Well-controlled Synthesis Techniques for Finely Tuned Catalysts for the Conversion of 2-butene

Authors: Brian S. Hanna, Timothy J. Kucharski, Maxim P. Bukhovko, Rachael O. Grudt, Michele L. Ostraat

ASC

To more efficiently utilize natural resources, low value components of the oil refinement stream can be advantageously redirected for the on-purpose synthesis of high demand commodity chemicals, such as propylene. As the demand for propylene is expected to outpace the quantity produced through conventional cracking processes, the on-purpose synthesis of this valuable commodity chemical via metathesis from underutilized feed stocks, such as 2-butene, would be a valuable and efficiency

enhancing process. Current methods for the on-purpose synthesis of propylene rely on the cross metathesis of 2-butene with ethylene, which is itself a highly desired commodity chemical. In order to eliminate the need for ethylene in the synthesis of propylene, catalysts that can produce propylene selectively using a feed stream of exclusively 2-butene are currently being explored.

As a further complication for a productive metathesis reaction to occur, some 2-butene in the feed stream must be isomerized to 1-butene. This requirement adds a level of complexity to the process, and creates interest for materials that can both control isomerization and perform olefin metathesis. The overall objective of this work is to demonstrate the development of finely tuned catalysts capable of efficient isomerization and metathesis of 2-butene. Using a well-controlled, highly tunable aerosol process, group 6 metal oxides are either simultaneously synthesized on silica-alumina supports in a single step or are deposited on the exterior of these particles in a second reactor step to create catalysts active towards the conversion of 2-butene to propylene. This catalytic transformation is endothermic and is typically run at elevated temperatures (550 °C), which leads to high levels of coke formation and requires high energy inputs. By lowering the reaction temperature and using an isomerization co-catalyst we can minimize the energy input, lengthen catalyst lifetimes, and demonstrate how lowering the temperature of the reaction effects the mechanism and the rate of isomerization. This talk will focus on the use of these novel processing techniques to adjust catalyst compositions to optimize propylene production as well as catalytic testing results under a range of reduced reaction temperatures.

Abstract (#19298)

Title: Superior Activity of Rh Nanoparticles in Olefin Hydrogenation

Authors: Abdullah Alhanash, Mhamed Benaissa, and Mohamed S. Hamdy

King Khalid University

Introduction

The hydrogenation of olefins is considered one of the most important reactions in petroleum as well as chemical industries [1]. The hydrogenation of cyclic-alkenes leads to valuable feedstocks such as cyclohexane, cyclooctane, and cyclododecane which consider the precursors for the production of different nylon types. The hydrogenation of cyclo-alkenes has attracted also the interest in fuel industry in which the diesel with low-aromatic-content is highly requested because of its cleaner-burning property [2]. Several homogeneous catalysts have been reported to catalyze the liquid phase hydrogenation of cyclohexene notably Wilkinson type catalysts [3]. However, due to the industrial problems associated with the use of homogeneous catalysis such as separation and reutilization, the use of heterogeneous catalysis has been targeted. Noble metals attracted a lot of interest in heterogeneous hydrogenation reactions due to their high activity. Moreover, the catalytic materials which consist of a proper support incorporate highly-dispersed and structurally-defined metallic nanoparticles seem smart alternative to bulk metal catalysts. This is because the high surface area of the catalyst and also its low cost compared to the bulk metal catalysts. Rhodium (Rh) is one of the most interesting metal that is used in hydrogenation reactions of olefins either in homogeneous or heterogeneous catalysts. In the current work, a new catalyst is introduced. The catalyst is consisted of Rh nanoparticles incorporated into the 3D mesoporous silica TUD-1. The activity of the prepared catalyst was investigated in the liquid phase, room temperature and

ambient H₂ pressure, hydrogenation of cyclohexene, cyclooctene, and cyclooctadiene.

Materials and Methods

Nanoparticles of Rh were incorporated into TUD-1 mesoporous silica material by using sol-gel technique by using triethanol amine as a bi-functional template. A sample with a Si/Rh ratio of 200 was synthesized by using the molar oxide ratio of 1SiO₂ : 0.02RhO : 0.5TEAOH : 1TEA : 15H₂O. The sample was hydrogenated in a tube furnace at 300°C for 3h to ensure the formation of Rh⁰ in the final product which coded as Rh-0.5. The prepared sample was characterized by XRD (Schimadzu 6000 DX instrument), FTIR (Agilent Cary 630 Spectrometer), Raman spectroscopy (Renishaw system 2000), Nitrogen sorption measurements (QuantaChrome NOVA 2000e) instrument, ICP (Thermo scientific, ICAP 7000), SEM (Jeol 6360), and HR-TEM (Philips CM30UT). The solvent-free hydrogenation of cyclo-alkene was performed in a stirred batch Parr reactor with 300 ml capacity. The concentration of the reactants and the products were analyzed by using a SHIMADZU GC-17 instrument equipped with RTX-5 capillary column and a flame ionization detector (FID).

Results and Discussion

XRD pattern of Rh-TUD-1 shows a broad band around 23-25° 2θ which can be characteristic to amorphous phase of silica, other peaks at 41.16°, 47.86°, and 70.17° 2θ indicate the presence of metallic Rh⁰ particles (JCPDS 05-0685). The N₂ sorption isotherm of Rh-TUD-1 sample shows type IV and exhibited H1 type of hysteresis loop which is characteristic to the mesoporous materials. Moreover, BET surface area was found to be 721 m²/g with an average pore size of 4.8 nm. HR-TEM micrographs show highly dispersed nanoparticles of Rh (average size = 3-5 nm) incorporated in the mesoporous matrix.

Figure 1. Left panel: The N₂ sorption isotherms of Rh-TUD-1 sample together with the pore size distribution. Right panel: HR-TEM micrograph of the sample.

The catalytic activity of Rh-TUD-1 was evaluated in the hydrogenation of several cyclo-alkenes at ambient conditions (room temperature and 1 atm. of hydrogen gas pressure), moreover, no solvents were used. The obtained results are listed in Table 1.

Catalyst	Substrate	T(K)	PH ₂ (atm)	Conversion %	TOF (S ⁻¹)
Rh-TUD-1	Cyclohexene	298	1	38.5	0.54
Rh-TUD-1	Cyclooctene	298	1	34.5	0.4
Rh-TUD-1	Cyclooctadiene	298	1	38.6	0.44

The results clearly show that Rh-TUD-1 is a super active catalyst in reduction reaction. Cyclohexene, cyclooctene and cyclooctadiene were hydrogenated with a reasonable conversion % to the corresponding cyclo-alkane. The results of other cyclo-alkanes, catalyst stability and recycling, effect of support, as well as the optimization of operating and catalytic parameters will be presented during the presentation.

Significance

The presented catalyst can be optimized to have the benefits of homogeneous catalysis (high rate, high selectivity, and operating ambient conditions) and the other benefits of heterogeneous catalysis (easy separation and easy recycling). In another word, the presented catalyst can close the gap between homogeneous and heterogeneous catalysis, which can be reflected on the petrochemical industry in the different hydrogenation reaction.

Session 5

Abstract (#19398)**Title:** Catalyst Control for the Synthesis of Cyclic Carbonates or Polycarbonates from CO₂ and Epoxides**Authors:** Hyunwoo Kim**KAIST**

Carbon dioxide (CO₂), an abundant and renewable C1 source, is actively used to prepare value-added commodity chemicals. In particular, reactions between CO₂ and epoxides to synthesize polycarbonates or cyclic carbonates are the promising industrial processes because these products are valuable materials such as functional polymers, monomers for polycarbonate production, electrolytes, and polar solvents. The research team at KAIST designed a new type of NO₃ ligands, which form stable complexes with Al(III) and Fe(III) sources. The detailed mechanistic and computational studies revealed that the geometrical constraints in the ligand stabilize penta- or hexa-coordinated intermediates and transition states, resulting in enhanced reactivity and selectivity compared to the previously reported metal catalysts. The research team reported that Fe-NO₃ is highly efficient for the formation of cyclic carbonates from internal epoxides (Catal. Sci. Technol. 2017, 7, 4375). A divergent coupling reaction between N-aryl epoxy amines and CO₂ to cyclic carbonates or oxazolidinones has been reported (Org. Lett. 2018, 20, 5036). Moreover, Al-NO₃ is found to be a highly effective catalyst for the formation of polycarbonates from CO₂ and cyclohexene oxide. Now the team is also pursuing synthesis of new CO₂-containing polymeric materials based on the established catalysts

Abstract (#19589)**Title:** Catalyst Technology for Maximize Light Olefin Yield in FCC-U**Authors:** Mitsunori Watabe**Presenter:** Takaki Mizuno**JGC C&C**

The demand of light olefin such as propylene and butene for petrochemicals have increased in the global market. JGCC&C have developed various advanced ZSM-5 additives to meet refiner's requirement to increase light olefins and commercialized them as "OCTUP series".

Abstract (#19189)

Title: Application of Inferential Models to Crude Distillation Process

Authors: Rashid M Ansari.

Saudi Aramco

The inferential models, based on fast and continuously available temperature, pressure and flow measurements reduce the negative impact of sample intervals and time delays with minimum compromise on accuracy. The resulting continuous and fast response keeps the product qualities on specifications and minimizes the quality giveaway.

A wide range of inferential models were developed on crude fractionation unit for various product qualities and implemented these models in real-time to form a closed-loop quality control using laboratory feedback mechanism. The model is updated using laboratory results as a basis to update the predicted values and a first-order filter to compensate for the noise in the flow measurements. The average deviation from the laboratory results is only 2 °C, and considering the repeatability of 4 °C in Naphtha FBP laboratory results, this prediction can be considered very accurate.

The development of 85% combined diesel inferential model was an innovative approach to inferential modelling by incorporating the blending concept in inferential model development which combined many streams from the two units to predict the quality of combined diesel and controlled that to required specification. The savings from these models are significant by eliminating the need of expensive analyzers and exclusively using the laboratory mechanism in closed-loop quality control system.

This article highlights the development aspects of correlations, use of inferential model in open and closed loop environment, integration of laboratory update mechanism, operator's acceptance and the benefits of inferential modelling.

Abstract (#19229)

Title: Non-Conventional Oxidative Dehydrogenation of Propane to Propylene: Influence of ZrO₂ Phase Structure.

Authors: Mohamed Mokhtar, Katabathini Narasimharao, Sulaiman Basahel, Salem Bawaked, Tarek Ali, Nabil Al-Yassir, Khalid Al-Majnouni, Abdulkarim Al-Mutairi, Ahmed Al-Zenaidi, Ahmed Toseef, Nagmeddin Elwaer

King Abdulaziz University

The motivation for developing active and selective catalysts that will dehydrogenate propane to propene is the ability to take an inexpensive and abundant alkane feedstock and convert it to a considerably more valuable and synthetically useful olefin. The thermal dehydrogenation process is energy intensive and because of the temperatures required, catalyst coking and undesired methane formation are inherent problems. Alternatively, oxidative dehydrogenation (ODH) relies on the oxidation of the H₂ by-product to H₂O and thus utilizes the heat of formation of water to turn an otherwise endothermic process into an exothermic one. In theory, ODH processes can be run at lower temperatures that allow for an improvement in selectivity and/or yield of propene. Unfortunately, the addition of oxygen also allows for competing combustion reactions of paraffin or olefins to carbon oxides. These competing reactions lower alkene selectivity and have thus far prevented the ODH process from becoming commercially viable. Alternatively, chemical looping (CL-ODHP) approach based on oxygen lattice is a promising approach as it preserves alkene selectivity while minimizing the thermodynamic limitation. In the present study the effect of support phase structure on oxygen liability for CL-ODHP was extensively studied. Analysis of the bulk structures shows that tetragonal and cubic phases of ZrO₂ are more reducible than monoclinic structure.

Session 6

Abstract (#19331)

Title: Optimizing an Industrial Methanol Reactor Using Aspen Plus

Authors: Shaker Haji, Omar Al Deeb, Ashraf Hassan

University of Bahrain

Using a Langmuir-Hinshelwood-Hougen-Watson kinetics, an existing industrial methanol staged-reactor was modeled in Aspen Plus® in an attempt to optimize its operation to maximize the methanol production. The kinetic model parameters and the heat loss terms were estimated and tuned to obtain a model that perfectly properly described the measured, responding process variables such as the beds' inlet and outlet temperatures and the reactor's outlet composition. These parameters/terms included the equilibrium and rate constants, catalyst activity factors, reactor's overall heat transfer coefficient, and the rate of heat transferred from the interstage/quenching compartments. After the model was established and verified, the optimization was carried out through four different approaches, in which the main feed and quenching streams' flow rates and temperatures were manipulated within their physical limits. The approach that lead to the best optimization result involved controlling the flow rate and temperature of the main feed to the reactor, as well as the temperature and flow rates of the quenching streams. The study concluded that the reactor performance was applaudable, but the methanol production rate could further be increased by up to 4%, as suggested by the best optimization approach.

Abstract (#19482)

Title: Exploring the Potential Energy Landscape of Zeolites to Understand Deactivation Pathways

Authors: Brian S. Hanna , Steven C. Hayden,¹ Huashan Li,² Elisha Converse, Arthur France-Lanord, Tatiana Headrick, Brian S. Hanna, and Jeffrey Grossman

ASC

The loss of activity associated with metal catalyst deactivation under the harsh conditions of industrial systems, is often addressed by frequent replacement or over-metallation in order to maintain the required activity. Many of these commonly used active metals are rare or expensive, such as platinum or gold, so conserving their usage is important to address both operational expenses as well as the overall sustainability of these processes.

As catalysts age, they are commonly regenerated to remove coke and other deposits that form on the material's surface during operation. During these regeneration cycles catalyst activity is lost due to the sintering of the active metal species, limiting the number of recycles the catalyst is capable of undergoing.

Catalyst deactivation in these systems generally proceeds by Ostwald ripening (OR) and/or particle coalescence/migration (PCM) mechanisms that depend strongly on the interaction between catalytically active surface particles and their support structure. By understanding these deactivation pathways, we can develop materials that are less prone to deactivation and are capable of surviving more regeneration cycles.

Combining both experimental and computational approaches, we explored gold-nanoparticle-doped zeolites containing various Si:Al ratios. The systematic alteration of the aluminum concentration in the zeolite framework allowed the potential energy landscape of the surface to be examined both experimentally (UV-Vis & TEM) and computationally (DFT and MD), and these analyses were used to determine the contributions of the surface binding energy profiles on OR and PCM. Recent findings will be presented in the context of potential exploitation of these interactions to suppress surface-supported catalyst deactivation pathways and thereby extend catalyst lifetimes.

Abstract (#19551)

Title: Selective Catalytic Reduction (SCR) of NO using H₂ under Lean Exhaust Conditions

Authors: Nawaf M. Alghamdi, Juan Restrepo-Cano, Dalaver H. Anjum, Christos Kalamaras, Jorge Gascon, and S. Mani Sarathy

KAUST

The utilization of H₂ to catalytically treat NO emissions under lean exhaust conditions in gasoline and diesel engines was studied over a series of Pt- and Pd-containing catalysts supported on CeO₂ and MgO. The catalytic performance was examined using a fixed-bed reactor where the dry effluent gas stream from the reactor was analyzed by an online FTIR NO/N₂O/NO₂ analyzer. The catalysts were evaluated in terms of NO conversion and N₂ selectivity in the range of 125-300°C with a feed gas composition of 0.05%NO/1%H₂/10%O₂/N₂. The CeO₂-based catalysts exhibited higher NO conversion compared to their MgO counterparts. The most effective catalyst was Pd/CeO₂, with a conversion of 67% at 230°C and a selectivity of about 70% near 230°C. The prepared solids were extensively characterized using different techniques (BET, ICP-OES, CO pulse chemisorption, STEM, EELS and EDS) in order to correlate the structural and morphological properties of the metallic phase (Pt, Pd) and the support (CeO₂, MgO) with the observed catalytic activity. For the two supports tested, CeO₂ is more effective as it yields higher metal dispersion and better facilitates the reduction of Pt and Pd.

Abstract (#19210)

Title: Synthesis of Amphiphilic Copolymers of Hyperbranched Polyethylene-based Core through a Combination

Authors: Ahlam I. Alsulami

University of Jeddah

Well-defined HBPE-based diblock copolymers with predictable amphiphilic properties are studied in the third part. The HBPE-b-poly(N-isopropylacrylamide) and HBPE-b-poly(solketal acrylate), were successfully synthesized by combining CWCP and ATRP. The synthetic methodology includes the following: a) synthesis of multifunctional initiator of HBPE-MI by direct copolymerization of ethylene with 2-(2-bromoisobutyryloxy)ethyl acrylate using η^2 -diimine Pd(II), and b) ATRP using the η^2 -bromoester groups on the HBPE-MI as initiation sites. The self-assembly behavior of the HBPE-based block copolymers of PNIPAM in water as selective mobile phase was studied. The synthesized copolymers revealed the core-shell nanostructure in a spherical micelle, as confirmed by combining dynamic light scattering, DLS, transmission electron microscopy, TEM, and atomic force spectroscopy, AFM. The proton nuclear magnetic resonance spectroscopy, ^1H NMR, gel permeation chromatography, GPC, and Fourier transform infrared, FT-IR, spectroscopy, were used for determining the molecular and composition structures. Also, differential scanning calorimetry, DSC, and thermogravimetric analysis, TGA, were used to record the melting temperature and to study the thermal stability, respectively.
